CHAPTER 1

General Aspects of Unsaturated Polysters, Halopolysters, Rocket Propellants and Their Inhibition and Nitroglycerine Migration
1.0 **UNSATURATED POLYESTERS**

The term 'Polyester' describes a class of materials formed as a result of condensation reaction of polyhydric alcohol and polybasic acid. This includes both saturated as well as unsaturated polyesters. By common usage, however, the term polyester when used alone is synonymous with unsaturated polyester.

They possess a number of unusually valuable properties immediately amenable to use for diverse applications. The major fields of applications of unsaturated polyesters are lamination, potting, moulding and surface coating. Polyester laminates are used in storage tanks for oils, water and certain chemicals. A wide variety of household articles and other articles are produced from polyester laminates. Glass fibre reinforced laminates are used for fuel cell backing boards in aircrafts, helmets etc. In office and industry, similar applications are found including machine housings, guards and cabinets although some of them are now replaced by thermoplastics.

In electronic industry, unsaturated polyesters have a number of applications such as encapsulation of electronic circuits, insulating sleeves, parts of television assemblies and capacitors.

Glass reinforced polyester resins are now used in the manufacture of helmets, vehicles and boats. Boat building is
one of the most unique applications of reinforced polyester resins is the wet lay-up process. The main feature being their resistance to salt water, sun light, termites, and rot. The polyester resin used for reinforced plastics are mostly liquids with viscosities varying from 200 to 2000 cPs. The polyester resins are also useful in fabrication of radar housings with complex aerodynamic shapes. Surface coatings (solventless wood lacquers) and impregnation (impregnation of wooden relics) are additional important applications of unsaturated polyesters. The surfacing of roads to produce non-slip surface along with their quick repair is another interesting application which has been reported recently. The scientists working in museums have succeeded in developing new techniques for the conservation of antiquities and works of art with the use of unsaturated polyesters. Hans has reported use of unsaturated polyesters for a completely different application i.e. "inhibition of rocket propellants". The use of unsaturated polyesters for inhibition of double-base (DB) and composite modified double-base (CMDB) rocket propellants has stimulated considerable interest in them and a number of unsaturated polyesters i.e. rigid, flexible, semi-rigid, semi-flexible, very flexible unsaturated polyesters, chloropolyesters and novel unsaturated polyesters have
recently been developed in this laboratory\textsuperscript{7-21}. The applications of unsaturated polyesters in the form of an application tree are shown in Fig.1.

The history of polyester can be traced back to as early as 1847 when a Swedish scientist, Berzelius\textsuperscript{22} obtained a white amorphous solid of resinous nature on heating with tartaric acid. Lorenzo\textsuperscript{23} reported a polyethylene succinate by heating ethylene glycol with succinic acid in 1863. The work of Berzelius was extended by Watson\textsuperscript{24} in 1902 who prepared a wide range of resinous products by such reactions, and named them 'glyptals'. With the advent of Staudinger's polymer concept\textsuperscript{25,26} in 1920 and his subsequent postulation of primary valence bonds followed by Meyer et.al.\textsuperscript{27}, Carothers\textsuperscript{28} was the first to prepare polyesters with well defined polymeric structures. In his introduction to general theory of condensation of polymers, he described these polymers and produced them by recurring condensation of monomers. In late thirties, Bradley and co-workers\textsuperscript{29-31} reported that unsaturated polyesters become infusible and insoluble on mixing with styrene monomer and curing because of the presence of unsaturation i.e. double bonds in the polyester chains. In 1933, American Scientist Ellis\textsuperscript{32} discovered that the rate of cure of unsaturated polyesters may be increased by more than 30 times if unsaturated monomers are present. The use of polyesters as laminating resins was made in the Second World War. The polyesters were
FIG. 1 - APPLICATION TREE OF UNSATURATED POLYESTERS
first offered in aircraft industry in 1946. The alkyd moulding materials were however, first produced in USA in 1948 and then in Great Britain in 1952.

Further, several types of polyesters were introduced in early sixties for various applications. Around 1966, polyethylene terephthalate was developed for moulding applications by injection moulding technique followed by the introduction of polybutylene terephthalate and polymethylene terephthalate in 1969. However, the vinyl esters were introduced for use in industries on a large scale quite late.

1.1 CHEMISTRY OF UNSATURATED POLYESTERS

Alcohols react with carboxylic acids, to give simple esters and water as shown in the following reaction:

\[
\begin{align*}
\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} & \rightarrow \text{CH}_3\text{C} = \text{O}\text{C}_2\text{H}_5 + \text{H}_2\text{O} \\
\text{ACETIC ACID} & \quad \text{ETHYL ALCOHOL} \\
& \quad \text{ESTER} \\
& \quad \text{WATER} \\
\text{Eqn.(1)}
\end{align*}
\]

This reaction cannot be carried out further as both the acetic acid and ethyl alcohol have only one reactive/functional group and at the same time, reaction product also has no functional group. But if a dicarboxylic acid or anhydride (phthalic anhydride or acid) is reacted with dihydric alcohol (ethylene glycol), a linear polyester i.e. poly (ethylene phthalate), consisting of long chain linear
molecules (thermoplastic) is formed as shown in the Eqn. (2) i.e.

\[
\begin{align*}
\text{CH}_2\text{OH} + \text{C}_6\text{H}_4\text{O}_4\text{C} \rightarrow \text{H}_2\text{O} + \text{O} = \text{C} \\
\text{CH}_2\text{OH} + \text{C}_6\text{H}_4\text{O}_4\text{C} \rightarrow \text{H}_2\text{O} + \text{O} = \text{C} \\
\text{ETHYLENE PHTHALIC WATER POLYETHYLENE PHTHALATE} \quad \text{Eqn}(2)
\end{align*}
\]

Similarly, 2:3 functionality may be illustrated by the Eqn. (3)

\[
\begin{align*}
\text{CH}_2\text{OH} + \text{C}_6\text{H}_4\text{O}_4\text{C} \rightarrow \text{H}_2\text{O} + \text{O} = \text{C} \\
\text{CH}_2\text{OH} + \text{C}_6\text{H}_4\text{O}_4\text{C} \rightarrow \text{H}_2\text{O} + \text{O} = \text{C} \\
\text{GLYCEROL PHTHALIC WATER POLYGLYCERYL PHTHALATE} \quad \text{Eqn}(3)
\end{align*}
\]
Maleic Acid is tetrafunctional [bifunctional because of two carboxyl groups and bifunctional because of unsaturation, \(-\text{CH} = \text{CH}-\)]. When it is reacted with ethylene glycol, a normal reaction of 2:2 functionality takes place first, as shown in Eqn.(4)

\[
\begin{align*}
\left[ \text{CH}_2\text{OH} \right] + \left[ \text{H-O-C-CH=CH-C-OH} \right] & \rightarrow \text{H}_2\text{O} + \text{H-O-CH}_2\text{CH}_2\text{O-C-CH=CH-C-O-CH}_2\text{CH}_2\text{O} \\
\text{ETHYLENE GLYCOL} & \quad \text{UNSATURATED ACID (MALEIC ACID)}
\end{align*}
\]

--- Eqn(4)

This polyester i.e. poly (ethylene maleate), contains reactive double bonds and is a linear polyester resembling a polyester made from reactants of 2:2 functionality as shown in Eqn.(2). If it is further heated, the reactive groups further start to crosslink the linear molecular chains, yielding a thermoset polyester resembling a resin made from reactants of 2:3 functionality as shown in Eqn.(3). This crosslinking is shown in Eqn.(5) where \( R \) is a divalent group.
A linear polyester, poly (ethylene maleate) [Eqn. (4)] crosslinks very readily if a monomer (such as styrene monomer) is incorporated, as illustrated in Eqn. (6)

1.2 **RAW MATERIALS FOR UNSATURATED POLYESTERS**

Polyesters are formed by the reaction of dibasic acids (saturated/unsaturated) with di/tri/tetrahydric glycols followed by their blending with polymerisable monomer. It means that the major components of polyesters are:

i) Alcohol/glycol component

ii) Acid (unsaturated/saturated) component

iii) Crosslinking component
i) **Alcoholic/Glycol Component**

This has an important influence on the properties of unsaturated polyesters. Flexibility, crystallinity, water and heat sensitivity are the properties which are mainly affected by the choice of glycol/alcohol. The principal glycols/alcohols along with their merits/demerits are given in Table.1

ii) **Acid Component**

A large number of dibasic acids are available for the synthesis of unsaturated polyesters on a commercial scale and resulting resin possess specific properties depending upon the dibasic acid. Since the unsaturated dihydric alcohols are not commercially available, the majority of the unsaturated polyesters derive their unsaturation from the acid component. Most of the unsaturated polyesters are made up of atleast two dibasic acids except in cases where it is desired. The most common acids alongwith their structures and primary characteristics are listed in Table.2

iii) **Crosslinking Monomer**

These are used to copolymerize with the unsaturation present in the polyester chains, (Eqn.6) in order to result crosslinked or thermoset structures. Monomers also serve as a solvent to dilute the viscous polyesters prior to occurrence of crosslinking reaction. A brief on various monomers is listed in Table.3

In addition to these main raw materials, there are a few minor components, such as esterification catalysts, stabilizers, curing catalysts and accelerators which are also used for the synthesis of unsaturated polyesters. Their brief account and merits/demerits are given below:
TABLE 1: ALCOHOLS/GLYCOLS FOR UNSATURATED POLYESTERS

<table>
<thead>
<tr>
<th>Glycol</th>
<th>Structure</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene glycol</td>
<td>$\text{CH}_2\text{OH}$</td>
<td>The resulting polyesters show strong tendency to crystallize and also have a limited compatibility with styrene.</td>
</tr>
<tr>
<td>Polymethylene glycols</td>
<td>$\text{HO CH}_2\text{(CH}_2\text{)}_n\cdot\text{CH}_2\text{OH}$</td>
<td>The resins suffer from the above defects and tendency to crystallize increases with the chain length of the glycols.</td>
</tr>
<tr>
<td>(tri, tetra and hexa methylene glycols)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>$\text{CH}_3\cdot\text{C}\cdot\text{HOH}$</td>
<td>Results in polyesters which are compatible with styrene and show little tendency to crystallize.</td>
</tr>
<tr>
<td>(propane-1,2-diol)</td>
<td>$\text{HO CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_3$</td>
<td>Yields polyesters having higher toughness and thermal softening point.</td>
</tr>
<tr>
<td>Glycol</td>
<td>Structure</td>
<td>Remarks</td>
</tr>
<tr>
<td>------------------------------</td>
<td>---------------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Diethylene glycol</td>
<td>$\text{HO·CH}_2\text{·CH}_2\text{·O·CH}_2\text{·CH}_2\text{·OH}$</td>
<td>The glycols having oxygen linkages also produce non-crystallizing polyesters. The flexibility increases with the chain length.</td>
</tr>
<tr>
<td>Dipropylene glycol</td>
<td>$\left[\text{CH}_3\cdot\text{CH}\cdot(\text{OH})\cdot\text{CH}_2\right]_2\text{O}$</td>
<td></td>
</tr>
<tr>
<td>Polyethylene glycol (mol. wt. 200, 400, 600)</td>
<td>$\text{HO}\left(\text{CH}_2\cdot\text{CH}_2\cdot\text{O·CH}_2\cdot\text{CH}_2\right)_n\text{·OH}$</td>
<td>Produces very flexible polyesters</td>
</tr>
<tr>
<td>Neopentyl glycol</td>
<td>$\text{HOH}_2\text{C}\cdot\text{C}\cdot\text{CH}_2\text{·OH}$</td>
<td>Produces flexible polyester</td>
</tr>
</tbody>
</table>
### TABLE 2: ACIDS/ANHYDRIDES FOR UNSATURATED POLYESTERS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Primary Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Saturated aromatic acid or anhydride</td>
<td><img src="image" alt="Phthalic anhydride" /></td>
<td>Most commonly used in commercial polyesters. Higher percentages yield, more flexible and less reactive resins.</td>
</tr>
<tr>
<td>Phthalic anhydride</td>
<td><img src="image" alt="Phthalic acid" /></td>
<td>Reacts slowly with glycols and gives high molecular weight polyesters which have superior strength, toughness, weathering characteristics, heat and chemical resistance.</td>
</tr>
<tr>
<td>Phthalic acid</td>
<td><img src="image" alt="Isophthalic acid" /></td>
<td></td>
</tr>
<tr>
<td>Isophthalic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>Structure</td>
<td>Primary Characteristics</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-----------------------------------------------</td>
<td>-----------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Aliphatic dibasic acids</td>
<td>HOOC-(CH₂)ₙ-COOH  ( n = 1 ) to 8</td>
<td>Results in flexible polyesters which are partially crystallizable and slow curing. Also these polyesters have poor strength and flexibility increases with chain length.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b) Unsaturated acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>i) Maleic acid or anhydride</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H-C-COOH | H-C-COOH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fumaric acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H-C-COOH | HOOC-C-H</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Itaconic acid</td>
</tr>
</tbody>
</table>
### Table 3: Crosslinking Monomers for Unsaturated Polyesters

<table>
<thead>
<tr>
<th>Crosslinking Monomer</th>
<th>Structure</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td><img src="https://example.com/styrene_structure" alt="Styrene structure" /></td>
<td>Most widely used because of low cost compatibility, availability, low volatility and good strength of cured resins. Resins based on styrene cure rapidly and have good weathering characteristics.</td>
</tr>
<tr>
<td>Diallylphthalate (DAP)</td>
<td><img src="https://example.com/diallylphthalate_structure" alt="Diallylphthalate structure" /></td>
<td>Low volatility and elevated temperature curing. The resulting polyesters are tougher and have higher thermal softening points, outstanding electrical properties, heat resistance and dimensional stability.</td>
</tr>
<tr>
<td>Diallylisophthalate (DAIP)</td>
<td><img src="https://example.com/diallylisophthalate_structure" alt="Diallylisophthalate structure" /></td>
<td>Gives better heat resistance than DAP but final products have low strength.</td>
</tr>
<tr>
<td>Trially cyanurate</td>
<td><img src="https://example.com/trially_cyanurate_structure" alt="Trially cyanurate structure" /></td>
<td>Imparts remarkable improvement in heat resistance.</td>
</tr>
<tr>
<td>Crosslinking Monomer</td>
<td>Structure</td>
<td>Application</td>
</tr>
<tr>
<td>------------------------------</td>
<td>-----------------------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
</tbody>
</table>
| Ethyl acrylate               | \[
\begin{array}{c}
    \text{CH}_2=\text{C}--\text{O}--\text{C}_2\text{H}_5 \\
    \text{H} \quad \text{O}
\end{array}
\] | The resulting products are too soft & flexible. It is generally used in conjunction with rigid polyesters. |
| Methyl methacrylate (MMA)    | \[
\begin{array}{c}
    \text{CH}_2=\text{C}--\text{O}--\text{CH}_3 \\
    \text{CH}_3
\end{array}
\] | Results in considerable improvement in weathering characteristics and lower smoke levels. |
| Vinyl toluene                | \[
\begin{array}{c}
    \text{CH}=\text{CH}\_2 \\
    \text{CH}_3
\end{array}
\] | Low volatility but suffers from the defect of delayed crosslinking. |
| \(\alpha\)-methyl styrene    | \[
\begin{array}{c}
    \text{CH}\_3 \\
    \text{C}=\text{CH}\_2
\end{array}
\] | Gives more flexible resins than styrene. It is normally used in potting compositions because of their reduced shrinkage on curing. |
I) **Esterification catalysts**

Esterification catalysts are introduced along with other ingredients in the beginning of the synthesis of unsaturated polyesters in order to reduce the reaction time and temperature. The esterification catalysts which are commonly used are as follows:

- Sulphuric acid, p-toluene sulphonate acid, anhydrous zinc chloride, tannic acid, pyrogallol, sodium hydroxysulphate and primary amines, i.e. aniline, phenylenediamine.

These esterification catalysts function by improving the efficiency of water removal.

II) **Stabilizers**

The function of stabilizers is to avoid gelling of unsaturated polyesters as such or containing crosslinking monomers at room temperature. The most widely used stabilizer is hydroquinone. This is used in the proportion 0.01 to 0.02% based on the weight of resin. The stabilizers for retarding/preventing free radical chain reactions fall into the following classes.

- **a) Inorganic substances**: Sulphur, copper and nitrites
- **b) Polyhydroxy aromatic compounds**: Hydroquinone, catechol, t-butyl catechol and pyrogallol.
- **c) Quinones**: Naphthaquinone, 1, 4-benzoquinone and phenantheraquinone
d) Aromatic nitro compounds: dinitrobenzene (DNB),
    trinitrotoluene (TNT) and
    picric acid

e) Amines: Pyridine,
    Phenyl-β-naphthylamine,
    primary and secondary
    amines (aniline and
    phenylenediamine).

III) Curing Catalysts and Accelerators

One of the valuable properties of polyester resins is
their ability to transform readily from the liquid state to
tough, hard and thermoset structure. This is achieved by the
addition of a chemical compound known as curing
agent/catalyst/initiator. The function of a catalyst is
activated by a compound called accelerator/activator.

In general, curing catalysts can be broadly classified
as "cold setting" and "hot-setting". There is a wide range
of compounds which can be used as catalysts and
accelerators and are listed in Table 4.

1.3 Synthesis of Unsaturated Polyesters

Polyesters are prepared by the dry method or azeotropic
method by following 1, 2 or 3-step processes.

The "Melt condensation" is rapid, continuous and does
not require removal of water and has been developed
recently. In this method, isophthalic acid and maleic
### TABLE 4: CATALYSTS AND ACCELERATORS FOR UNSATURATED POLYESTERS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Curing temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Catalyst/initiator</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diaroyl peroxide (Benzoyl peroxide, BPO)</td>
<td>$\text{Ph} \cdot \text{C} \cdot \text{O} \cdot \text{O} \cdot \text{C} \cdot \text{Ph}$</td>
<td>Critical temperature is 70°C</td>
</tr>
<tr>
<td>Diacyl peroxides (Diacetyl Peroxide)</td>
<td>$\text{H}_3\text{C} \cdot \text{C} \cdot \text{O} \cdot \text{O} \cdot \text{C} \cdot \text{CH}_3$</td>
<td>Elevated temperature</td>
</tr>
<tr>
<td>Dialkyl peroxides (di-t-butyl peroxide)</td>
<td>$(\text{CH}_3)_3 \cdot \text{C} \cdot \text{O} \cdot \text{O} \cdot \text{C} (\text{CH}_3)_3$</td>
<td>Critical temperature is 100°C and is used when long pot life is desired</td>
</tr>
<tr>
<td>Alkyl hydroperoxides (t-butyl hydroperoxide)</td>
<td>$(\text{CH}_3)_3 \cdot \text{C} \cdot \text{OOH}$</td>
<td>-</td>
</tr>
<tr>
<td>Peracids (Peracetic acid)</td>
<td>$\text{CH}_3 \cdot \text{C} \cdot \text{COOH}$</td>
<td>-</td>
</tr>
<tr>
<td>Aralkyl hydroperoxides (Cumene hydroperoxide)</td>
<td>$\text{Ph} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{OH}$</td>
<td>Critical temperature is 100°C but often used in conjunction with BPO at 70°C.</td>
</tr>
<tr>
<td>Compound</td>
<td>Structure</td>
<td>Curing temperature</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>---------------------------------------</td>
<td>-----------------------------------------</td>
</tr>
<tr>
<td>Peresters (t-butyl perbenzoate)</td>
<td>[\text{Ph} \cdot \text{C} \cdot \text{O} \cdot \text{C} \cdot \text{Me}_3]</td>
<td>Critical temperature is 90°C</td>
</tr>
<tr>
<td>Lauroyl peroxide</td>
<td>[\text{C}<em>{11} \text{H}</em>{23} \cdot \text{C} \cdot \text{O} \cdot \text{O} \cdot \text{C} \cdot \text{C}<em>{11} \text{H}</em>{23}]</td>
<td>Medium temperature</td>
</tr>
<tr>
<td>Mixed peroxides</td>
<td></td>
<td>Room temperature</td>
</tr>
<tr>
<td>derived by the oxidation of ketones</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[methyl ethyl ketone peroxide] (MEKP)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>and cyclohexanone peroxide (CHP)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b) Accelerator/activator</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lauroyl mercaptan</td>
<td>[\text{C}<em>{12} \text{H}</em>{25} \cdot \text{SH}]</td>
<td>Acts in conjunction with EPO at room temperature</td>
</tr>
<tr>
<td>Cobalt naphthenate</td>
<td></td>
<td>Acts with hydroperoxides such as MEKP and CHP. Little or no reactivity with peroxides.</td>
</tr>
<tr>
<td>Tertiary amines (Dimethyl amine, diethylamine and diethyl-p-toluidine)</td>
<td></td>
<td>Specifically with peroxides.</td>
</tr>
</tbody>
</table>
anhydride/acid are reacted first to form polyanhydride which, in turn, is reacted with an excess of propylene/ethylene oxide to produce polyester. In other azeotropic method, solvent such as xylene is used at the time of esterification reaction to facilitate the removal of water easily.

The polyesters are generally prepared by 1- and 2-step processes. In "1-step" process, all reactants i.e. acid, glycol and unsaturated acid/anhydride are reacted at a time and condensation reaction is carried out either in the presence of catalyst or without catalyst. In this process, higher temperature of the reaction not only increases random distribution of unsaturated and saturated acids but also converts maleic to fumaric configuration. It is also reported that unsaturation > 13% is lost if unsaturated acid is treated with diols at higher temperatures in '1-step' process. As a result, a number of available sites for crosslinking with styrene or other crosslinking monomer are also lost. The reaction may be shown as below

\[
\text{G} + \text{IP} + \text{MA} \rightarrow -\text{IP-G-MA}/\text{FA-G-MA}/\text{FA-G-MA}/\text{FA-G-MA}/\text{FA-G-IP-G-} \quad \ldots \text{eqn (7)}
\]

where -G = Glycol Moiety

MA/FA = Maleic/fumaric acid moiety

IP = Isophthalic acid moiety
In "2-step" polyesterification process, a polyester is prepared by reacting aromatic acid/anhydride with the entire quantity of diol to produce low molecular weight product. This is then treated with unsaturated acid/anhydride at low temperature. The low temperature transesterification gives a product of regular structure because second step does not tend to scramble the order which is already built in. In addition, the reaction of maleic acid/anhydride in the 2nd step results in unsaturated portions at the end of the resin chain, which impart better heat resistance, flexibility and a more regular structure.

This reaction can be shown as below:

\[
\text{Glycol (G) } + \text{ Acid (IP)} \quad \downarrow
\]

\[
\overset{\text{G-IP-G-IP-G}}{\text{MA}} \quad \downarrow \quad \overset{\text{MA}}{\text{MA/FA-G-MA/FA-G-IP-G-IP-G-MA/FA-G-MA/FA-G- ... Eqn(8)}}
\]

The "3 Step Polyesterification Process" has recently been patented by Agrawal et.al and novel unsaturated polyesters synthesised with the use of this process, possess a unique combination of two contradictory properties i.e. higher elongation and lower NG absorption or better chemical resistance.

In "3-step" process, an aromatic acid is generally
first reacted with the entire quantity of glycol and condensation is carried out to achieve desired acid value. Then aliphatic acid is reacted with this product in the second step and condensation is again continued to achieve desired acid value. Finally, in the third step, unsaturated acid/anhydride is reacted with "2nd step" product to achieve final product. e.g.

\[
\begin{align*}
G + \text{IP} & \\
\rightarrow & \\
\sim G-\text{IP}-G-\text{IP}-G & \ldots \text{First step} \\
\rightarrow & \\
\sim G-\text{DA}-G-\text{DA}-G-\text{IP}-G-\text{IP}-G-\text{DA}-G-\text{DA}-G & \ldots \text{Second step} \\
\rightarrow & \\
\sim \text{MA/FA-G-MA/FA-G-DA-G-DA-G-IP-G-IP-G-DA-G-DA-G-MA/FA-G} & \ldots \text{eqn (9)}
\end{align*}
\]

where DA = Dibasic acid Moiety

1.4 Quality Control

Quality control is one of the most important aspect of synthesis of unsaturated polyesters in order to produce uniform and good quality product. Following measures may be adopted for quality control while preparing polyester resins.
i) **Raw Materials**

While selecting and using raw materials, their purity (assay), melting/boiling points and other impurities etc. are tested. The preference is always given to the indigenous and low cost materials provided they conform to their respective specifications.

ii) **Duplication of Reaction Conditions**

This is one of the most important aspect in order to avoid batch to batch variation i.e. to produce uniform quality of the final product. The following points are strictly maintained while running the reaction

(i) Maintenance of desired temperature at the time of reaction

(ii) Continuous and slow stirring throughout the reaction

(iii) Completion of reaction without any break i.e. preferably in one go.

iii) **Acid Number**

The acid number is the most important parameter and is used to monitor the polyesterification reaction during the synthesis/manufacture of unsaturated polyesters. It is determined at regular intervals. In addition to acid number, amount of water liberated, viscosity are other important parameters which are measured during the course of reaction in order to keep its track.
1.5 Characterization

The characterization of unsaturated polyesters may be done in the following manner:

A. Characterization of Uncured Polyesters

(i) Characterization of virgin polyester
- Acid value
- Viscosity
- Molecular weights and their distribution

(ii) Characterization of styrenated polyester
- Gel time and exotherm peak temperature
- Viscosity

B. Characterization Of Cured Unsaturated Polyesters

The cured unsaturated polyesters are generally characterized for various properties. In order to obtain most favourable properties of any cured resin, it is important to achieve maximum crosslinking. The important among them are

i) Tensile strength and % elongation

ii) Cross-link density

iii) Heat deflection temperature (HDT)

iv) Vicat softening temperature

v) Glass transition temperature (T_g)

vi) Heat resistance or Thermal stability

A. Characterization of Uncured Polyester

Acid Value

Acid value of a polyester is defined as the number of milligrams of KOH required to neutralize 1 gm of resin. It
is generally kept between 10 to 50 depending on requirement. It is extensively reported in the literature\textsuperscript{38} that acid number of a polyester is related to number average molecular weight ($M_n$) whereas the viscosity to weight average molecular weight ($M_w$). Polyesters consist of a number of molecular chains having different chain lengths. If the polyesterification reaction continues, number of terminal carboxyl groups slowly decreases and molecular chains becomes longer i.e. number of terminal carboxyl and hydroxyl groups slowly decrease as the molecular chains become longer during polyesterification reaction and that is why, the course of reaction is followed by determining the number of these end groups. If acid value of polyesters made in a series is same, the number average molecular weight ($M_n$) is also same. With the use of this concept and the concept of molecular weight per unsaturated group, a number of properties like gel time, exotherm peak temperature, elongation, tensile strength etc. may be explained.

**Viscosity**

Viscosity of a fluid is a measure of its resistance to flow caused by its 'internal friction' and depends upon the shear rate at which it is measured. The viscosity of resins is usually measured with a rotating spindle instrument such as Brookfield Viscometer and is highly temperature dependent. In general, following relationships exist between molecular structure and viscosity of resins.
i) Long chain glycol based polyesters have lower viscosity than short chain glycol based polyesters.

ii) The substitution generally results in decrease in viscosity but viscosity does not necessarily decrease in direct proportion to the length of substituted chain.

iii) The increase in viscosity is proportional to the molecular weight of starting materials.

**Molecular Weights and Their Distribution**

The molecular weights of polymers are generally expressed as the average of the molecular weights of all the molecules present in them. The most commonly expressed molecular weights are number average molecular weight ($\bar{M}_n$) and weight average molecular weight ($\bar{M}_w$).

The number average molecular weight ($\bar{M}_n$) is defined as the total weight of all solute species divided by the total number of moles present i.e.

$$\bar{M}_n = \frac{\sum_{i=1}^{i=n} M_i N_i}{\sum_{i=1}^{i=n} N_i} \quad \text{Eqn. (10)}$$

where

- $N_i$ = number of moles of solute of species $i$
- $M_i$ = Molecular weight of species $i$
- $M_i N_i$ = Actual weight of species $i$
It is highly sensitive to the presence of small number of fraction of low molecular weight macromolecules. It is determined by membrane osmometry, cryoscopy and end group analysis, which take into consideration number of molecules present.

The weight average molecular weight ($\overline{M}_W$) is defined as

$$\overline{M}_W = \frac{\sum_{i=1}^{n} N_i M_i^2}{\sum_{i=1}^{n} N_i M_i}$$

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 weight of the solute. The fractional precipitation and thin layer chromatographic methods have also been used for the determination of molecular weights and their distribution. The most powerful and rapid technique for resin fractionation and determination of molecular weight distribution is by gel permeation chromatography (GPC). This involves a column packed with particles of an inert crosslinked gel network. The polymer sample is dissolved in a solvent whose polarity is similar to that of the gel, usually tetrachloroethylene (THF), and is introduced into the column. The column is also eluted with the same solvent. The extent to which each molecular species is able to diffuse into the gel network, determines its elution time. Polymer concentration in the outflowing
solution is determined by the difference in refractive index between the polymer solution and the solvent.

(ii) Characterization of styrenated polyester

Gel time and Exotherm Peak Temperature

Gel time ($G_t$), and exotherm peak temperature ($E_{pT}$) are important properties of unsaturated polyesters from the angle of their processing and use. This is defined as the time corresponding to sudden buildup of viscosity (known as gelling) of specified weight of resin at a definite temperature after adding known percentage of accelerator and catalyst. The gel time is measured by Gelation Timer whereas $E_{pT}$ is measured by a laboratory thermometer, during gel time determination. The knowledge of $G_t$ is useful at the time of application of unsaturated polyesters and may be altered by varying the percentage of accelerator/catalyst and also temperature.

B. CHARACTERIZATION OF CURED STYRENATED UNSATURATED POLYESTERS

i) Tensile Strength and % Elongation

Tensile strength and % elongation are most important mechanical properties. These are measured by ASTM method using Instron machine. The knowledge of these properties is useful at the time of selection of unsaturated polyesters for various applications.

ii) Crosslink Density or Degree of Cure

The crosslink density which determines the ultimate
properties such as rigidity, flexibility etc. of cured resins depends on various parameters such as the nature of the resin, its functionality, nature of curing agent and distance between the reactive groups etc. For example, crosslinking density is increased not only by increasing functionality of the reacting molecules but also by decreasing the distance between the functional groups. A comprehensive study of the relationship between the resin structure and physical properties has been reported by Burhans et al.\textsuperscript{43}

The crosslinking density is determined by a thermomechanical analyser (TMA). A uniform sheet of cured polyester resin of thickness 2 to 3 mm is placed on a holder below the plunger and the extent of penetration obtained by applying different forces is recorded. From the slope of graph, $\Delta L/L$ versus force $F$ (in grams) [where $L$ is the initial thickness and $\Delta L$ is the decrease in the thickness of the sample], crosslinking density ($Ve/V$) is calculated in the following manner

$$\frac{Ve}{V} = \frac{F/A}{RT[\alpha - \frac{1}{\alpha^2}]}$$ \hspace{1cm} \text{Eqn.(12)}$$

where $F =$ Force (in grams)

$A =$ Area of Probe

$R =$ Gas constant

$\alpha = 1 + \epsilon$ (where $\epsilon = \frac{\Delta L}{L}$)
iii) **Heat Deflection Temperature**

The heat deflection temperature \(^{44}\) (HDT) is a guide to determine the optimum cure cycle and in general, indicates the extent of crosslinking for ascertaining the effect of curing temperature. It is desirable to plot cure time divided by HDT against cure time for various temperatures. If HDT is independent of the curing temperature, within the range of temperatures under consideration, all lines so plotted coincide, but if the HDT is dependent on curing temperature, the lines differ in their slopes\(^{45}\).

It is determined by ASTM method\(^{44}\). A test specimen (rectangular bar) of cured resin, supported at each end, is loaded in the middle with a weight designed to give a uniform fibre stress of 264 psi. The sample is then immersed in silicone oil bath with a temperature control and deflection measuring dial indicator. The temperature of the oil bath is raised at a rate of 20°C/min. HDT is recorded as a temperature of the oil bath when the test bar has deflected by 0.25% mm under a uniform fibre stress.

iv) **Vicat Softening Temperature**\(^{46}\)

It is also an important property of polymers and is defined as the temperature at which the flat ended needle of 1 mm circular cross-section, penetrates the specimen to a depth of 1 mm under a uniform fibre stress using a selected rate of temperature rise. It is measured by a method similar to HDT.
v) **Glass Transition Temperature**

Glass Transition Temperature \((T_g)\) is one of the properties that dictates the possible uses for a polymer. There are several structural characteristics that affect the \(T_g\).

\(T_g\) is defined as the temperature or a narrow range of temperature below which an amorphous polymer is in a glassy state and above which it is rubbery. It is obtained from a curve of specific volume as a function of temperature. The specific volume-temperature curve has an abrupt change in the slope at \(T_g\). Below \(T_g\), molecular motions are frozen and there is not sufficient thermal energy to allow segments of molecular chains to move as a whole. At \(T_g\), increase in thermal energy becomes sufficient to allow the movement of relatively large molecular segments which can jump from one position to another by rotation about carbon-carbon bonds\(^{47}\).

The most convenient method for \(T_g\) determination is by differential thermal analysis (DTA). This technique, which has been fully described in the literature\(^{48,49}\), consists of heating material under test and inert reference material, side by side, under identical conditions and continuously recording the temperature difference \((\Delta T)\) between the two materials. Any exothermic or endothermic process occurring in the sample is recorded as a positive or negative peak in the thermogram.
\( T_g \) detects the extent and nature of crosslinking of cured resin and is also used as a measure of its thermal stability. \( T_g \) is, now-a-days, replacing HDT as a method of evaluating and comparing different polymer systems.

vi) **Heat Resistance or Thermal Stability**

The heat resistance or thermal stability of cured polyesters has assumed increasing importance over the last few years, reflecting the growing use of these resins in rockets and high performance aircrafts. The heat ageing studies seeking to compare various systems are often carried out by the prolonged heating of samples at a fixed temperature in an oxidising atmosphere. The "change in weight" is taken as a measure of thermal stability.

Thermogravimetric analysis gives a more reliable indication of the thermal stability of polymers, together with the kinetics and overall activation energy of the degradation reaction. DTA has also been extensively used to study thermal degradation of polyesters.

1.6 **Curing Mechanism of Polyesters**

The curing of unsaturated polyesters is based on the "free radical mechanism" and involves following steps:

a) Initiation

b) Chain Growth or Propogation

c) Chain termination

During initiation, free radicals are formed in the resin medium and initiate the curing process. The rate of
formation of these free radicals largely determines the rate of polymerization. The free radical polymerization is often very rapid and once initiated, chain formation being terminated only when the molecules are no longer active.

The general formula of organic peroxides is R.O.O.R' and its thermal decomposition with the help of an accelerator at room temperature is essentially homolytic cleavage of -O-O-bond to give two free radicals RO and OR.

**Curing Reactions**

A. Benzoyl Peroxide (BPO) releases two free Radical at 90°C

\[
\text{PhC.O.O.C.Ph} \xrightarrow{90^\circ C} 2\text{Ph.C.O}^* \\
\text{Eqn(13)}
\]

B. Benzoyl peroxide also releases free radical with lauroyl mercaptan at room temperature.

\[
\text{PhC.O.O.C.Ph} + \text{C}_{12}\text{H}_{25}\text{SH} \rightarrow \text{Ph.C.O}^* + \text{PhCOOH} + \text{C}_{12}\text{H}_{25}\text{S} \\
\text{Eqn(14)}
\]

C. Organic peroxides or hydroperoxides such as methyl ethyl ketone (MEK) peroxide releases free radicals with cobalt naphthenate in the following manner.

\[
\text{R.O.OH} + \text{Co}^{++} \rightarrow \text{RO}^* + \text{OH}^- + \text{Co}^{+++} \\
\text{Eqn(15)}
\]

\[
\text{R.O.OH} + \text{Co}^{+++} \rightarrow \text{RO.O}^* + \text{H}^+ + \text{Co}^{++} \\
\text{Eqn(16)}
\]
This cycle continues till all the hydroperoxide or peroxide decompose into free radicals. These free radicals attack and add onto the double bonds of the crosslinking monomer resulting in activated molecules which, in turn, attack double bonds present in the polyester backbones. This continues till the whole mass gets converted into a solid three dimensional network as shown in Eqn.6.

If nitro bodies such as 2-nitrodiphenylamine (2-NDPA), trinitrotoluene (TNT) and dinitrotoluene (DNT) are present in propellants, and unsaturated polyesters are allowed to cure in their contact, nitro bodies interfere with the polymerization process of these polyesters. This results in incomplete curing of polyesters and leads to weak bonds between propellant and polyesters. The nitrobodies interfere like

\[
\begin{align*}
AR \cdot N^\equiv O + 2 R \cdot (\text{FREE RADICALS}) \\
\downarrow
\end{align*}
\]

\[
\begin{align*}
AR-N-O^- + R^* \\
\downarrow
\end{align*}
\]

\[
\begin{align*}
AR-NO + RO \cdot R \quad \text{---- Eqn.(17)}
\end{align*}
\]

The study of reaction kinetics indicates that oxygen of nitro group is the actual point for retardation of polymerization process. This is supported by IR studies where presence of nitroso compounds is observed.
1.7 ROCKET PROPELLANTS AND THEIR INHIBITION

The main function of a propellant is to impart motion to a projectile. For space exploration and military applications both solid and liquid propellants are used. However, from the point of view of safety, reliability, simplicity and long storage life, solid propellants are preferred over liquid propellants.

The solid rocket propellants are classified as:

i) Double-base (DB) Propellants
ii) Composite Propellants (CP)
iii) Composite Modified Double-base Propellants (CMDB)

i) Double Base Rocket Propellants

These are also called as colloidal or homogeneous propellants and have nitroglycerine (NG) and nitrocellulose (NC) as their principal ingredients. Some ingredients may be added in small proportions to serve as stabilizers, non-explosive plasticizers, coolants, lubricants, opacifiers and burning rate modifiers or other additives to impart desirable properties to the propellants. The well known ballistic modifiers are finely powdered metal oxides, metallic salts of organic acids like lead salicylates, lead acetyl salicylate, lead 2,4-dihydroxy benzoate, lead-2-ethylhexanoate or lead stearate etc. These propellants are processed into the desired shape by two methods: Extrusion and Casting. They find wide applications in anti-tank missiles.
ii) **Composite Propellants**

These are also called as heterogeneous propellants and are essentially made up of a binder in which inorganic oxidizer is dispersed. The binder which also acts as the fuel, constitutes the matrix that retains solid oxidizers such as ammonium nitrate, ammonium perchlorate and governs largely the physical properties of propellants. Unlike DB propellants, plasticizer is not explosive in nature in composite propellants, but only fuel based on hydrocarbons. For higher specific impulse ($I_{sp}$), a higher oxidizer loading is necessary but this adversely affects the mechanical properties of the propellant. The best and most commonly used oxidizer is ammonium perchlorate (AP). A number of binder such as carboxy terminated polybutadiene (CTPB), hydroxy terminated polybutadiene (HTPB), lactone terminated polybutadiene (LTPB) and butadiene-acrylic acid-acrylonitrile terpolymer (PBAN) etc. are now available and the choice depends upon the availability, cost, ease of processing and specific impulse required\cite{58, 59}. The $I_{sp}$ can be substantially increased by incorporating aluminium or magnesium powder in the propellant formulation. Aluminium powder (18 to 22%) gives higher $I_{sp}$. The compounds such as ferric oxide, prussion blue, aluminium dichromate, copper chromite, ammonium sulphate etc. are used as ballistic modifiers for composite propellants. These propellants are manufactured by
casting technique similar to DB propellants. India's four stage Satellite Launch Vehicle-3 (SLV-3) which put ROHINI Satellite in orbit on July 18, 1980, utilized a composite propellant based on butadiene-acrylic acid-acrylonitrile terpolymer (PBAN) for the first and second stage motors and lactone terminated polybutadiene (LTPB) based composite propellant for the third and fourth stage motors.

iii) **Composite Modified Double-Base (CMDB) Propellants**

CMDB propellants combine both DB and composite propellants. In this type of propellants, crystalline oxidiser (ammonium perchlorate) and metallic fuel (aluminium powder) are incorporated in DB matrix (NG-NC matrix) making these propellants highly energetic. They are characterised by high energy output (specific impulse, $\approx 260-270$) and higher combustion temperatures ($\approx 3500^\circ K$). These are manufactured by Advance Casting Powder (ACP) technique or slurry cast techniques (SCT).

Considering overall functional requirements of rockets/missiles, rocket propellant technologists desire the propellant to burn in a definite pattern. This is achieved by applying polymeric materials over the propellant surface, which do not readily burn. This inert polymeric material is called "**Inhibitor**" or "**Inhibiting Material**" and process of their application is known as "**Inhibition**".
There are three main types of pressure-time (P-t) profiles corresponding to the mode of burning of propellant. The mode of inhibition is governed by the desired pattern of pressure-time (P-t) profile namely, neutral, progressive and regressive as depicted in Fig.2. This may be exemplified by the inhibition of a tubular propellant grain. If, it is inhibited on both ends only, it possesses a constant burning surface during combustion which results in a neutral pattern of burning (Fig.2A). If, in addition to the ends, the entire outer periphery of the propellant is also inhibited, the pattern of burning is progressive (Fig.2B). If, however, the propellant is inhibited on the inner surface, in addition to the ends, the pattern of burning is regressive, (Fig.2C). Therefore, the performance of the rocket/missile depends not only on the propellant grain and its geometry but also on the mode of inhibition of the rocket propellants.

Depending upon the requirement, rocket propellant technologists choose a propellant system and accordingly, develop inhibiting material/inhibitor. Considering the characteristics of an ideal inhibitor, inert organic polymeric materials are considered best for this purpose. The choice of an inhibiting material depends upon a number of factors such as the type of propellant, availability and physical properties of inhibiting material with special reference to ballistic requirements.
FIG. 2-MODE OF INHIBITION AND CORRESPONDING PRESSURE - TIME PROFILES
1.8 **Characteristics of Inhibitors**

i) Chemical compatibility with the double-base rocket propellants i.e. not promoting its deterioration.

ii) Absorption of NG, stabilizer and plasticizer from propellants should be as small as possible. This is to ensure that the physical properties and ballistic performance during its stipulated storage life are not adversely affected to the extent vitiating their serviceability. Its ingredients should have high molecular weight in order to eliminate their migration. It should not preferably warrant the use of a barrier layer in between the propellant and the inhibitor.

iii) Should have high softening point. Its physical properties should closely match with that of propellant.

iv) High level of "tear strength" or "peel off strength" or "bond strength" is also desirable.

v) Should have a low density and volatile content.

vi) Should have effective ablative and thermal insulating characteristics as evidenced by reproducible high "burn through time" and self-heating characteristics.

vii) Should not exhibit "corrosivity" characteristics when placed in intimate contact with steel and aluminium alloy motors. Should possess compatibility with varnish applied to inner surface of motor tubes in some calibers.

viii) In case of inhibitors in the form of a moulding powder,
it should lend itself formed without requiring to be heated beyond +100°C to permit direct application in bulk production by conventional production techniques. Should form a proper weld with propellant on bonding and resist delamination/cracking or interface separation due to self-stressing. On the other hand, in case of liquid inhibitor, ability to bond itself onto the propellant on direct application by casting, without the aid of an adhesive, is considered as an added attribute.

ix) Ability to produce a sufficient degree of translucent finish is desirable, in order to permit visual inspection after inhibition.

x) Low cost of production and indigenous availability of ingredients.

xi) Ingredients should retain desired physical state when stored in original packing under controlled conditions of temperature humidity.

xii) Recycling of rejects to a maximum extent without fall in properties.

xiii) The functional test viz. successful performance of inhibited propellants during static evaluation at ambient, cold (-40°C) and hot (+50°C) temperatures after conditioning. This is a most important test and even if a polymer meets all other requirements but fails in this test, it cannot be used for inhibition of rocket propellants.
1.9 **TESTING OF INHIBITORS**

The properties such as gel time and exotherm peak temperature, tensile strength and percent elongation, bond strength with propellant, nitroglycerine/plasticizer absorption, heat resistance, flame retardance and ballistic evaluation of inhibited propellants after conditioning over a wide range of temperatures, constitute an important criterion to evaluate suitability of a polymer as an inhibitor. These properties are assessed by the methods already reported in the literature\(^7,9,20,60,61\) and described in Chapter 2.

1.10 **TECHNIQUES OF INHIBITION**

Inhibition is generally carried out by one of the techniques indicated below:

i) **Sleeve Technique**

A sleeve of definite size and shape is extruded out of plasticized ethyl cellulose and fixed on the propellant using ethyl cellulose adhesive cement.

ii) **Tape Winding Technique**

Alternately, ethyl cellulose tape of uniform thickness and width is wound and bonded around the propellant with the help of a suitable adhesive cement either manually or on lathe machine.

iii) **Casting Technique**

The sleeve and tape techniques, are not suitable for large sized grains and grains having complicated geometry.
The ease of operation in the casting technique attracted wide interest for inhibition of rocket propellants by this technique. The propellant surface for inhibition is prepared either by rubbing with an emery paper or by giving a light cut on a lathe machine, the dust being removed with a brush. This propellant grain is placed in a mould and the inhibitor containing catalyst and accelerator is poured around the grain and is allowed to cure. In case of inhibition of the propellant containing nitroodies such as dinitrotoluene (DNT), trinitrotoluene (TNT) and 2-nitrodiphenylamine (2-NDPA) etc., interpositioning of barrier layer, resistant to ingress of nitroglycerine and other nitroodies, is necessary. This is done by applying coatings of rigid and fast gelling polymeric materials to the propellant by brushing, before final assembly of the inhibition mould.

iv) **Case-Bonding Technique**

In order to accommodate more quantity of propellant and as a result, to increase payload/range of the rocket/missile, case bonding technique is preferred and is more common in composite propellants where migration of plasticizer is not considered so significant. In case bonded propellants, insulation to inside of the motor is achieved by applying thick layers of filled rubbers to the interior of the motor by methods such as casting, automated trowelling, dipping or
spray process. In order to provide a strong bond between insulating material and propellant, it is necessary to add a thin liner which is cured to a tacky state just before casting of propellant into the motor. The propellant is then cast in the insulated and lined motor and is cured as per the optimized curing cycle.

1.11 NITROGLYCERINE MIGRATION

The development of inhibitors/inhibiting materials for DB and CMDB rocket propellants has always been a difficult problem because of the presence of nitroglycerine (NG) in these propellants and its subsequent migration from propellants towards inhibitors\textsuperscript{62,63}. This is regarded as one of the most important physical factors which affects the useful Service life of a solid propellant rocket motor. A low NG migration between propellant and inhibitor is generally beneficial to the adhesive bond between them\textsuperscript{62} but extensive migration results in several problems enumerated below:

i) Excessive NG migration from rocket propellants to inhibitor affects propellant ballistics i.e. gives lower performance and at the same time, increases combustion of inhibitor, resulting in exposure of more surface than desired.

ii) The inhibitor swells and becomes mechanically weak and soft due to excessive NG migration. This results in bond
failure defeating the very purpose of inhibition of rocket propellants.

iii) Excessive NG migration also results in delamination/separation of inhibitor from propellant.

iv) The migration of NG also leads to coning of burning propellants especially in an end-burning propellant. The coning arises from an increased burn-rate at the side walls of a propellant because of an increase in NG content as a result of its migration.

These problems are serious and as a result, a number of physical and chemical methods have been reported to reduce the problem of NG migration.

1.12 CONCEPTS AND EVIDENCES

There are a number of concepts which explain NG migration qualitatively and accordingly, methods to prevent/reduce the extent of its migration, have been reported in the literature. These can be briefly described as follows:

(i) "Force of Attraction" Concept: This is based on the fact that the electrostatic force of attraction between NG, a major ingredient (≈ 25-40%) of DB and CMDB propellants and inhibitor operates and leads to migration of NG from rocket propellant to inhibitor. This may be exemplified in a very lucid manner by taking an unsaturated polyester as an inhibitor. The structures of NG and an unsaturated polyester
(inhibitor) based on a diol, unsaturated acid/anhydride (maleic anhydride, MAn) and an aromatic acid (phthalic acid) are shown in Fig.3. It is clear from the structures that an unsaturated polyester has a number of electron donor sites, whereas NG has a number of electron acceptor sites. As a result, electrostatic force of attraction operates between them and leads to migration of NG from propellant to unsaturated polyester (inhibitor). The introduction of electron acceptor groups such as chloro/bromo groups in phthalic acid and condensation with glycol and maleic anhydride results in a chloro/bromo unsaturated polyester (Fig.3), capable of reducing electrostatic force of attraction between propellant and inhibitor. This ultimately results in the reduction of NG migration from propellant to inhibitor. Similarly, if a crosslinking monomer with chloro/bromo i.e. chloro/bromo styrene is used in place of styrene or chlorinated/brominated plasticizer is used in conjunction with styrene, NG absorption of the cured products come down considerably.

This is supported by the work of several investigators who have proved that the introduction of electron acceptance groups such as chloro/bromo groups in aromatic/aliphatic/unsaturated acid or glycol giving chloro/bromo polyester or addition of chlorinated/brominated crosslinking monomers or plasticizers
FIG. 3 - STRUCTURES OF NITROGLYCERINE AND UNSATURATED NON HALO/HALO POLYESTERS
considerably reduces the extent of NG migration from propellant to inhibitor. It has been reported from our laboratory that NG absorption of a rigid polyester (PR-3)\(^8\) and semi-rigid unsaturated polyester (SRUP-2)\(^{17}\) after 96 hours is \(\approx 2\%\) whereas in case of chloropolyester\(^{15}\) (CP-1), it is only 0.45\% (Table.5). It has also been reported\(^{15}\) that NG absorption decreases as chlorine percent increases in polymers (Table-8).

(ii) "Polymer Weight" Concept: Polymers which are generally used for inhibition of rocket propellants are macromolecules with loose structures. NG being small in size, can easily seep into the structures of polymers. The NG migration comes down on addition of fillers to polymers.

French scientists\(^{66,67}\) have suggested that fillers, when added to inhibitors, reduce NG migration by physically blocking the pores of loose structures of polymers used as inhibitors. On the other hand, Agrawal et.al\(^{11,12,68,69}\) are of the view that the extent of NG migration is lowered on addition of fillers to polymers because of their dilution effect on polymers and it is directly proportional to the quantity of polymer present in the filled systems i.e. polyester/chloro polyester-filler systems. Further, it goes on decreasing with the decrease in the quantity of polymer in filled polymer systems.
**TABLE 5 : NG MIGRATION ($M_\infty$) FOR NONHALO AND HALO POLYESTERS**

<table>
<thead>
<tr>
<th>HALO POLYESTER</th>
<th>NG MIGRATION ($M_\infty$) AFTER 14 DAYS, %</th>
<th>NON HALO POLYESTER</th>
<th>NG MIGRATION ($M_\infty$) AFTER 14 DAYS, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP-1</td>
<td>0.45</td>
<td>PR-3</td>
<td>2.3</td>
</tr>
<tr>
<td>FCPM-90</td>
<td>6.71</td>
<td>FUP-9</td>
<td>10.0</td>
</tr>
<tr>
<td>FCPM-90(I)</td>
<td>18.21</td>
<td></td>
<td>--</td>
</tr>
</tbody>
</table>

**TABLE 6 : CHLORINE PERCENT AND NG ABSORPTION DATA OF CHLOROPOLYESTERS**

<table>
<thead>
<tr>
<th>CHLOROPOLYESTER</th>
<th>THEORETICAL CHLORINE CONTENT, %</th>
<th>NG MIGRATION AFTER 14 DAYS, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP-2</td>
<td>12.9</td>
<td>Specimen shattered into pieces due to excessive NG migration</td>
</tr>
<tr>
<td>CPM-2</td>
<td>13.7</td>
<td>6.7</td>
</tr>
<tr>
<td>CPM-4</td>
<td>14.6</td>
<td>5.4</td>
</tr>
<tr>
<td>CPM-6</td>
<td>15.8</td>
<td>3.1</td>
</tr>
<tr>
<td>CPM-8</td>
<td>16.2</td>
<td>2.5</td>
</tr>
<tr>
<td>CPM-9</td>
<td>17.8</td>
<td>2.0</td>
</tr>
<tr>
<td>CP-1</td>
<td>18.5</td>
<td>0.45</td>
</tr>
</tbody>
</table>
The NG absorption of unfilled and filled semi-flexible unsaturated polyester resin-4 and chloropolymers blend-4 are already reported in the literature and it has been shown that the NG absorption decreases with the increase of filler in unsaturated polyester/chloropolyester-filler systems. The kinetics of migration of NG through these systems has already been reported. The diffusion coefficient (D) and NG migration at infinite time (M_\infty) are also given in Table-7 and Table-8. It is seen from the data that M_\infty regularly decreases as the quantity of filler increases. This provides ample evidence that the NG migration depends on the quantity of resin and as it decreases from polyester/chloropolyester-0% filler to polyester/chloropolyester-80% filler, NG migration also decreases. On the contrary, D data do not follow any specific trend. If the fillers, on their addition to polymers, reduce NG migration by physically blocking the pores, it is expected that migration through the filled resin systems will be retarded with the increase in the filler quantity leading to regular decrease in the value of D. The fact that D does not regularly decrease with the increase in the quantity of fillers also indirectly supports the validity of proposition of Agrawal et.al.

(iii) "Crosslink density" Concept: The NG absorption data for a wide range of polymers i.e. thermosets, thermoplastics
### Table 7: Diffusion Coefficient (D) and M<sub>∞</sub> for Semi-Flexible Unsaturated Polyesters

<table>
<thead>
<tr>
<th>Filler</th>
<th>Diffusion Coefficient (D) cm&lt;sup&gt;2&lt;/sup&gt;/s x 10&lt;sup&gt;-8&lt;/sup&gt;</th>
<th>NG transferred at equilibrium (M&lt;sub&gt;∞&lt;/sub&gt;) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.11</td>
<td>2.5</td>
</tr>
<tr>
<td>20</td>
<td>7.19</td>
<td>1.50</td>
</tr>
<tr>
<td>40</td>
<td>5.11</td>
<td>1.20</td>
</tr>
<tr>
<td>60</td>
<td>4.16</td>
<td>1.0</td>
</tr>
<tr>
<td>Filler</td>
<td>CPB-4-Alumina trihydrate</td>
<td>CPB-4-Antimony trioxide</td>
</tr>
<tr>
<td>--------</td>
<td>---------------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>%</td>
<td>Diffusion coefficient (D)</td>
<td>Diffusion coefficient (D)</td>
</tr>
<tr>
<td></td>
<td>cm²/s x 10⁻⁸</td>
<td>cm²/s x 10⁻⁸</td>
</tr>
<tr>
<td>0</td>
<td>3.41</td>
<td>3.41</td>
</tr>
<tr>
<td>20</td>
<td>3.27</td>
<td>2.58</td>
</tr>
<tr>
<td>40</td>
<td>4.37</td>
<td>3.09</td>
</tr>
<tr>
<td>60</td>
<td>4.78</td>
<td>3.89</td>
</tr>
</tbody>
</table>
and rubbers is given in Table-9. It is evident that the reduction in the mobility of the polymer chains resulting from crosslinking (thermosets) or high degree of crystallinity (linear thermoplastics) is accompanied by a marked decrease in the ability of NG molecules to diffuse into polymers i.e. more compact nets oppose migration of NG. A wide range of unsaturated polyesters, novel unsaturated polyesters and chloropolyesters—rigid, semi-rigid, flexible, semi-flexible and very flexible, have been studied in this laboratory\(^{8-9,15-17,20}\) and it has been established beyond doubt that if the chain length of polyester backbones is less, NG absorption is small whereas if chain length of polyester backbone is long, NG absorption is high\(^{9,15-17,73}\). The crosslinking density and NG absorption data for chloropolyesters based on tetrachlorophthalic anhydride, maleic anhydride and mixed glycols (in different molar proportions) are given in Table-10, which also proves the validity of this concept. The interpositioning of barrier coats (barrier coats are usually of polymers possessing high crosslink density) between propellant and inhibitor in order to prevent/reduce NG migration from propellant to inhibitor, supports this concept. The polymers absorbing low amount of NG appear to be very promising for inhibition of DB and CMDB rocket propellants but may or may not be suitable in view of other considerations such as bond strength (BS) with
### Table 9: Absorption of Nitroglycerine by Polymers

<table>
<thead>
<tr>
<th>Low (&lt; 10%)</th>
<th>Moderate (= 10-20%)</th>
<th>High (&gt; 20%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyolefine</td>
<td>Ethyl cellulose(EC)</td>
<td>Cellulose acetate</td>
</tr>
<tr>
<td>Substituted Polyolefine</td>
<td>Flexible epoxide</td>
<td>Very flexible Polyester (PVF)</td>
</tr>
<tr>
<td>Polyolefine copolymers</td>
<td>CTPB polymer No.2</td>
<td>Filled flexible Polyester (PFF)</td>
</tr>
<tr>
<td>Modified PVA copolymer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flexible epoxide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyurethane rubber</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neoprene rubber</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polystyrene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyamide</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Note: The table lists polymers and their absorption properties for nitroglycerine.*
<table>
<thead>
<tr>
<th>Chloropolyester</th>
<th>Crosslink density ((V_e/V)), moles/cm(^3)</th>
<th>NG Migration, (M_\infty) % (after 14 days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP-2</td>
<td>---</td>
<td>Specimens shattered into pieces</td>
</tr>
<tr>
<td>CPM-2</td>
<td>(2.6 \times 10^4)</td>
<td>6.3</td>
</tr>
<tr>
<td>CPM-4</td>
<td>(3.2 \times 10^4)</td>
<td>4.75</td>
</tr>
<tr>
<td>CPM-6</td>
<td>(4.3 \times 10^4)</td>
<td>1.78</td>
</tr>
<tr>
<td>CPM-8</td>
<td>(7.7 \times 10^4)</td>
<td>1.06</td>
</tr>
<tr>
<td>CP-1</td>
<td>(9.6 \times 10^4)</td>
<td>0.9</td>
</tr>
</tbody>
</table>
propellant, high elongation, tensile strength and compatibility with propellant. The elongation and NG migration are interrelated properties and if one is higher, the other is also higher and vice versa. It is only recently that the Novel Unsaturated Polyester-7(III) abbreviated as NUP-7 (III) i.e. NUP(III)-A, NUP(III)-B, NUP(III)-C and NUP(III)-D synthesized by "3-Step Polyesterification Process", possess lower NG absorption and higher elongation - a combination of two contradictory properties.

1.13 PREVENTION/REDUCTION OF NG MIGRATION

These concepts i.e. "Force of Attraction" concept, "Polymer Weight" concept and "Crosslink Density" concept, explain the phenomenon of NG migration from DB and CMDB rocket propellants in a lucid manner and accordingly, methods have been suggested to prevent/reduce NG migration. It may therefore, be considered as an additional evidence in support of these concepts in addition to the above. The following methods suggested for this purpose are:

(i) Use of Chloro Resins and Compounds in Place of Conventional Resins/Compounds: The NG migration of chloro/bromo unsaturated polyesters, unsaturated polyester - (50% styrene monomer + 50% chloro/bromo styrene monomer), unsaturated polyester - (styrene monomer + chlorinated/brominated plasticizer) systems etc. is less as compared to conventional unsaturated polyesters and therefore, conventional resins have been replaced by
halogenated resins. SNPE, France prefers use of halogenated polyesters for inhibition of DB rocket propellants.

(ii) **Use of Inorganic Fillers:** The use of inorganic fillers such as alumina trihydrate, antimony trioxide, lithophane, titanium dioxide, asbestos powder etc. in inhibitors reduces NG migration from propellant to inhibitor and thus, supports "Polymer Weight" concept. The fillers being cheap, this method of reduction of NG migration appears to be very attractive but it is restricted to applications where opacity is not objectionable. It also increases the cost of inspection of inhibited rocket propellants because x-ray radiography of propellants is essential if propellants are opaque.

(iii) **Use of Barrier Coats:** The interpositioning of a barrier coat, between a propellant and inhibitor is, sometimes essential to resist NG migration. Most of the barrier layers absorb a small amount of NG and are not completely impermeable to NG/plasticizer. At least a 5 fold increase in storage life has been reported by Stenson with the use of barrier coats between propellant and main inhibitor. The fast curing resins, rigid and semi-rigid polyesters, possessing high crosslink density, are generally used for this purpose if a very flexible unsaturated polyester is used for inhibition of DB & CMDB rocket propellants. Similarly, a number of other polymeric
materials—urethane prepolymer\textsuperscript{74}, poly (dimethyl siloxane)\textsuperscript{75}, butyl rubber\textsuperscript{76}, carboxy terminated polybutadiene (CTPB) and hydroxy terminated polybutadiene (HTPB) rubbers\textsuperscript{77} have also been patented for this purpose.

The genesis behind the application of a barrier coat is to prevent migration of NG or nitrobodies before curing of inhibitor otherwise it interferes with the curing process of inhibitor resulting in incomplete cure and weak bond between propellant & inhibitor.

These methods of prevention of migration of NG from DB and CMDB propellants are considered very useful and selection of the method, depends upon the overall requirements of the propellant-inhibitor system. These methods of prevention of NG migration appear to be attractive but introduce some other disadvantages to the system. The introduction of electronegative groups such as chloro or bromo groups, impairs mechanical properties of inhibitor adversely. On the other hand, incorporation of fillers introduces problems like settling of filler before curing, opacity etc. The application of barrier coats and subsequent inhibition depends, to a large extent, on the judgement, expertise and skill of the individual carrying out inhibition and thus makes it cumbersome for bulk production.

The phenomenon of NG migration has been dealt in a qualitative manner so far and attempts have recently been
made by Vergnaud et al.\textsuperscript{70-72,78} to study the kinetics of NG/DEP migration which is likely to offer better insight to understand the NG migration.

1.14 **HALO POLYESTERS** :

Halo polyesters are defined as the polyesters when one of the ingredients i.e. glycol or acid or crosslinking monomer consists of halogens (fluorine, chlorine, bromine and iodine) in their structures.

Lyons\textsuperscript{79} concludes as a result of exhaustive study that on an equal molar basis, the ease of halogen liberation is \( I > Br > Cl > F \) and accordingly, their effectiveness is directly proportional to their atomic weights namely 

\[ F : Cl : Br : I : : 1 : 1.9 : 4.2 : 6.7 \]

The role of halogens is, therefore to increase the total mass of the material which must be vapourised per unit time without an equivalent increase in heat flux from the flame to fuel\textsuperscript{80}.

Of the four halopolymesters, it is very difficult to prepare fluoropolymesters as fluorine binds too tightly to carbon. Even if fluoropolymesters are synthesized, they are not likely to impart flame retardant characteristics as potentially active HF is not released at the appropriate time for functioning as a flame retardant. Several bromopolymesters have also been synthesised\textsuperscript{81,82} and studied in detail including their flame retardant characteristics.
However, these could not become popular because of their uncertain curing characteristics. Further, chloropolyesters are less effective than bromopolyesters which is due to the fact that, C-Br bond is weaker than C-Cl bond, which helps to generate Br radicals easily and thus interfere with the flame in a more favourable manner during combustion. Also, effective burning agent HBr is liberated at a higher concentration and at a lower temperature range as compared to HCl. On the other hand, polyesters based on iodine have not yet been reported in the literature and are likely to be too unstable to be used as flame retardants. Further, their use will be limited on the basis of their high cost and their instability to heat and light. The literature survey reveals that most of the investigations deal with the halo polyesters based on chlorine and bromine.

1.15 CHEMISTRY, SYNTHESIS AND CURING MECHANISM OF HALO POLYESTERS

The chemistry, synthesis and curing mechanism of halo polyesters is generally similar to that of unsaturated polyesters except that the time required for their synthesis is higher as compared to unsaturated polyesters. Curing of halo polyesters is also similar to that of unsaturated polyesters except that the time required for curing of these polyesters is more in case of chloropolyesters and is still more for bromopolyesters.
1.16 **RAW MATERIALS OF HALO POLYESTERS**

The principal ingredients required for the synthesis of halopolyesters are as follows:

i) **Halo glycols**:

The halo glycols are not commercially available. Some research work with the use of halo glycols/their derivatives for the synthesis of halo polyesters has been reported in the literature and are listed in Table-11.

ii) **Halo Acids or Anhydrides**:

A large number of dibasic halo acids/anhydrides have been reported for the synthesis of halo polyesters. The most common halo acids/anhydrides along with their structures are listed in Table-12.

iii) **Halo Crosslinking Monomers**:

These are used to copolymerize with the unsaturation present in the polyester chains. These halo crosslinking monomers also act as solvents for diluting viscous halopolyesters/polyesters, prior to their use similar to styrene monomer. Major halo crosslinking monomers are given in Table-13.

1.17 **COMPARISON OF NONHALO AND HALOPOLYESTERS**

An extensive work reported in the literature on the characterization of unsaturated polyesters and halo polyesters suggests that halo polyesters possess better flame retardance than unsaturated...
<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Dichloro/bromo penta erythritol(^{82})</td>
<td>![Structure for Dichloro/bromo penta erythritol] (x = Cl/Br)</td>
</tr>
<tr>
<td>2. Trichloro/bromo penta erythritol(^{82})</td>
<td>![Structure for Trichloro/bromo penta erythritol] (x = Cl/Br)</td>
</tr>
<tr>
<td>3. Cyclic bromodiol(^{88})</td>
<td>![Structure for Cyclic bromodiol]</td>
</tr>
<tr>
<td>4. 2,3,5,6 tetrachloro phenylene 1,4 diol(^{89})</td>
<td>![Structure for 2,3,5,6 tetrachloro phenylene 1,4 diol]</td>
</tr>
</tbody>
</table>
5. B-B' (4,6 dibromo 1,3 phenylenedioxy) dialkanols$^{90}$

6. Aliphatic diols$^{82}$

7. Halogenated diols$^{91}$

8. Diamine derivative of Polyhalogenated biphenyl$^{92}$

9. Dibromo neopentyl glycol
10. Halogenated polyol \textsuperscript{93}

11. 1-(Pentachloro phenyl) 1,2,5 pentane triol \textsuperscript{82,94}

12. \(\alpha,\alpha'\)-bis (2-hydroxyethoxy)-
    2,3,5,6 tetrachloro p-xylene \textsuperscript{95}

13. \(\alpha,\alpha'\)-bis (2-hydroxyethoxy)
    2,4,5,6 tetrachloro m-xylene \textsuperscript{95}
<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 1,4,5,6,7, 7-hexachloro-bicyclo [2.2.1] hept-5-ene 2,3-dicarboxylic anhydride (chlorendic anhydride)</td>
<td>![Structure 1]</td>
</tr>
<tr>
<td>2. Tetrabromophthalic acid</td>
<td>![Structure 2]</td>
</tr>
<tr>
<td>3. Tetrachlorophthalic acid</td>
<td>![Structure 3]</td>
</tr>
<tr>
<td>4. Tetrachlorobisphenol-A</td>
<td>![Structure 4]</td>
</tr>
<tr>
<td>Name</td>
<td>Structure</td>
</tr>
<tr>
<td>--------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------</td>
</tr>
<tr>
<td>5. Tetrabromobisphenol-A</td>
<td><img src="image" alt="Structure of Tetrabromobisphenol-A" /></td>
</tr>
<tr>
<td>6. 2,3-dicarboxy-5,8-endomethylene-5,6,7,8,9</td>
<td><img src="image" alt="Structure of 2,3-dicarboxy-5,8-endomethylene-5,6,7,8,9" /></td>
</tr>
<tr>
<td>hexachloro-1,2,3,4,4a,5,8,8a-octahydnaphthalene anhydride (chloran)</td>
<td><img src="image" alt="Structure of Hexachloro-1,2,3,4,4a,5,8,8a-octahydnaphthalene anhydride" /></td>
</tr>
<tr>
<td>7. Tetrachloro-p-xylene dichloride</td>
<td><img src="image" alt="Structure of Tetrachloro-p-xylene dichloride" /></td>
</tr>
<tr>
<td>8. Diallyl chlorendate</td>
<td><img src="image" alt="Structure of Diallyl chlorendate" /></td>
</tr>
<tr>
<td>Name</td>
<td>Structure</td>
</tr>
<tr>
<td>------------------------------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>1. 2 chlorostyrene</td>
<td><img src="structure1.png" alt="Structure" /></td>
</tr>
<tr>
<td>2. 2,5 dichlorostyrene</td>
<td><img src="structure2.png" alt="Structure" /></td>
</tr>
<tr>
<td>3. Allyl trichloroacetate</td>
<td><img src="structure3.png" alt="Structure" /></td>
</tr>
<tr>
<td>4. Diallyloxytetrachloro-83 m-xylene</td>
<td><img src="structure4.png" alt="Structure" /></td>
</tr>
<tr>
<td>5. Diallyl chlorendate</td>
<td><img src="structure5.png" alt="Structure" /></td>
</tr>
</tbody>
</table>
polyesters.

The synthesis and characterization of chloro/bromo polyesters and comparison of their effectiveness as flame retardants/heat resistants has been a matter of discussion by a number of investigators\(^\text{81,82,87}\) in the field. A brief account of comparison of their properties is shown in Tables 14-17. The conclusion of their exhaustive study is that bromopolyesters are better flame retardants/heat resistants than chloropolyesters. Nametz\(^\text{82}\) suggested that, at least 25-30% aromatically bound chlorine is needed to impart self-extinguishing properties in polyesters whereas 12-15% bromine is considered enough for the same level of flame retardancy. Further, the addition of compounds such as triethyl phosphate, triallyl phosphate, antimony trioxide, zinc borate and alumina trihydrate etc. impart synergistic effect on both chloro and bromo polyesters.
<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Non halo polyester (PR-3) moles</th>
<th>Halo polyester (CP-1) moles</th>
<th>Method of synthesis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene glycol,</td>
<td>1.4</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>Isophthalic acid,</td>
<td>0.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetrachlorophthalic anhydride,</td>
<td>-</td>
<td>0.5</td>
<td>By &quot;2-Step&quot; polyesterification process</td>
</tr>
<tr>
<td>Maleic Anhydride,</td>
<td>0.66</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Reaction time, hours</td>
<td>20-22</td>
<td>22-25</td>
<td></td>
</tr>
<tr>
<td>Gel time at 40°C, min.</td>
<td>6.0</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td>Theoretical chlorine, %</td>
<td>0.0</td>
<td>18.5</td>
<td></td>
</tr>
<tr>
<td>Styrene, %</td>
<td>25</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Properties</td>
<td>Non halo polyester (PR-3)</td>
<td>Halo polyester (CP-1)</td>
<td></td>
</tr>
<tr>
<td>------------------------------------</td>
<td>---------------------------</td>
<td>-----------------------</td>
<td></td>
</tr>
<tr>
<td>Tensile strength, kg/cm²</td>
<td>300</td>
<td>340</td>
<td></td>
</tr>
<tr>
<td>Elongation, %</td>
<td>8.0</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>Bond strength</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>with DB propellants, kg/cm²</td>
<td>85</td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>Nitroglycerine absorption after 14 days, %</td>
<td>2.5</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>Burning rate, mm/sec</td>
<td>Burns freely</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>Ingredients</td>
<td>Composition</td>
<td>Method of synthesis</td>
<td></td>
</tr>
<tr>
<td>-----------------------------------</td>
<td>-------------</td>
<td>-----------------------------------------</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Non halo polyester [FUP-9] (Moles)</td>
<td>Halo polyester [FCPM-90] (Moles)</td>
<td></td>
</tr>
<tr>
<td>Diethylene glycol,</td>
<td>0.9</td>
<td>0.9</td>
<td>{ }</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>By &quot;2-step&quot; polyesterification process</td>
</tr>
<tr>
<td>Polyethylene glycol, (Mol Wt. 200)</td>
<td>0.1</td>
<td>0.1</td>
<td>{ }</td>
</tr>
<tr>
<td>Isophthalic acid,</td>
<td>0.66</td>
<td>-</td>
<td>{ }</td>
</tr>
<tr>
<td>Tetrachlorophthalic anhydride,</td>
<td>-</td>
<td>0.5</td>
<td>{ }</td>
</tr>
<tr>
<td>Maleic anhydride,</td>
<td>0.5</td>
<td>0.5</td>
<td>{ }</td>
</tr>
<tr>
<td>Reaction time, hours</td>
<td>25</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Gel time at 40°C min.</td>
<td>41.0</td>
<td>29.0</td>
<td></td>
</tr>
<tr>
<td>Theoretical chlorine, %</td>
<td>0.0</td>
<td>14.9</td>
<td></td>
</tr>
<tr>
<td>Styrene, %</td>
<td>25</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>------------------------------------------------</td>
<td>-----------------------------</td>
<td>--------------------------</td>
<td></td>
</tr>
<tr>
<td>Tensile strength, kg/cm²</td>
<td>112</td>
<td>97.8</td>
<td></td>
</tr>
<tr>
<td>Elongation, %</td>
<td>20.0</td>
<td>24.8</td>
<td></td>
</tr>
<tr>
<td>Bond strength, kg/cm² with DB propellants</td>
<td>29.0</td>
<td>49.5</td>
<td></td>
</tr>
<tr>
<td>Nitroglycerine migration after 14 days, %</td>
<td>10.0</td>
<td>3.71</td>
<td></td>
</tr>
<tr>
<td>Burning rate, mm/sec</td>
<td>-</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td>Ingredients</td>
<td>Halo polyester (FCPM-90) Moles</td>
<td>Halo polyester (FCPM-90(I)) Moles</td>
<td>Method of synthesis</td>
</tr>
<tr>
<td>-----------------------------------------</td>
<td>-------------------------------</td>
<td>----------------------------------</td>
<td>---------------------------------------------</td>
</tr>
<tr>
<td>Diethylene glycol,</td>
<td>0.9</td>
<td>0.9</td>
<td>}</td>
</tr>
<tr>
<td>Pol yethylene glycol, (Mol.Wt.200)</td>
<td>0.1</td>
<td>0.1</td>
<td>}</td>
</tr>
<tr>
<td>Tetrachlorophthalic anhydride,</td>
<td>0.5</td>
<td>0.5</td>
<td>}</td>
</tr>
<tr>
<td>Maleic anhydride,</td>
<td>0.5</td>
<td>0.25</td>
<td>}</td>
</tr>
<tr>
<td>Dichloro maleic anhydride,</td>
<td>-</td>
<td>0.25</td>
<td>}</td>
</tr>
<tr>
<td>Reaction time, hours</td>
<td>30</td>
<td>35</td>
<td>}</td>
</tr>
<tr>
<td>Gel time at 40°C min.</td>
<td>25.0</td>
<td>36.5</td>
<td>}</td>
</tr>
<tr>
<td>Theoretical chlorine, %</td>
<td>17.15</td>
<td>20.21</td>
<td>}</td>
</tr>
<tr>
<td>Styrene, %</td>
<td>25</td>
<td>25</td>
<td>}</td>
</tr>
<tr>
<td>Properties</td>
<td>Halo polyester [FCPM-90]</td>
<td>Halo polyester [FCPM-90(I)]</td>
<td></td>
</tr>
<tr>
<td>--------------------------------</td>
<td>---------------------------</td>
<td>----------------------------</td>
<td></td>
</tr>
<tr>
<td>Tensile strength, kg/cm²</td>
<td>80.8</td>
<td>17.00</td>
<td></td>
</tr>
<tr>
<td>Elongation, %</td>
<td>36.33</td>
<td>60.80</td>
<td></td>
</tr>
<tr>
<td>Bond strength, kg/cm²</td>
<td>46.17</td>
<td>9.61</td>
<td></td>
</tr>
<tr>
<td>with DB propellants,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitroglycerine absorption after</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14 days, %</td>
<td>6.71</td>
<td>16.21</td>
<td></td>
</tr>
<tr>
<td>Burning rate, mm/sec</td>
<td>0.388</td>
<td>0.465</td>
<td></td>
</tr>
</tbody>
</table>
## Table 17: Combustion Behaviour of Non Halo and Different Halo Polyesters*<sup>87</sup>

<table>
<thead>
<tr>
<th>Properties</th>
<th>Non Halo polyester based on phthalic anhydride</th>
<th>Chloropolyester based on (TCPAn)</th>
<th>Chloropolyester based on chlorendic anhydride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction time, hrs</td>
<td>16</td>
<td>13</td>
<td>18</td>
</tr>
<tr>
<td>Acid number</td>
<td>43</td>
<td>48</td>
<td>40</td>
</tr>
<tr>
<td>Chlorine, %</td>
<td>0.0</td>
<td>2.3</td>
<td>29.2</td>
</tr>
<tr>
<td>Styrene, %</td>
<td>30.0</td>
<td>30.0</td>
<td>30.0</td>
</tr>
<tr>
<td>Burning rate, mm/sec</td>
<td>Burns freely</td>
<td>0.79</td>
<td>0.18</td>
</tr>
<tr>
<td>Time to flame out, sec</td>
<td>---</td>
<td>180</td>
<td>150</td>
</tr>
<tr>
<td>Self-extinguishing</td>
<td>Burns easily</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>
1.18 **OBJECT OF THE PRESENT WORK**

Unsaturated Polyesters possess a number of unusually valuable properties immediately amenable to use for various applications. The major fields of applications of unsaturated polyesters are lamination, potting, moulding and surface coating. Their use for inhibition of double-base (DB) propellants was mentioned as back as in 1964 in Europe but they did not disclose the type of the unsaturated polyesters used for this purpose. An extensive study of unsaturated polyesters and novel unsaturated polyesters for the inhibition of DB and CMDB rocket propellants has been carried out in this Laboratory in last decade.

Literature survey reveals that no work has been done on "comparative account of various nonhalo and halo polyesters containing diethylene glycol, maleic anhydride, tetrachlorophthalic anhydride, tetrabromophthalic anhydride and phthalic anhydride and effect of different percentage of styrene monomer on them has not been reported as yet. Also, kinetics of NG migration through these nonhalo and halo polyesters, has not been reported as yet. It was, therefore, considered of interest to undertake a comparative study of nonhalo and halo polyesters.

1.19 **PLAN OF PRESENTATION OF THIS STUDY**

The plan of the work have been presented in the following manner:
Chapter I

This chapter deals with the general aspects of nonhalo unsaturated polyesters and halo polyesters viz. their chemistry, applications, historical background, raw materials and methods of their synthesis. Further, chemistry of halo polyesters including their flame retardancy, inhibition of double-base propellants as well as concepts and prevention of NG migration have also been included in this chapter. This is followed by the object and plan of presentation of this study.

Chapter II

In this chapter, details of methods used for the synthesis of nonhalo and halo unsaturated polyesters along with their specifications and source of supply have been given. In addition, methods for characterization of nonhalo and halo polyesters in terms of acid value, viscosity, infrared (IR) spectra, nuclear magnetic resonance (NMR), gel time (Gₜ) and exotherm temperature (Eₚₜ), tensile strength (TS), elongation, thermal conductivity (λ), bond strength (BS) with DB propellants, oxygen index (n), heat resistance and flame retardance have also been explained in detail.

Chapter III

This chapter describes the structural aspects of nonhalo and halo prepolymer/polyesters with the help of IR and NMR, followed by data on their characteristics such as TS,
BS, with DB propellant, $G_\tau$, $E_p\tau$, thermal conductivity, oxygen index, heat resistance and flame retardance for 25% as well as 35% styrene monomer containing nonhalo and halopolyesters. Further, structures of these nonhalo and halo polyesters have also been co-related with different characteristics. The data of static evaluation of DB propellants inhibited with 'CP'35' at ambient temperature is also given in this chapter.

Chapter IV

This chapter reports study of kinetics of nitroglycerine migration through nonhalo and halo polyesters (containing 25% as well as 35% styrene monomer). The diffusion coefficients (D) of NG through these polyesters have been calculated using 'Fick's Law' and their solutions. The concentration profiles which build up at different time intervals and at various locations in the sheet of nonhalo and halopolyesters have also been calculated.
The material presented in this thesis forms subject matter of the following papers

1. All About Unsaturated Polyesters
   Agrawal J.P., Satpute R.S. and Kulkarni K.S.
   Popular Plastics, 30 (8) (1985) 31

2. Comparative Study of Halo and Non halo Polyesters and Their Application For The Inhibition of Double-base Rocket Propellants
   J.P. Agrawal and K.S. Kulkarni

3. Kinetics of Nitroglycerine Migration Through Halo and Nonhalo Polyesters
   J.P.Agrawal and K.S. Kulkarni
   Polymer Bulletin, Japan, 1993 (Communicated)
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