INTRODUCTION

1.1 Use of Oils in Surface Coatings:

Oils have been used for centuries in traditional ways for food, printing inks, lubricants, paints and varnishes etc. The paints and varnishes were mainly used for painting purposes i.e. for decorative purposes. People in those days concentrated mainly on using linseed oil only as it was a drying oil and was available in abundance. The use of oils for making paints was discovered by the Egyptians and later on by Chinese and Indians. In recent past the use of oils from different origins were explored for their use in surface coatings. Afterwards with the development in the science and technology much research work was carried out to eliminate the drawbacks of natural oils and their modified forms were introduced with improved properties.

The natural oils which are used in paints, varnishes and oil modified resins and as plasticizers in nitrocellulose lacquers are obtained from the seeds, nuts of certain plants, trees and from a few species of fish. They are referred to as vegetable and marine oils. These are further classified as drying,
semi-drying and non-drying oils. This classification is related to their ability to dry when spread in relatively thin films and exposed to normal atmospheric conditions.

The drying or changing from a liquid to a solid film is due to absorption of atmospheric oxygen leading to polymerisation. Semi-drying oils do not form satisfactory films at room temperature but these oils may be used in air drying alkyd resins and in stoving finishes. Non-drying oils are not used in air drying finishes and are used as plasticizers or softeners in nitro-cellulose lacquers and in non-oxidising alkyd resins.

**Chemical Composition:**

Vegetable oils are triglycerides of higher fatty acids having predominantly 18 carbon atoms. But those from marine origin like fish oil, etc. have a wider distribution of chain length and varies from C$_{14}$ to C$_{24}$. The fatty acids contained in the oils are saturated and unsaturated. The unsaturated fatty acids may be conjugated or non-conjugated type.

The important unsaturated fatty acids are oleic acids, Linoleic acid, Linolenic acid, eleosteric acid, Licanic acid etc.
Linseed oil which is widely used in surface coatings contains about 55-65% linolenic acid having three isolated ethylenic linkages, Tung oil on the other hand consists of about 80-90% eleostearic acid having three conjugated ethylenic linkages.

The degree and rate of drying of an oil depends on the amount and type of unsaturation present in the oil molecule. The extent of unsaturation is determined by the iodine value of the oil.

1.2 Mechanism of drying of oils:

When a thin film of an oil is applied on any surface the oil film transforms from liquid state to solid state leaving behind a hard transparent film which is insoluble in common solvents.

The oil takes oxygen from air through the unsaturated position and undergoes cross-linking to form a long chain molecules i.e. polymer. It forms the polymer by oxygen activation and hydro peroxide formation. This is known as auto-oxidative polymerization. The unsaturation in oils is towards the middle of the 18 carbon chain of the fatty acid radical and is known as non-terminal unsaturation. Auto-
oxidative polymerization is associated with non-terminal unsaturation and addition polymerization with terminal unsaturation. However addition polymerization may take place between molecules having non-terminal unsaturation.

The naturally occurring oils have definite limitation in drying properties and dried film characteristics. These depend on the following:

1. **Ethylene group**: The average number of ethylene molecules are responsible for the degree of film formation.

2. **Types of Ethylene groups**: Whether they are isolated or conjugated.

3. **Geometric isomers**: Geometric form of ethylene group is responsible for rate of drying properties.

4. **Cross-linking via addition agents**: Reaction takes place through the ethylene group and thus the oil molecules are increased in molecular weight with or no decrease in ethylene functionality.
1.3 **Modification of oils for use in Surface Coatings**

The modification of natural drying and semi-drying oils with a view to improve their film forming properties has been practised for so many years as the film from an unmodified oil is liable to show a number of deficiencies described below:

1) They are slow in drying.
2) The dried film is not hard enough.
3) The dried films have poor water resistance.
4) The films possess less gloss than a resin film.
5) They have poor alkali and acid resistance.
6) The oil films are not durable on exterior surfaces unless they are protected from u.v. light absorption by using an opaque pigment.
7) They possess less mechanical strength than resin film.
8) Their films generally yellow on aging specially in the case of oils rich in linolenic acid.

It is a well known fact that the conjugated unsaturation imparts better drying and faster bodying characteristics to an oil than the equivalent amount of non-conjugated unsaturation. This fact provides an incentive to develop a method for changing drying,
semi-drying and other non-conjugated oils to their conjugated isomers. The modification of the oils can be done in two ways:

1) Modification of glyceride part
2) Modification of fatty acid part

a) **Glyceride Part**: The glycerol part may be replaced by higher alcohols like pentaerythritol or sorbitol, etc. which produce faster drying oils having improved properties. The above mechanisms can be carried out by following methods:

1) Oil splitting and re-esterification
2) Alcoholysis or ester interchange

b) **Fatty acid part**: The other modification may be made in the fatty acid radicals which include the following treatments:

1) Heat treatment
2) Dehydration
3) Isomerisation
4) Segregation
5) Oil splitting and reesterification
6) Chemical treatment
7) Copolymerization
(1) **Heat treatment of Oil** :- The oldest and most conventional method for the modification of oils is polymerisation by heat treatment under various conditions. The operating conditions and the rate of reaction depend to a great extent on the degree and the type of unsaturation present in the oil. Heat treated oils are used in varnishes and enamels because they are superior to raw oils because a considerable degree of polymerisation assumes two stages to the reaction, first the migration of the double bonds from the isolated to the conjugated configuration and in the second stage, the conjugated system so formed is assumed to react with double bond in another molecule according to Diels-Alder pattern forming a cyclohexanising compound.

(a) **Boiled oil** :- The process of oil boiling has as its object the production of a drying oil that will dry in twenty four hours or less when exposed to the air in a thin film. It is therefore, applicable only to those oils that give smooth films without being subjected to a special thermal treatment, i.e. oils rich in linolenic or linoleic acids. Linseed oil is the most important raw material. Soyabean oil is also used occasionally.
Boiled oil is a viscous liquid of a colour ranging from pale yellow to reddish yellow or brown. It is perfectly clear and bright. The odour is characteristic and peculiar. Boiled oil is used by painters to mix with white or coloured paste paints without the further addition of driers.

(b) **Blown Oil** :- The blown oil produced commercially, mainly for use in surface coatings, are generally made at temperature below 140°C. No driers are used in this process. A plentiful supply of air is introduced in such a way as to cause the oil to foam, thus presenting a large surface to oxidation. The temperature chosen for the process has a marked effect upon the rate of bodying of the oil and the colour and acid value of the final product. The acid value tends to be lower at the higher temperatures, owing to the greater loss of volatile acids, but the colour is adversely effected beyond to a certain point, and the best results are obtained at about 120°C. Blown linseed oil can be produced having a specific gravity slightly greater than unity, and a very high viscosity, being only just fluid at ordinary temperatures. Blown oil is a good wetting agent,
and a small quantities are sometimes added to raw oil to aid the dispersion of pigment pastes. Blown linseed oil and soyabean oil have excellent gloss and flow properties and find applications in certain enamels and flat paints for architectural purposes. Blown fish oil may be used if it is refined to eliminate the objectionable odour.

(c) **Heat bodied oils (Stand oil)** :- Heat bodied oil is obtained by heating the refined oil to a predetermined temperature and holding at this temperature for the time required to produce a specified increase in viscosity.

The time required to heat body an oil will depend on the type of oil, the viscosity required and the temperature. In general the drying oils body more quickly than the semi-drying oils. There is no significant increase in viscosity when the non-drying oils are held at high temperature. It will be apparent that the rate of bodying is related to the degree and type of unsaturation in these oils. The increase in viscosity is due to polymerization at the points of unsaturation. The rate of polymerization increases with temperature therefore, it would appear desirable to body the oils at the highest possible temperature.
However, other factors must be considered since the flash point of the oils is about 320°C, care must be taken to avoid fires. This danger could be averted to a certain extent by heating in closed kettles with a blanket of inert gas over the oils, but oils are organic compounds, are susceptible to decomposition at high temperature. The decomposition products are free fatty acids and acrolein from the triglycerides and some dark coloured compounds. These lower the value of the oil for many paint purposes therefore, the maximum bodying temperature which can be used, is governed by the degree of decomposition which can be tolerated.

During the heat treatment of oil the following changes take place:

1. The acid no. increases with time of heating and the increase is greater as the temperature is raised. This indicates that the free acids are produced by thermal decomposition, but there are also some free acids formed as the result of oxidative decomposition. These will be reduced when the oil is bodied under vacuum because there is less air in the system. Since some of the acids are volatile they will be removed by the vacuum.
(2) The iodine no. decreases with increase in viscosity indicating polymerisation or cross linking at the points of unsaturation.

(3) The mol.wt. increases, suggests that the polymers are mostly dimers with a small % of trimmers. There will also be some residual monomer.

(4) The colour of the oil is darker as the temperature of bodying is increased. Pale colour is obtained with the vacuum bodied oils because there is less oxidation under vacuum.

The thermal polymerisation of drying oils produce essentially the addition type of polymer by the formation of crosslinking between the unsaturated section of the fatty acids radicals. If the thermal polymerisation is continued long enough, it will result in an insoluble, infusible gel because oil molecule is a triglyceride, having three fatty acid radicals and a potential functionality of 3.

The type and degree of unsaturation in the fatty acid radical effect the rate of thermal polymerisation and the type of gel structure formed. The rate of polymerisation is measured conveniently by increase of viscosity with time of heating. The non-drying oils
such as cotton seed and coconut show no significant increase in viscosity when maintained at (315°C) for prolonged periods of time. The rate of thermal polymerisation increases and the bodying temperature may be decreased as the non-conjugated unsaturation increases from soyabean to fish oil, but there is rapid increase in rate of polymerisation and a sharp drop in bodying temperature when the type of unsaturation is changed from non-conjugated to conjugated.

(2) **Dehydration:** Dehydration of non-drying castor oil to produce a drying oil is a well known reaction. The dehydration of castor oil is a simple process, and the many modifications used by different manufacturers have as their object the production of pale-coloured material of low acid value and good drying properties. Castor oil is the only oil that can be dehydrated because it contains hydroxyl group. When the oil is heated in presence of some catalyst under controlled conditions, water is split off at the hydroxyl group. This results in removal of hydrogen atom and the introduction of a second double bond adjacent to the original double bond, consequently drying properties are acquired by the oil. It finds its principal application in the protective coating industry but it is also used though to a lesser extent in the manufacture of printing inks and linoleum. The important properties are rapidity of bodying, film
durability, flexibility and colour retention.

(3) **Isomerization** :- Isomerization is a process by which a normal oil that contains two or more isolated bonds is converted to a conjugated oil by shifting the positions of the double bonds from isolated to conjugated position. The reaction differs from conjugation of castor oil in that no water is formed and no additional double bond is created. It is a well known fact that the conjugated unsaturation imparts better drying and faster bodying characteristics to an oil than the equivalent amount of non-conjugated unsaturation. This fact provides an incentive to develop a method for changing drying, semi-drying and other non-conjugated oils to their conjugated isomers.

(4) **Segregation or fractionation of oil** :-

Segregation means the separation of an oil into two or more portions that differs substantially in composition and properties especially in degree of unsaturation. Fish oils are well known for their high degree of unsaturation but because of presence of significant amounts of saturated fatty acids, leave after tack in their films after drying. Such oils can be advantageously improved
by segregation. The principle underlying the prevailing method is that a suitable solvent may have a relative solvency for the various oil constituents that differs with change of temperature. The most notable processes are, the furfural process and the solexol process. Solvent segregation is adoptable to all of the notable oil but has bot been extensively used with them. It is most effective with fish oil because it has the widest disparity between the composition and solubility of the saturated and unsaturated constituents.

(5) Oil splitting and re-esterification :- In this process the oil is first split into glycerol and fatty acids. The later are then esterified with selected polyols to produce a new oil which is known as reconstituted oil.

Reconstituted oils are made by replacing glycerol in natural oils with a different polyol i.e. penta erythritol, sorbitol, dipentaerythritol etc. while glycerol contains two primary hydroxyls and one secondary hydroxyl, penta erythritol has four hydroxyls which can react with four molecules of fatty acids producing thereby greater complexity of the molecules. This results in
faster drying, better hardness and faster heat bodying. The most promising application of this process seems to be to tall oil fatty acids, since one of the two operations would be eliminated and tall oil acids are not expensive.

(6) Chemical treatment:- Chemically modified oils are widely used in surface coatings. The modifying chemicals are reacted with the molecular structure of the oils, of course, and form new coating materials of generally improved performance characteristics compared with the raw and processed oils.

(a) Maleinised oils:- Maleinised oils form an interesting groups of water soluble binders for use in surface coatings. Drying oils with dienoic or trienoic unsaturation form adducts with maleic anhydride. When maleic anhydride is heated with unsaturated oils it reacts differently according to whether the oils is conjugated or not. With a conjugated oil such as tung oil or D.C.O, the product is formed primarily by Diels-Alder reaction.

\[
\begin{align*}
R-\text{CH}=\text{CH}-\text{CH}=\text{CH}-R' + \text{CH} = \text{CH} & \rightarrow \\
R-\text{CH} & \text{CH} = \text{CH}-\text{CH}-R'
\end{align*}
\]
With a non-conjugated oil, the hydrogen atom of the active methylene group in \( \alpha \)-position to the double bond adds to the double bond of maleic anhydride resulting in the formation of a substituted succinic anhydride compound.

\[
R-\text{CH}=\text{CH}-\text{CH}_2-R' + \text{CH} = \text{CH} \rightarrow \]

\[
R-\text{CH}=\text{CH}-\text{CH}-\text{CH}=\text{CH}-R'
\]

This treatment is relatively simple and the products have definite advantages over the original natural oil. These oils are known as maleic treated oils or maleinised oils. The increased complexity and unsaturation of maleic treated oils explain their improved properties. The process is most profitably applied to the slow drying oils with isolated double bond. Maleinised oils are at present of significant interest of air drying oil for water based coatings.

(b) **Epoxidised oils:** Unsaturated oils or their fatty acids can be converted into oxidised products, having an oxyrane ring by reaction with
various per-acids, such as per-benzoic, performic and peracetic acids.

Mono and diunsaturated fatty acids and their esters including the glycerides are converted to epoxy derivatives by oxidation under mild conditions with the above organic per-acids, thus generating the per acids in situ.

\[
\text{CH}_3(\text{CH}_2)_7\text{CH} = \text{CH}(\text{CH}_2)_7\text{COOH} + \text{CH}_3\text{COOH}
\]

\[
\text{Oleic acid} \quad \text{Peracetic acid}
\]

\[
\text{CH}_3(\text{CH}_2)_7\text{CH} - \text{CH}(\text{CH}_2)_7\text{COOH} + \text{CH}_3\text{COOH}
\]

9,10 epoxy stearic acid

Trienoic and more highly unsaturated compounds react in a somewhat abnormal fashion yielding oxyrane derivatives only in part.

The epoxidised oils can react with polyfunctional compounds having active hydrogen atoms such as polyamines, polyamides etc. to yield resinous products in the same manner as the epoxy resins.
Epoxidised soya oil is the most important commercial product. Its chief application is as a stabilizer in polyvinyl chloride compositions or for other halogens containing polymers. The oil also, at the same time serves as a plasticizer for these polymers. The other important fields for the use of epoxidised oils are as latent polyols for the preparation of alkyd type resins and as starting materials for the preparation of polyether compounds.

(c) Urethane oils:- The introduction of urethane linkage into the oil molecules increases the hardness and abrasion resistance. To prepare urethane oils, the oil is converted into monoglycerides, after the preparation of monoglycerides and diglycerides 2,4 toluene, di-isocyanate (TDI) is added at lower temperature to get urethane oils.

\[
2 \text{CHOOCR} + R(NCO)_2 \rightarrow \text{CH}_2\text{OOCR} \text{CHOOCR} \text{CH}_2\text{OOCR}
\]

Urethane oil
The amount of isocyanate added for modification of oils is equivalent to or slightly less than the amount of free hydroxyls present in ester, curing takes place through the unsaturated bond of fatty acid radical of the molecule which is activated by paint drier.

Urethane oils are completely miscible with petroleum spirit, even at high dilution, and the lower viscosity products have excellent film building properties owing to the small amount of thinner required to reduce them to brushing consistency. When exposed to air as a thin film, urethane oils dry rapidly to give a tack free coating with a high resistance to water and dilute alkalis.

(7) **Copolymerisation** :- The physical and chemical properties of the oils for use in organic finishes can also be modified with incorporation of resin to the oil. The resins improve the characteristic of the oil films in the following manner:

1. They reduce the drying time of the oil.
2. They increase the hardness of the oil film.
3. They improve the water and chemical resistance of the oil film.
4. They improve the gloss of the oil film.
5. They increase the mechanical strength and durability of oil film.

The resins can be incorporated into the oil by gum running or by copolymerisation of oil with some unsaturated organic monomer. The monomers most commonly used are styrene, α-methyl styrene, cyclopentadiene etc.

![Chemical structures of Styrene, α-methyl styrene, and Cyclopentadiene]

Styrene  α-methyl styrene  Cyclopentadiene

Among the various materials available for copolymerising the oil, styrene is perhaps the most promising as an ingredient of surface coatings due to its easy commercial availability and low cost as compared to other monomers. The oils copolymerised with styrene are known as styrenated oils. Resins obtained by the polymerisation of styrene are colourless completely neutral materials, having good electrical properties, and a high resistance to water, alkalis and aqueous chemicals generally.
Styrene copolymerisation of tung oil was studied by 'Brunner & Tucker' and 'Peterson' by bulk and solvent methods and it was reported that a better product was obtained by the solvent method of copolymerisation, since a certain degree of homopolymerisation of styrene during the bulk polymerisation resulted in a hazy product. Several workers studied copolymerisation of D.C.O. with styrene and reported improvements in drying and film characteristics of the oil. Studies on unsaturated oils having fatty acids with isolated double bonds revealed that a certain degree of conjugated unsaturation was essential in order to have a clear and homogenous product and for the purpose of styrenation they had to incorporate certain quantities of oils having conjugated unsaturation.

Valuable characteristics of styrenated oils are as follows:

1. Rapid initial drying by solvent.
2. Low acid value and good stability towards pigment.
3. Moderate wetting properties by providing an excellent suspension medium for pigments.
4. Pale colour, good colour retention and absence of dirt retention.
5. Good water resistance.
6. Good insulating properties.

Due to the above qualities the styrenated oil have been used extensively in gloss, semi-gloss and flat wall paints, anticorrosive paints for structural steel and ships etc. They are also used in paper and fabric impregnations, leather finishing industry, printing ink, electrical insulating materials etc.

Styrenated alkyds of different oils were also prepared by different workers and it was reported that styrene copolymerisation after the preparation of alkyd gave a better product than obtained by preparing the alkyd of the styrenated oil.

1.4 Less known or Minor Oil Seeds:

There is a vast potential of minor oil seeds or less known oil seeds which if, properly tapped can substantially augment the overall supply of vegetable oils and can help in bridging the wide gap between their demand and supply. India is a major oil seeds producing country and oilseeds occupy an important
position in the Indian economy. The increasing demand for vegetable oils for edible purposes have necessitated the utilization of minor oils in place of conventional oils currently used in industries after suitable processing and modifications. There are as many as hundred of oilseed bearing plants in the Indian forests out of which only Mahua, Neem, Karanja, Kusum and Sal have been commercially exploited. The yield of minor oilseeds varies from tree to tree and year to year. The technological problems associated with the processing of minor oilseeds have by and large been resolved and now the organised sector has also started using these oils.

The industrial development of a country depends primarily upon its capacity to research and utilise its own raw materials, by intensive research, collection, modification and exploration of its natural wealth. India has unlimited natural wealth and is blessed with abundance of oilseed bearing trees and plants which grow widely and wildly. Many surveys have been made in the past by many organisations like Khadi & Village Industries Commission, Indian Central Oilseeds Committee etc. to explore this hidden wealth. Considering the oil shortage the need for achieving further exploitation of less known oilseeds cannot be over
emphasised. Unfortunately inadequate organisational set up for timely collection of minor oilseeds, lack of adequate transport, storage facilities collection of oilseeds before the monsoon sets in and the undesirable characteristics of their oils like dark colour, unpleasant odour and taste, high cost of processing and refining of these oils act as major hinderences in the exploitation of these oilseeds. Agencies for collection of the minor oilseeds and suitable technological innovations for their better utilisation will lead in getting more and more oil under this class.

Although, a number of minor oil seeds have been analysed during the last 2-3 decades yet all of them can not be deemed as industrially important. Therefore, out of all the known minor oilseeds, a selection can be made of those which have sufficient economic importance because of their possible availability in large quantities for industrial application. Some of the unusual minor oilseeds of commercial importance are

- Rayana-seed (Amoora rohituka),
- Malkangi-seed (Celastrus paniculatus),
- Tobacco-seed (Nicotiana tabacum)
- Gokhru-seed (Xanthium strumarium)
- Babul-seed (Acacia arabica)
- Niger-seed (Guizotia abyssinica)
Rubber-seed (Hevea brasiliensis), and
Pindara-seed (Trewia nudiflora)

Most of these above oils are semi-drying and are rich in linoleic acid and thus have a potential for utilization after due processing and modification in surface coating industry. Although a number of semi-drying oils such as Niger seed oil, Tobacco seed oil, Teak oil, Rubber seed oil and Babul oil etc. are available indigenously but out of all these, Niger seed has sufficient economic importance because of their possible availability in large quantities and hence is ideally suited for utilisation in surface coatings by copolymerising it with styrene.

Niger seed (Guizotia abyssinica):

It is an erect, annual, smooth herb, 1-6 ft. high cultivated widely as an oilseed crop in India and parts of East Africa. In India, it is grown extensively in M.P., Hyderabad, Orissa, Bombay and Mysore and to some extent in Bihar, Andhra Pradesh, Madras and Bhopal. The chief areas of cultivation in different states are Chindwara, Jabalpur, Bilaspur and Buldana district in M.P. Gulbarga, Nanded, Bir, Bidar, Osmanabad district in Hyderabad, Ratnagiri, Poona, Ahmadnagar, Dharwar and Satara district in Bombay, Bellary, Chickmagalur and Shimoga district in Mysore,
Chota Nagpur district in Bihar, Srikakulam and Vishakapatnam district in Andhra and Coimbatore district in Madras.

Niger grows well on the black and light soils of Deccan, it is grown either pure or mixed with ragi, horse gram, cotton and to certain extent groundnut. The tree grows widely in India. The production of niger seed oil and cake in different states are given in Table 1.1.

Table-1.1

<table>
<thead>
<tr>
<th>State</th>
<th>Quantity crushed</th>
<th>Yield of oil%</th>
<th>Output of oil</th>
<th>Output of cake</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bombay</td>
<td>110.8</td>
<td>33</td>
<td>36.6</td>
<td>74.2</td>
</tr>
<tr>
<td>Hyderabad</td>
<td>67.2</td>
<td>24</td>
<td>16.1</td>
<td>51.1</td>
</tr>
<tr>
<td>M.P.</td>
<td>844.8</td>
<td>25.7</td>
<td>217.1</td>
<td>627.7</td>
</tr>
<tr>
<td>Mysore</td>
<td>12.1</td>
<td>28.1</td>
<td>3.4</td>
<td>8.7</td>
</tr>
<tr>
<td>Orissa</td>
<td>128.4</td>
<td>31.0</td>
<td>39.8</td>
<td>88.6</td>
</tr>
<tr>
<td>Others</td>
<td>242.0</td>
<td>33.0</td>
<td>80.5</td>
<td>161.5</td>
</tr>
<tr>
<td>Total</td>
<td>1,405.3</td>
<td></td>
<td>393.5</td>
<td>1,011.8</td>
</tr>
</tbody>
</table>
NIGER SEED (Guizotia abyssinica)
Niger seed resembles sunflower seed in shape, but is much smaller in size (3.9-4.7 mm long). Number of seeds per gram are (234-295) and are quite black. It bears a fairly thick adherent seed coat (20% of the wt. of seed) and can be stored for a year or so without deterioration. The characteristics of niger seed are given in Table 1.2.

Table-1.2

<table>
<thead>
<tr>
<th>Characteristics of Niger seed (Wt.%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>7.8</td>
</tr>
<tr>
<td>Protein</td>
<td>19.40</td>
</tr>
<tr>
<td>Fatty Oil</td>
<td>31.3</td>
</tr>
<tr>
<td>Carbohydrates (by difference)</td>
<td>39.47</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.05</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.18</td>
</tr>
<tr>
<td>Ash</td>
<td>1.80</td>
</tr>
</tbody>
</table>

The oil content of niger seed varies from 30 to 50%. The oil resembles very closely the safflower oil. The alkyd prepared from the niger seed oil is extremely pale, non-yellowing and dries quickly. The oil has not been seriously exploited except for edible purposes. This oil deserves all the encouragement. The oil content reaches the maximum value of the end of about 45 days after the flower opening. The synthesis of
lower saturated acid precedes that of higher and unsaturated acids, during the later stages of ripening the iodine value increases from 90 to 126.

The bulk of niger seed produced in India is crushed for the extraction of oil. In part of Hyderabad, Mysore and Bombay, the seed is used for making chutneys, it is also fried and eaten. Niger seed oil is extracted either by cold or hot pressing or by a combination of both.

Niger seed oil is pale yellow or orange in colour with little odour and a pleasant nutty taste. The physico-chemical characteristics of Niger seed oil as per American Oil Chemists Society (AOCS) are given in Table 1.3.

**Table-1.3**

<table>
<thead>
<tr>
<th>The AOCS value for Niger seed oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Sp. gravity at 25°C</td>
</tr>
<tr>
<td>2. Refractive index at 25°C</td>
</tr>
<tr>
<td>3. Iodine value</td>
</tr>
<tr>
<td>4. Saponification value</td>
</tr>
<tr>
<td>5. Unsaponifiable matter %</td>
</tr>
<tr>
<td>6. Acid value</td>
</tr>
<tr>
<td>7. R.M. value</td>
</tr>
<tr>
<td>8. Polenske value</td>
</tr>
<tr>
<td>9. Colour 1&quot; cell</td>
</tr>
<tr>
<td>10. Free fatty acid</td>
</tr>
</tbody>
</table>
The fatty acid composition of Niger seed oil are given in Table 1.4.

Table 1.4
Fatty acid composition of Niger seed oil (wt.\%) 

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Myristic (including capric and lauric)</td>
<td>1.7-3.4</td>
</tr>
<tr>
<td>2</td>
<td>Palmitic</td>
<td>5.0-8.4</td>
</tr>
<tr>
<td>3</td>
<td>Stearic</td>
<td>2.0-4.9</td>
</tr>
<tr>
<td>4</td>
<td>Oleic</td>
<td>31.1-38.9</td>
</tr>
<tr>
<td>5</td>
<td>Linoleic</td>
<td>51.6-54.3</td>
</tr>
</tbody>
</table>

Niger seed oil is a semidrying oil used to a limited extent as a paint oil compared to linseed oil, it has poor drying properties but by suitable heat treatment and incorporation of driers such as lead, manganese and cobalt soaps, the drying properties can be improved. The incorporation of red lead with processed oil gives compositions suitable for outdoor coatings. Raw oils containing driers give tack free films within 2 hr. when dried at 100°C.

1.5 Refining and Bleaching:

1.5.1 Refining: Refining is done in the oil to remove free fatty acids, phosphatides, mucilaginous materials or other gross impurities
in the raw oil. The main object of refining is to remove the objectionable impurities in the raw oil with the least possible damage to the glycerides and with the least possible loss of oil. The main methods of refining are given below:

1) Acid refining: - Refining by means of acids is generally more effective in removing break constituents from oils and also attacks the colouring matter to some extent. Before the introduction of methods of refining by means of alkalies, acid refined linseed oil was widely used for the manufacture of paints, and oleoresinous and lithographic varnishes. Several reagents have been proposed for this process, but in practice strong sulphuric acid is most commonly used. This method helps in the precipitation of phosphatides and other impurities. But the oil refined by this method becomes dark and its odour becomes bad.

2) Steam refining: - In steam refining method the high temperature of the steam breaks the oil and the insoluble material gets precipitated, if phosphatides are present in large amount. But if moderate amount of phosphatides is present no
visible separation of solid material will occur, but the oil will become darker due to the decomposition of associated carbohydrates. This process is not applied in surface coating industry.

3) **Degumming** :- This method removes phosphatides and mucilaginous material from the oil but does not reduce the free acidity of the oil and colour of the oil. Gums, if left in the oil, tend to produce high refining losses and create trouble by settling out in storage tanks. These gums, after simple treatment are marketed as commercial lecithin.

4) **Alkali refining** :- It is the most important method of refining of the oils used for heat bodying, for varnishes and for alkyd resins in surface coating industry. This method is commonly employed for refining of edible oils.

The alkali refining completely removes phosphatides from oils. The alkali commonly employed for refining of oils is caustic soda. Caustic soda however has the disadvantage of saponifying a small proportion of neutral oil in addition to reacting with free fatty acids.
The success of alkali refining depends on proper choice of alkalies, amount of alkalies, and refining techniques, to produce the desired purification without excessive saponification of neutral oil.

1.5.2 **Bleaching**: Bleaching means reducing the colour of the oil. The standard method of bleaching is adsorption bleaching i.e. treatment of the oil with bleaching earth or carbon. Natural bleaching earth also known as Fuller's earth, comprises various earths or clays consisting basically of a hydrated aluminium silicate. The yellow red colour of most vegetable oils is reduced without difficulty by treatment of the oil with bleaching earths or earth and carbon mixture. Natural bleaching earths may be replaced by acid activated clays to obtain better results. Besides bleaching clay the other adsorbent used is activated carbon. Because of its relatively high cost and its very high oil retention, carbon is rarely used alone on most vegetable oils but is employed in admixture with bleaching clay in a ratio of about 5 to 20 parts by weight of clay to 1 part of carbon (16). Carbon is also a superior
adsorbent for traces of soap in refined oils. Bleaching of oils by adsorption involves the removal of pigments which are either dissolved in the oil or are present in the form of colloidally dispersed particles. Because of the greater protection afforded to the oil against oxidation, bleaching is conducted under vacuum.

1.6 **Isomerisation**

Isomerisation means a molecular transformation without change in the number of atoms in a molecule but their positions are changed. Such a positional change is illustrated by the shift from a non-conjugated position to a conjugated position shown below:

Non-conjugated  \[ \text{R-CH} = \text{CH-CH}_2 = \text{CH} = \text{CH} - \text{R} \]

Conjugated  \[ \text{R-CH} = \text{CH-CH} = \text{CH} - \text{CH}_2 - \text{R} \]

The rate of copolymerisation of oils with styrene may be increased by increasing the extent of conjugation in the oil either by isomerisation of non-conjugated oils or by blending of non-conjugated oils and conjugated oils like Tung and D.C.O. The isomerisation of oils is done by heating the oil in presence of catalysts like alkali, nickel on carbon, sulphurdioxide,
halogens compounds, organic compounds like anthraquinone. Among these, catalysts isomerisation with alkali, nickel on carbon and organic compounds have gained importance and are described below:

1) **Isomerisation with alkali:**- Bradley & Richardson (7) isomerised soyabean and linseed oil by alkali and reported 30-50% conjugation in the fatty acids. The oil can be reconstituted by reesterification with glycerol. Cowan(24) pointed out the following drawbacks of alkali isomerisation:

(a) 'After tack' was observed in the films of varnishes prepared from isomerised oils.

(b) High cost of re-esterifying the fatty acids obtained in the process to get the oils.

2) **Isomerisation in presence of nickel on carbon:**- This method developed by Cowan and his cowokers (15,16) does not involve splitting of the oil and appears to be simpler than alkali isomerisation. It was also pointed out that this process does not produce as much conjugation as obtained by alkali isomerisation. Describing the advantages of this method over alkali isomerisation they mentioned that:
(a) Oil can be isomerised without splitting.
(b) Retention of the glyceride structure without need for re-esterification.
(c) The treated oil does not possess the defect of 'after-tack'.

3) Isomerisation with organic compounds: In 1946, Terrill (17) proposed the hypothesis that anthraquinone and similar compounds increase the rate of polymerisation of oils because they actually isomerise the poly-unsaturated fatty acid radicals to conjugated configuration prior to polymerisation and do not have a catalytic affect on the polymerisation mechanism. In 1948, the isomerisation of soybean oil in presence of number of organic compounds was studied by Falkenburg et al. (18) by heating with 2 percent catalyst at 280°C for 2 hours. Out of all the compounds investigated the quinones were the only ones to possess marked activity which readily induced conjugation. Out of various quinone compounds investigated, anthraquinone had the advantage that about 97 percent of it could be crystallised out on cooling and could be reused. The isomerisation with anthraquinone has the following advantages:

(a) It produces oils of good colour which exhibit much less 'after-tack' than Nickel-carbon isomerised
oils.

(b) It is relatively inexpensive.

(c) It can be easily separated out from the oil on cooling by filtration.

(d) Anthraquinone crystallises out almost completely on cooling and can be reused after separation.

(e) It is relatively simple and economical to isomerise vegetable oils on a large scale by the treatment of anthraquinone.

**Mechanism of Isomerisation with anthraquinone:**

The mechanism by which the quinoid type catalysts operate may be analogous to that proposed by Kass and Skell (11) for the alkali isomerisation of oils. They postulated that isomerisation occurred by means of a prototropic shift and this can be represented in the case of anthraquinone and linoleic acid as shown below.

\[
\begin{align*}
\text{CH}_3 - (\text{CH}_2)_4 - \text{C} &= \text{C} - \text{CH}_2 - \text{C} = \text{C} - (\text{CH}_2)_7 - \text{C} \\
+ &\quad \text{O} \\
\text{9,12 linoleic acid} \\
\text{anthraquinone}
\end{align*}
\]
CH₃-(CH₂)₄ - C = C - C - C = C - (CH₂)₇ - C - OH

\[ \text{heat} \rightarrow \]

CH₃-(CH₂)₄ - C = C - C - C = C - (CH₂)₇ - C - OH

\[ \rightarrow \]

9,11 linoleic acid

anthraquinone
Considering the advantage of anthraquinone to be used as a catalyst for isomerisation of oils, niger seed oil was isomerised in the presence of anthraquinone and optimum conditions of isomerisation were established.

1.7 **Styrene monomers:**

Styrene was first isolated in the 19th century from the distillation of storax, a natural balsam. Although styrene was known to polymerise, no commercial applications were attempted for many years because the polymers were brittle and cracked easily. Commercial manufacture of styrene began on a small scale shortly before World War II. Since that time the production of the monomer has shown enormous growth. Several factors have contributed to this success.

1. Styrene (bp 145°C) is a liquid which can be handled easily and safely;
2. The activation of the vinyl group by the benzene ring makes styrene easy to polymerize and copolymerize under a variety of conditions; and
3. Polystyrene is one of the least expensive thermoplastics on a cost per inch basis.
Manufacture: Many different techniques have been investigated for the manufacture of styrene monomer. Of these, the following methods have been used or considered for commercial production:

1. Dehydrogenation of ethylbenzene.
2. Oxidative conversion of ethylbenzene to \( \alpha \)-phenyl-ethanol via acetophenone and subsequent dehydration of the alcohol.
3. Side chain chlorination of ethylbenzene followed by dehydrochlorination.
4. Side chain chlorination of ethylbenzene, hydrolysis to the corresponding alcohols, followed by dehydration.
5. Pyrolysis of petroleum and recovery from various petroleum processes.
6. Oxidation of ethylbenzene to ethylbenzene hydroperoxide which is reacted with propylene to give \( \alpha \)-phenylethanol and propylene oxide. The alcohol is then dehydrated to styrene.

In India styrene is manufactured by:

1. M/s Polychem. Ltd., Bombay
2. M/s Hindustan Polymer Ltd., Vishakapatnam
3. M/s Synthetic & Chemicals Ltd., Bareilly (U.P.)
Bottling of imported styrene is done by many factories and the chief bottler is M/s Amrut Industrial Products, Bombay.

The annual production of styrene monomer in India in 1970 was 9,300 tons. The present production of styrene in our country is estimated to be 1,00,000 tons.

**Properties:**

**Physical Properties:**

<table>
<thead>
<tr>
<th>No.</th>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Boiling point at 760mm Hg, °C</td>
<td>145.0</td>
</tr>
<tr>
<td>2.</td>
<td>Freezing point, °C</td>
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</tr>
<tr>
<td>3.</td>
<td>Flash point, °F, Tag open cup</td>
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</tr>
<tr>
<td>4.</td>
<td>Refractive Index, n_D20</td>
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<tr>
<td>5.</td>
<td>Viscosity, CP at 20°C</td>
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</tr>
<tr>
<td>6.</td>
<td>Surface tension, dyne/cm at 20°C</td>
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</tr>
<tr>
<td>7.</td>
<td>Density, g/Cm³ at 20°C</td>
<td>0.9059</td>
</tr>
<tr>
<td>8.</td>
<td>Specific heat, liquid, Cal/(g)(°C) at 20°C</td>
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</tr>
<tr>
<td>9.</td>
<td>Solubility at 25°C, %</td>
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<tr>
<td></td>
<td>(a) Monomer in H₂O</td>
<td>0.032</td>
</tr>
<tr>
<td></td>
<td>(b) H₂O in monomer</td>
<td>0.070</td>
</tr>
</tbody>
</table>

**Chemical Properties:**

Styrene polymerises readily and the temperature and pressure required are both moderate. In addition to
polymerisation styrene also undergoes all of the normal reaction of a typical unsaturated compounds. Resins obtained by the polymerisation of styrene are colourless, completely neutral materials, having good electrical properties and a high resistance to water, alkalis and aqueous chemicals.

Uses: Styrene plastics are now the major outlet for the monomer. These products include polystyrene, rubber modified polystyrene, styrene-butadiene copolymer, styrene acrylonitrile copolymer (SAN) and acrylonitrile butadiene styrene terpolymer (ABS). Styrene homopolymer is used for packaging toys, housewares, appliances etc. Expanded form of polystyrene have excellent heat insulating and flotation properties and find applications in construction and refrigeration. Rubber modified polystyrene generally referred to as "impact polystyrene" is used in appliances, luggage and other products that require breakage resistance. ABS is used as instrument panels and in refrigerator interior and telephone housings.

1.8 Styrenation:

1.8.1 Copolymerisation of oil with styrene: 'Copolymerisation' is the joint polymerisation of two or more monomer species. The high molecular mass compound so formed is called "Copolymer".
Copolymerization has found extensive practical usage because it enables variation of properties of high molecular mass compound over a wide range.

Various methods of copolymerisation of oil with styrene are Bulk (mass) method, solvent method, Emulsion method, High pressure method and styrene vapour method. But here only two methods, i.e. Mass and Solvent have been tried.

(1) **Mass Method** :- In this method copolymerisation of styrene and oils is done in the absence of any solvent. This method though being considerably faster has the following drawbacks:

1. The temperature control is difficult.
2. There is excessive increase in viscosity of the product.
3. Film of styrenated oil prepared by mass method are found to soften at elevated temperature.
4. There is a tendency for the styrene to homopolymerise than to copolymerise.

(2) **Solvent Method** :- In this method styrene, oil and a solvent is refluxed for 10-30 hours till copolymerisation is complete as indicated
by the viscosity and clarity of the product. This process has the following advantages over the mass method:

1. The good temperature control of the reaction.
2. The tendency of styrene to homopolymerise is less.
3. The handling of the product is easy due to lower viscosity.

1.8.2 Mechanism of addition polymerisation

The process of free radical polymerisation takes place in three general stages, i.e. initiation, propagation and termination.

(1) Chain initiation: The chain initiation involves a decomposition of an initiator to yield a pair of free radicals and the subsequent addition of the free radical to a monomer molecule.

\[ I \rightarrow 2R' \]

\[ R' + CH_2 = CH \rightarrow R - CH_2 \text{-CH} \]

(2) Propagation: Propagation involves the successive addition of monomers to the radical formed. This is the growth step in which the active free radical is maintained at the end of
the chain in the successive addition and thus, once the initiation step has generated a free radical, the active centres remain active until its death.

\[ R - CH_2 - CH + CH_2 = CH \xrightarrow{X} R - CH_2 - CH - CH_2 - CH \]

\[ R - CH_2 - CH - CH_2 - CH \xrightarrow{CH_2 = CH} R - (CH_2 - CH)_n - CH \]

(3) **Termination:** Termination can occur in any of the following three ways:

1. By molecular coupling of two growing chains.
2. Disproportionation through transfer of a hydrogen atom (free radical) from one growing chain to another.
3. Chain transfer through transfer of a hydrogen atom (free radical) on other atom of the solvent or other molecules foreign to the growing chain.

The reactions can be represented as follows:

1. \[ R - (CH_2 - CH)_n - CH_2 - CH + R - (CH_2 - CH)_m - CH_2 - CH \xrightarrow{X} R - (CH_2 - CH)_n - CH_2 - CH - CH_2 - (CH - CH_2)_m - R' \]
1.8.3 **Mechanism of copolymerisation of oil with styrene**:

In the copolymerisation of oil with styrene a number of reactions take place simultaneously. The reaction with the fastest rate will be the dominant reaction and frequently it will determine, the type of product formed. It is generally believed that the styrene polymerises to some degree and the styrene chains then become attached to the unsaturated portions of the fatty acid radical of the oil. It is also possible that a growing styrene chain may connect two oil molecules by becoming attached to unsaturated sections of each oil molecule.

Polymerisation reactions usually involve three steps namely, initiation, propagation and
termination as described in 1.8.2. Initiation is necessary to activate the monomer and may be accomplished by heat, light, catalyst free radical or other means. Propogation by a chain reaction assumes chain growth and molecular size and usually proceeds more readily than initiation. Termination stops the chain growth and is the result of loss of energy, stearic hindrance, reaction of chain end with an inhibitor or a free radical from the catalyst or solvent or some other mechanism.

Benzoyl peroxide, which is widely used as an initiator is believed to decompose and form free phenyl radicals as follows:

\[
\begin{align*}
\text{Benzoyl peroxide} & \quad \rightarrow \quad \text{Benzoyl radical} \\
\quad & \quad 2 \text{Phenyl radical} + 2\text{CO}_2
\end{align*}
\]

The free phenyl radical may then activate the styrene monomer and so initiate chain growth. A free radical also may terminate the growing chain as indicated below:
Hewitt et al. (14) were the first to study the reaction of styrene with drying oils in xylene and also to put forward the free radical mechanism to explain the reaction mechanism. They suggested that with conjugated oils, styrene formed true copolymers as in styrene butadine reactions, and addition compounds by chain transfer through the active methylene group in the case of non-conjugated oils. Chain transfer reactions being slower than the rate of polymerisation of styrene, heterogenous products were obtained from non-conjugated systems. But styrene-oil copolymerisation being faster than chain transfer reaction, homogenity was expected and found in the case of mixtures of conjugated and non-conjugated oils. The reactions can be represented as follows:--
Conjugated system:

Non-conjugated system:

They believed that a similar situation exists when styrene is copolymerised with an oil, such as D.C.O. containing diene unsaturation. Therefore three possibilities exist which have been shown diagrammatically below:

1) Addition of chain which has one end terminated with a free radical (R)

\[
\text{Styrene chain} + \text{oil molecule} \rightarrow \text{copolymer}
\]
2) Addition of growing chains which will be terminated by a free radical (R)

\[
\text{Styrene chain} \rightarrow R + \text{Oil molecules} \rightarrow R + \text{Coolymer}
\]

3) Termination of a growing chain by reaction with the unsaturation or another oil molecule

\[
\text{Styrene chain} + \text{Oil molecules} \rightarrow \text{Copolymer}
\]

It is quite possible that xylene may act as a chain transfer agent and Armitage et al. (23) proved that dipentene was an effective chain transfer agent for the formation of clear styrenation products from conjugated as well as non-conjugated oils.

1.9 Alkyd Resins:

The name alkyd is a euphonious rendition of acid, and was coined to indicate that alkyd resins are made from alcohols and acids. The most important group of resins which are generally indicated by the term alkyd resin, is that of the oil modified glyceryl phthalate resins. They are the reaction products of the
trihydric alcohol (glycerol) and the dibasic acid (phthalic acid) modified with either drying or non-drying oils.

1.9.1 *History* :- The history of alkyds is very much interesting. The alkyds are a result of dedicated hard work of many individuals who from time to time have initiated many useful changes in the methods, processing and equipment of the alkyds.

Brezelius¹ (1847) obtained first condensation product from tartaric acid and glycerol. The history of alkyd resin comes of the electrical industry. In 1889 Arthur Smith used the reaction product of phenol and aldehyde for insulation. As the time passed the industry made use of hardening under heat and pressure, and produced plastic articles. In 1912 bakelite was standard insulation. In 1901 Watson Smith (2) was successful in producing a transparent mass, insoluble in water, soluble in hot glycerol. He found that the fusability of product varied as the glycerol was distilled within a transparent slab containing glycerol and anhydride in ratio 2:3. Further heating
resulted in a brittle residue. General Electrical Co. investigated in 1912 that when a part of phthalic anhydride was replaced by a monobasic acid product was flexible and had better stability. All this formed the basis of the modern alkyds. The first alkyd resins sold commercially were made by General Electrical Co. of U.S.A. named "GLYPTAL".

Alkyds constitute about 65% of total synthetic resin consumption in India and 95% of this is consumed in coating industry. The development and production rate is readily increasing. In India, in 1948 there was only one factory manufacturing alkyds and the production in that year was about 8 tons. In 1955, there were five factories manufacturing alkyds with a capacity of 962 tons per annum and produced 713 tons. Apart from the expected increase in demand even for our present requirement there is an ample scope for increasing the capacity and production of alkyd manufacture.

1.9.2 **Raw materials** :- The raw materials used in the manufacture of alkyds are mentioned below:
1. Polyhydric alcohols
2. Polybasic acids
2. Oils and fatty acids
4. Modifiers
5. Driers

1) Polyhydric alcohols:
   1) Dihydric alcohols
      e.g. ethylene glycol
      \[ \text{CH}_2 - \text{CH}_2 \]
      \[ \text{OH} \quad \text{OH} \]

2) Trihydric alcohols
   \[ \text{CH}_2 - \text{OH} \]
   \[ \text{CH} - \text{OH} \]
   \[ \text{CH}_2 - \text{OH} \]

3) Tetrahydric alcohols
   a) Penta erythritol
      \[ \text{HOH}_2\text{C} - \text{C} - \text{CH}_2\text{OH} \]
      \[ \text{HOH}_2\text{C} - \text{CH}_2\text{OH} \]
   b) Dipentaerythritol
      \[ \text{HOH}_2\text{C} - \text{C-H}_2\text{C-O-CH}_2\text{-C} - \text{CH}_2\text{OH} \]
      \[ \text{HOH}_2\text{C} - \text{CH}_2\text{OH} \]
4) Sorbitol

\[
\begin{align*}
\text{CH}_2 &- \text{CH} - \text{CH} - \text{CH} - \text{CH} - \text{CH}_2 \\
\text{OH} &- \text{OH} - \text{OH} - \text{OH} - \text{OH} - \text{OH}
\end{align*}
\]

5) Mannitol

\[
\begin{align*}
\text{CH}_2 &- \text{CH} - \text{CH} - \text{CH} - \text{CH} - \text{CH}_2 \\
\text{OH} &- \text{OH} - \text{OH} - \text{OH} - \text{OH}
\end{align*}
\]

2) Polybasic acids and their anhydrides

1) Phthalic acid

\[
\begin{align*}
\text{COOH} &- \text{COOH}
\end{align*}
\]

2) Phthalic anhydride

\[
\begin{align*}
\text{O} &- \text{O}
\end{align*}
\]

3) Maleic acid

\[
\begin{align*}
\text{H} - \text{C} &- \text{COOH} \\
\text{H} - \text{C} &- \text{COOH}
\end{align*}
\]

4) Maleic anhydride

\[
\begin{align*}
\text{O} &- \text{O}
\end{align*}
\]

5) Succinic acid

\[
\begin{align*}
\text{H}_2\text{C} &- \text{COOH} \\
\text{H}_2\text{C} &- \text{COOH}
\end{align*}
\]

6) Succinic anhydride

\[
\begin{align*}
\text{O} &- \text{O}
\end{align*}
\]
7) Sebacic acid
\[
\begin{align*}
&\text{H}_2\text{C} - \text{COOH} \\
&(\text{CH}_2)_3 \\
&\text{H}_2\text{C} - \text{COOH}
\end{align*}
\]

8) Terphthalic acid

9) Isophthalic acid

3) **Oils and fatty acids**

The various drying, non-drying or semi-drying oils which can be used are:

1. Tung oil
2. Linseed oil
3. Oiticica oil
4. Soyabean oil
5. Safflower oil
6. Cottonseed oil
7. Fish oil
8. Tall oil
9. Coconut oil

4) **Modifiers**

The modifiers generally used to prepare alkyds of varying properties are as below:

1. Natural resins such as Congo ester, rosin ester, etc.
2. Synthetic resins
   such as phenolic resins

5) Driers:

0.015-0.05% of Cobalt based on non-volatiles is the best drier for the alkyds. A mixture of cobalt, lead and calcium has been found to give a good resistance to wrinkling, blooming and gas checking.

1.9.3 Classification: Alkyd resins for protecting and decorative purposes are generally classified as under:

(1) Drying oil modified or oxidising alkyds:

Here, the amount of unsaturated structure present in sufficient quantity in the monobasic acid causes the thin films of the alkyd to polymerise in the presence of oxygen, at room temperature to give a coherent solid film. These are often used alone in coating vehicles.

(2) Non-drying oil modified alkyds:

In non-drying type of alkyds, particularly no polymerisation occurs because of low amount of unsaturated structure in monobasic fatty acids. These non-drying alkyds are blended with other polymeric materials to give finished
product.

As a matter of nomenclature, the alkyds that are intermediate in behaviour are sometimes classified as semi-drying.

(3) Natural resin modified alkyds:
This group includes those resins which are modified by natural resins such as ester gum.

(4) Synthetic resin modified alkyds:
The example of this type of alkyds are those which are modified by synthetic resins such as:

1. Phenolic resins
2. Maleic resins
3. Urea or amino resins etc.

(5) Other classification:
Alkyds are also classified according to the amount of oil and phthalic anhydride present in the alkyd. The generally recognised compositions are as follows:

(a) Short oil alkyds: They contain 30-45% oils. They have fast set, fair air dry and flexibility, when baked, the short oil oxidising
alkyds are more durable than the longer oil oxidising alkyds. Short oil alkyds have high viscosity and require strong solvents such as xylene. Coatings made by them are generally applied by spraying and dipping.

(b) **Medium oil alkyds** :- These are most versatile in alkyd resin family and contain 46-55% oil. They give excellent gloss, durability and flexibility and short set times. They are used in air drying or baking enamels, maintenance paint and metal decorative coatings.

(c) **Long oil alkyds** :- These have 55-70% oil and are soluble in mineral spirits and compatible with many oils. They have good overnight dry and flexible film properties.

(d) **Very long oil alkyds** :- These contain 70% oil and are soluble in mineral spirits. These are the slowest drying and have good brushing properties, used in printing inks etc.

1.9.4 **Manufacture of alkyd resins** :- The alkyd resins may be manufactured by the following methods :-

1. Fatty acid process
2. Monoglyceride process
The processing of alkyd resins by the above methods can now be done either by direct fusion of materials (Fusion method) or by fusion in presence of some solvent. So depending upon the processing two more methods are there i.e.

3. Fusion method
4. Solvent process

(1) **Fatty acid process** :- In the fatty acid process polyhydric alcohol, dibasic acids and fatty acids (obtained by splitting oils) are introduced in the reaction kettle and heated at a temperature ranging from 210°C to 240°C or higher. The batch is held at the reaction temperature until the required viscosity and acid value are attained. It is then pumped or blown by inert gas pressure into the thinning kettle and reduced to required solid content.

The temperature of processing is determined by the oil length and the various modifiers used. Short oil alkyds react more rapidly than the long oil resins.

Maleic anhydride can be used as a modifier to accelerate the reaction and to improve the colour of the resin.
(2) **Monoglyceride process (Alcoholysis process)**:–

In the monoglyceride process the oil is first converted into the monoglyceride. This is accomplished by heating a mixture of oil and glycerol with catalyst until the product makes a clear solution in methyl alcohol. After the formation of monoglyceride, rest of the ingredients are placed in the reaction kettle and heated at temperature ranging from 220°C to 240°C. This process is considered more economical than fatty acid process as no splitting of oil is required and hence the alkyd resin can be prepared in only one operation.

(3) **Fusion Process**:– While manufacturing alkyds by this process, all the reactants are charged in the reaction kettle and heated under an inert atmosphere at a temperature ranging from 210°C-240°C. As the name fusion suggests, here the fluidity of the mass in the reaction kettle is developed by heat alone. The advantages of this method are:

1. Less fire risks as no solvent used in this process.
2. Lower equipment cost.
We can prepare alkyds by fusion process employing the fatty acid process as well as the monoglyceride process. While preparing alkyd resins by fatty acids under fusion method, all the reactants are charged directly into the kettle.

For the monoglyceride process, the oil (Monoglyceride) and polyhydric alcohol are heated together with a catalyst at 250-270°C, when interaction is complete, the other reactants are added.

(4) **Solvent Process** :- When the resin is processed in presence of some solvent, we call it the solvent process. The suitable solvent, generally xylol is added to the reaction mixtures. The solvent volatilized with the water of reaction passes out to the condenser where it is collected with water in a separator. Here water is withdrawn and the xylol is recirculated to the kettle. The reaction temperature can be controlled by the type and amount of solvent used. Advantages of this methods are :-

1. Lower raw material losses.
2. Lighter colour product.
3. Easier cleaning up of the material.

1.9.5 **Mechanism of alkyd formation**: In alcoholysis process, the oil is firstly heated with the polyol to about 240°C in the presence of a basic catalyst (e.g. calcium hydroxide). Typically, the oil is heated with glycerol using a molar ratio of 1:2 in the presence of litharge and calcium oxide and the principal product is a monoglyceride.

\[
\begin{align*}
\text{Oil} & \quad \text{Glycerol} \quad \text{Monoglyceride} \\
\text{CH}_2-OOCR & \quad \text{CH}_2-OH \quad \text{CH}_2-OOCR \\
\text{CH} \quad \text{OOCR} & \quad +2 \quad \text{CHOH} \quad \rightarrow \quad 3 \quad \text{CHOH} \\
\text{CH}_2-OOCR & \quad \text{CH}_2OH \quad \text{CH}_2OH
\end{align*}
\]

After the monoglyceride is formed the dibasic acid is added to the monoglyceride at 180°C and the esterification reaction is carried out at about 240°C.

The structure of resin obtained by the simple reaction of glycerol with phthalic anhydride may be represented as follows -
The material based on a structure of this type are brittle and of little practical use. However, the incorporation of fatty acid residues into such a structure leads to highly successful surface coating vehicles. The detailed structure of the latter materials depends on the method of preparation. In the fatty acid process, the fatty acids react simultaneously and it has been shown that the primary hydroxyl groups of glycerol react more readily with phthalic carboxyl groups than with fatty acids whilst the reverse applies to the secondary hydroxy groups. It is to be expected,
therefore, that in an alkyd resin prepared by
the fatty acid process the following type of
structure would be predominant.

In the alcoholysis process there is no fatty
acid competing in the esterification reaction.
It is expected that alkyd resin prepared by this
process has the following type of structure:

A number of reactions other than the esterifi-
cation may occur during the production of
alkyd resins and these results in some
deviations from the ideal structure shown above.
For example, in the case of glycerol, acid
catalysed esterification may also take place
during polyester formation resulting in the
formation of a tetrafunctional alcohol having
following structure:

\[
\begin{align*}
2 \text{CH}_2\text{OH} & \xrightarrow{H^+} \text{CH}_2\text{OH} \\
\text{CHOH} & \xrightarrow{} \text{CH}_2-0- \text{CH}_2-\text{OH} \\
\text{CH}_2\text{OH} & + \text{H}_2\text{O}
\end{align*}
\]

1.9.6 **Styrenated Alkyds** :- Styrenated alkyds were made available commercially in 1948 and now they have established a definite position in the field of fast air-drying and baking coatings. In some respects the styrenated alkyds may be considered resin modified alkyds, the resin being polystyrene.

Polystyrene is tougher and more durable than the natural resin modifiers generally used and the styrenated alkyds show similar advantages of better toughness and durability. However, they are not as durable on exterior exposure as the pure oil modified alkyds. The styrenated alkyds are faster baking than the straight alkyds, but the surface hardness may be improved by addition of amino resins. Polystyrene has good water and alkali resistance, and this quality is imparted to the styrenated alkyd.
Styrenated alkyds are available as solutions in both mineral spirits and xylene. For fastest setting and air drying, the xylene solutions is better, but for grinding with pigment and best flow in high gloss finishes the slower evaporating mineral spirit is preferred. The styrenated alkyds are practically incompatible with the pure oil modified alkyds. Therefore, blends of these resins cannot be made. The usual lead and cobalt combination of driers is added to air-drying styrenated alkyd finishes. They dry with the speed of lacquers, i.e.

Set to touch 3-6 minutes
Dry hard within 10 minutes
Dry through within 20 minutes
Full hardness within 72 hours

From the above discussion, it is evident that the styrenated alkyds are suitable for fast air-drying finishes on such objects as toys, implements and wood and metal furniture, and for interior applications which require resistance to alkaline cleaning solutions but are not subject to contact with oils and greases.
1.9.6.1 **Manufacture of styrenated alkyds** :-

The styrenated alkyds can be manufactured by the following four methods :-

1. Styrenate the fatty acid, and then combine styrenated fatty acid with phthalic anhydride and glycerol.

2. Styrenate the monoglyceride, then combine with phthalic anhydride and more glycerol, if necessary.

3. Styrenate the oil, react with glycerol to form the monoglyceride, then combine with phthalic anhydride and additional glycerol if necessary. This method is known as prestyrenation.

4. Styrenate the completed alkyd resin directly. This process is known as post-styrenation process.

Out of the above general methods for the preparation of styrenated alkyds the last two methods, i.e. pre-styrenation and post-
styrenation processes, have been tried in the present work because these methods are known to be easier and cheaper.