INTRODUCTION

Introduction

Fats and oils:

Fats and oils are the most important lipids found in nature. They are one of the three major "food factors" needed for human body. They are widely distributed in foods. Fats and oils come from a variety of sources:

1- **Animals sources:**

Animal fats are located particularly in adipose tissue cells. These are distended with oily droplets at body temperature but solid after death. Thus we have tallow from cattle, sheep and goats, and lard from hogs.

2- **Vegetable sources:**

Vegetable oils are chiefly present in seeds and nuts of plants. They are stored in seeds to serve as nourishment for the germination of embryo. There are quite a few seeds and nuts which are rich in fat content. Thus, soya bean, groundnut, coconut and palm kernel, rape or mustard, sesame seeds, cotton seeds, and higher are all important sources of edible oils. Linseed, castor seed and mowrah give non edible oils in various industries.

Rice was produced in more than 100 countries, accounting for about 25% of all cereal grain production (1). More than 534 million tons were produced in 1994. Rice is not a common source of edible oil compared to other traditional cereal or seed sources such as corn, cotton , sunflower , or soya bean among others. However recent research has demonstrated that rice bran oil can be recommended for the replacement of saturated fat in the diet , as unsaponifiable ingredients such as oryzanol, a mixture of ferulic acid esters of sitosterol and cycloartenol, which are unique to rice bran oil, have the ability to reduce blood cholesterol levels, particularly low density lipoprotein (LDL)-cholesterol (2).

3- Marine sources:

Marine oils are obtained from water animals-sardines, herrings, salmons, whales, dolphins, seals, porpoises etc.

Not only the edible fats and oils occupy a place of pride in human diet but the importance of vegetable oils in industries such as foods , soaps , cosmetics and pharmaceuticals has been well documented (3,4). It is used as raw material for manufacture of synthetic detergents, paints and varnishes, polishes, glycerol, lubricants, drying oils and printing inks.

Most of oils used in alkyd resins are derived from vegetable oils with important proportions of polyunsaturated fatty acids called drying oils. Their high drying index (5) allows their use in the manufacture of oil based paints and varnishes and especially for the creation of works of art.The more common drying and nondrying oils used in the formation of alkyd resin are: linseed oil, castor oil, soy bean oil, tung oil, coconut oil, cottonseed oil, tall oil, dehydrated caster oil and safflower oil.

The drying oils owe their value as raw materials for decorative and protective coatings for their ability to polymerize or "dry" after they have been applied to a surface to form tough, adherent, impervious, and abrasion resistant films.

Their film-forming properties are closely related to their degree of unsaturation, since it is through the unsaturated centers or double bonds that polymerization takes place.

In recent years, there have been significant advances in processing methods for the separation of fatty acids. This has stimulated research on the use of fatty acid modifiers in alkyd resins. Moore D.T. (6) using known mixtures of the various fatty acids present in drying and semidrying oils has shown a number of quantitative relationships between film forming properties and fatty acid composition in alkyd containing 47% fatty acids.This work has confirmed that the rate of drying is function of polyunsaturated or polyenoic acid content.

Polyesters and alkyd resins:

Polyesters may be classed as heterochain macromolecular compounds that posses a plurality of carboxylate ester group (-COO-) as components of their skeletal structure. They are distinguished from other ester-containing polymers such as cellulose ester, polyacrylate, and polyvinylesters in which the carboxylate groups or part of substituent entities pendant from the back bone structure (7).

Polyesters can be also defined as the poly condensation product of dicarboxylic acids with dihydroxy alcohols. These compounds may be modified by monocarboxylic acids, monohydroxy alcohols, and even small amount of poly carboxylic acids or poly hydroxy alcohols. This definition does not include materials commonly known as alkyd which are usually modified by the fatty acids and drying oils (8).

The formation of polyesters with resinous characteristics have long been studied(9-11).

A hard brittle polymers was prepared by the reaction of glycerol with phthalic anhydride(13-16). When a part of phthalic anhydride is replaced with monobasic acids, such as butyric or oleic acid, more flexible and more soluble resin result(17).

The term "alkyd" was originally used by Kienle to describe the reaction product of polyhydric alcohols and poly basic acids. It now tends to specify polyester products composed of polyhydric alcohols, polybasic acids, and monobasic fatty acids or oil. These materials are used chiefly in the coating industry (18).Alkyd resins may be considered a successful chemical combination of oil or oil fatty acids into polyester polymer structure, thus enhance the mechanical properties, drying speed and durability of these oleoresinous varnish better than the oil themselves (19).

These resins form the largest group of synthetic resins available to the paint industry and the consumption is greater than that of other resins. In spite of large number of other synthetic resins being available for use in paint formulation, the alkyd resins are the most important one of them, low-coast and combining abroad spectrum of performance properties. More than one polyhydric alcohol or polybasic acid may be used in the same alkyd resin to obtained special properties, therefore it will be seen that the term "alkyd resins" include a very wide variety of resinous product(20).The most important group of this resins is the oil modified glycerol phthalate resins; they are produced from the reaction of the trihydric alcohol (glycerol) and the dibasic acid (phthalic acid) modified with either drying or non drying oils.

Classification of alkyd resins:

The following widely used classification is related chiefly to the kind of fatty acid or the oil used in alkyd:

a) Kind of fatty acids:

i- **Drying alkyds:**

The fatty acid has an unsaturated structure present in sufficient quantity to cause a thin film of the alkyd to polymerize in the presence of oxygen at room temperature to give a coherent and solid film.

ii- **Nondrying alkyds:**

The amount of unsaturated structure in the fatty acid is so low that little or no polymerization occurs with oxygen.

b) ***Kind of oil length :***

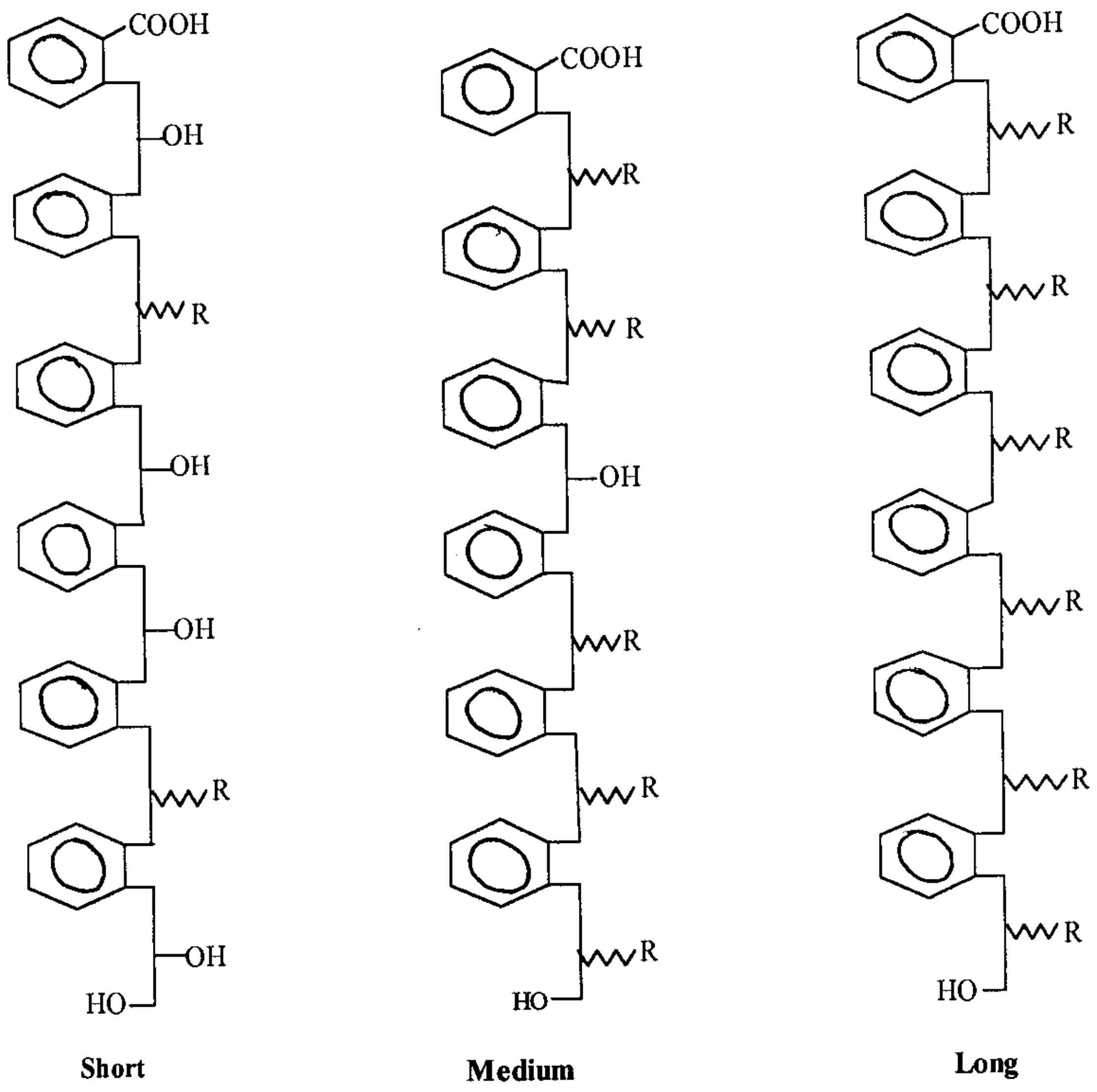
Traditional alkyds are formulated with significant drying oil or fatty acids content. Alkyds containing oil are typically described as having a given "oil length" which relates to percent of oil in the formulation.

So alkyds are classified according to the amount of oil and phtalic anhydride present in the resin(21). The generally recognized compositions are given in the table (1).

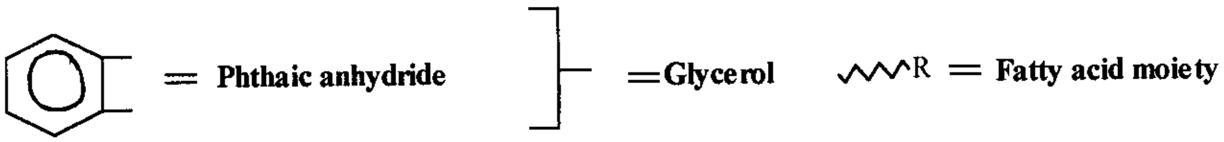
Table (1): Types of alkyd resins

Oil length	Oil content %	Phthalic anhydride
Short	35-45	> 35
Medium	46-55	30 – 35
Long	56-70	20 –30
Very long	71 up	< 20

The following scheme represents the classification of alkyds according to the oil length (22):



where :



= **Phthaic anhydride**

=**Glycerol**

= **Fatty acid moiety**

Manufacture of alkyd resins:

Four basic methods for manufacturing most alkyd resins are recognised: the fatty acid method, the fatty acid-oil method, oil dilution method, and alcoholysis method (23).

I- Fatty acid method:

The entire charge of fatty acid, polyhydric alcohol, and dibasic acids is heated to reaction temperature (usually 210-250°c, but as high as 280°C may be used) and maintained until alkyd specifications are met. A variation in which the polyol is reacted with dibasic acid before addition of the fatty acid gives rapid viscosity rise, wide alkyd molecular weight distribution, poor stability with the driers, a tendency towards surface drying, and often gel formation in films (23-25).

II- Fatty acid- oil method:

The entire charge of fatty acid, oil, polyhydric, alcohol and dibasic acid is added to the reaction kettle, and the temperature is raised to 210-280°C and maintained in this range until specifications are reached. Alkyd resins made by this method give coating with more rapid top drying and slower through drying than those from the alcoholysis method. It was important that the fatty acid to oil have the correct ratio (26).

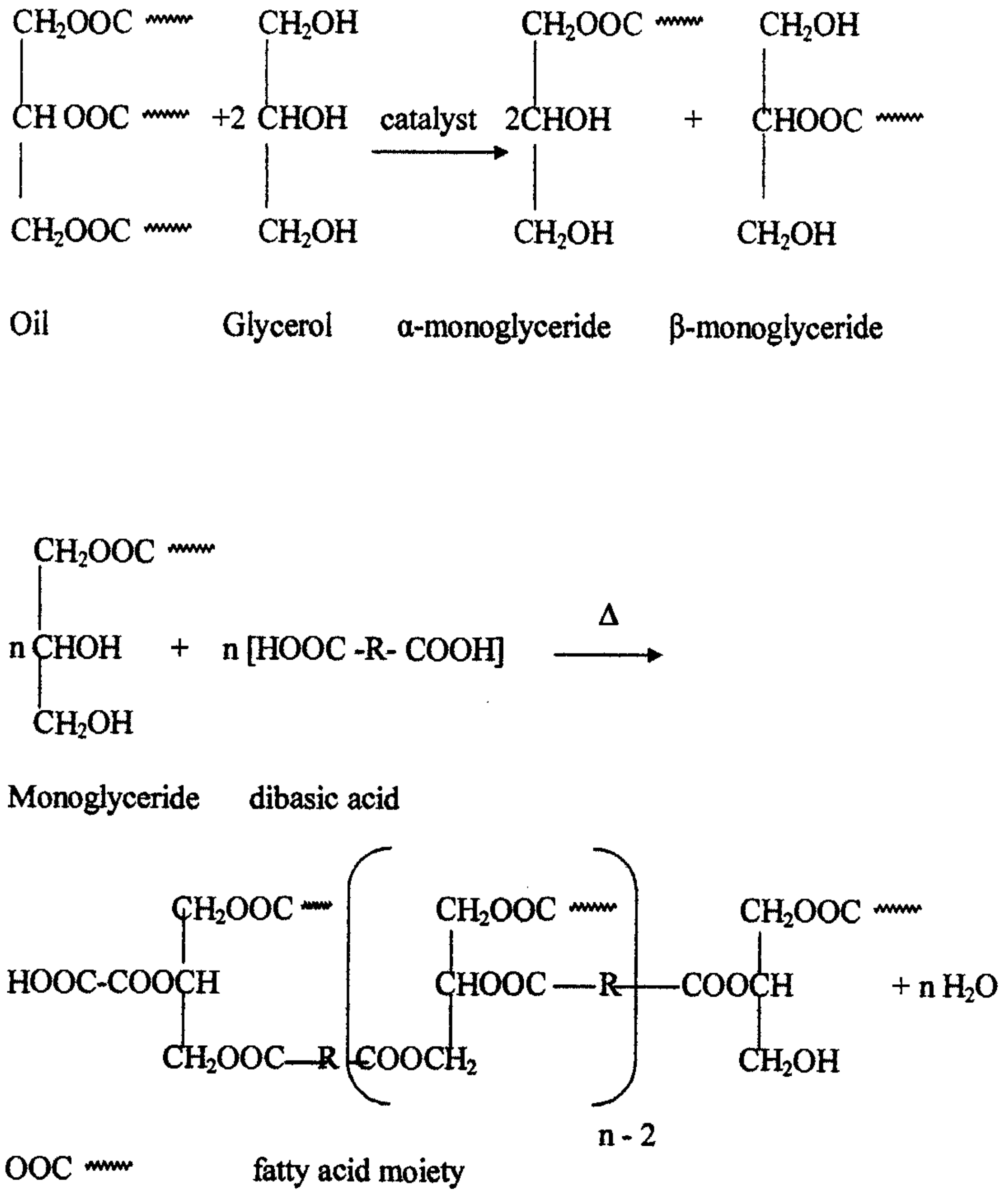
III- Oil dilution method:

The base alkyd is prepared by either the fatty acid, fatty acid-oil, or alcoholysis method. This alkyd is diluted with oil at elevated temperature to the desired oil content ratio. Alkyd prepared by this method usually exhibit better brushing characteristics, but produce somewhat softer coating with poor colour retention and durability than alkyd prepared by the fatty acid or alcoholysis method.

IV- Alcoholysis method:

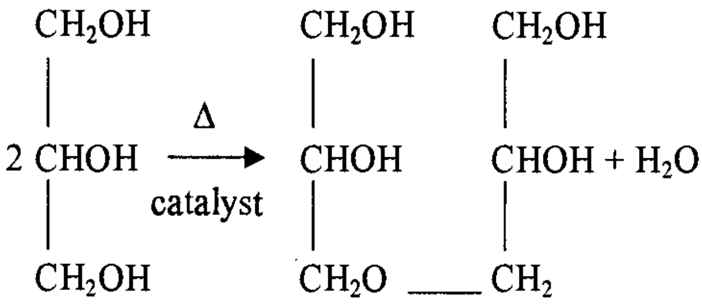
Large proportions of alkyd resins are made by alcoholysis of triglyceride oils, such as soya and linseed, with pentaerythritol or glycerol as the polyol added. The partial esters, which now have free hydroxyl groups are esterified with dibasic acid such as phthalic anhydride.The uncatalysed reaction takes place readily only at 280°C or above. Acid materials are relatively ineffective as catalysts. The alcoholysis or triglyceride oil in making alkyd is usually base catalysed with alkali or other metalic components. Alkali metal hydroxides are effective as alcoholysis catalysts but tend to give alkyds of darker colour and make the alkyd film more water sensitive. A study of the base catalysed alcoholysis of soya oil with pentaerythritol showed that on an equal mole basis (0.00224 mole catalysts/ 100 gm oil), lead compounds were most efficient, followed closely by lanthanium naphthenate, calcuium naphthenate, cerium naphthenate, calcium acetate and lithium salt. In most commercial alkyd preparations, sublimed litharge has been the preferred alcoholysis catalyst, since it gives faster esterification rate, equivalent colour, and higher viscosity than the other alcoholysis catalysts, such a calcium and lithium salts the litharge concentrations usually ranges from 0.01-0.05% metal based on the weight of triglyceride oil. For rapid and successful alcoholysis, the processing equipment should be cleaned and free of carboxylic materials such as residual phthalic anhydride from previous alkyd preparation or highly acidic oils. The general alcoholysis involves heating the oil to 230-250°C followed by addition of the sublimed litharge and polyol then the mixture is reheated to 230-250°C. One way to follow the course of alcoholysis reaction is by observing the solubility of the mixture in anhydrous methanol, where the triglyceride is insoluble in anhydrous methanol, on the other hand monoglyceride is soluble. When at least two volumes of methanol per volume of alcoholysis mixture give a clear solution, the phthalic anhydride is added and the alkyd is completed at the reaction temperature of 210-250°C to the desired specification (26).

When oil and polyol are first mixed, they are incompatible and very little reaction occurs even at high temperature. However, as soon as a small amount of monoester has been formed, the components become compatible and the reaction takes place(27). In the following, the schematic representation of alkyd polymer formation is depected (28).



Schematic representation of alkyd polymer formation.

Actually, the alcoholysis reaction present in the equation is an over simplification. In reality, the alcoholysis results in an equilibrium, which consists of monoglyceride, diglyceride, unchanged triglyceride, and free glycerol. The degree of alcoholysis has an important bearing on the properties of resulting resin (29).The alcoholysis reaction is further complicated by the tendency of the polyol under the influence of heat and alkaline catalyst used for alcoholysis to undergo interetherification with the resultant loss of available hydroxyl groups and the formation of higher functional polyol (30). In case of glycerol, the reaction is:



$$2\,\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow[\text{catalyst}]{\Delta} \begin{array}{ccc} CH_2OH & & CH_2OH \\ | & & | \\ CHOH & & CHOH \\ | & & | \\ CH_2O & — & CH_2 \end{array} + H_2O$$

Today the fatty acid and alcoholysis methods are the most important process used for producing alkyd resins (31). Other manufacturing methods are used when necessitated by such considerations an unusual chemical or physical properties of modifiers, special characteristics required of the finished resin or variables in processing equipments.In comparison the alcoholysis method with fatty acid method, the alcoholysis method gives the following difference in alkyds; higher and more rapidly attained viscosity, gelation at low degree of esterfication and softer and slower drying coating films. Other differences that have been observed for the two procedures are listed below (32) .

- **Monoglyceride (alcoholysis) procedure:**

a- The rate of esterification slows down at higher acid values.
b- Gelation occurs at slightly higher acid values.
c- The alkyd tends to be marginally softer and tackier.
d- The alkyd tolerates more aliphatic hydrocarbon thinner.

- **The fatty acid procedure:**

a- Low acid values are more rapidly attained.
b- Bodying and gelation occur at lower acid values.
c- The alkyd tends to be somewhat harder and less tacky.
d- The alkyd tolerates less aliphatic hydrocarbon thinner.

Fusion versus solvent processing (32):

The four methods described above, which vary only in order of addition of ingredients, can be further modified in point of technique during the esterfication cycle. The four methods are carried out as described, the process is called "fusion process", a term presumably signifies that the fluidity of the mass is developed by heat. The technique of adding an azeotropic solvent as an aid to remove water during the esterfication reaction can also be used in alkyd processing. When this is done, the process is referred as a "solvent or azeotropic process".

In the fusion process, the evolved water of esterification is vented to the atmosphere or collected in a fume-scrubber system. In the solvent process, the amount and kind of solvent (aromatic types are preferred), usually 3-10% of batch charge, is adjusted so that a vigorous refluxing occurs at the desired esterification temperature.

The vapours are condensed and collected in an automatic decanter that removes the water and returns the solvent to the reaction kettle. Aliphatic solvents are generally not used in the solvents processing of alkyds because they are poor solvents for phthalic anhydride, which can sublime and plug the reflux condenser tubes. In the solvent process, better temperature control is possible by the addition of withdrawal solvent than by the regulation of heat.

In the solvent processing alkyds made by the fatty acid method, the usually procedure is to charge all the ingredients and solvent. In the alcoholysis the solvent is held after the alcoholysis completed, the solvent is then added after the dibasic acid.

The solvent process for preparing alkyds has the following advantages over fusion process:

a) Faciliate the removal of water and gaseous contaminants owing to the continuous sparging action of the solvent, which is condensed and continuously returned to the alkyd kettle.
b) Give better temperature and viscosity control, as the presence of the solvent provides a more mobile mixture.
c) Better colour and polymer uniform alkyd which is free from skinning and polymerized gels.
d) Faster esterification and easier cleaning of the kettle after the batch is completed.

Despite this advantages, the fusion cook is popular processing method for the following reasons:

a) Certain alkyds such as the isophthalic alkyd are more easily made by fusion process.
b) Requires less initial outlay of equipment, as no water condenser is necessary.
c) No heat input is required for refluxing of solvent.

Effect of composition upon the characteristics of alkyd resins(33):

Each of the main ingredients of alkyd contributes to its properties in a predictable manner:

I- Polyhydric alcohols:

The most commonly polyhydric alcohol used in alkyd resins are pentaerythritol and glycerol. Because of high functionality of pentaerythritol, it is widely used as polyol for long oil alkyds, and blended with either glycerol or glycol in case of medium and short oil alkyds. Alkyds containing pentaerythritol tend to have higher viscosity and higher molecular weights, dry more rapidly, better gloss retention, better heat yellowing resistance, better chemical and water resistance, and better exterior durability than glycerol alkyds with comparable oil content.Other polyhydric alcohols may be used in more limited amounts to improve special properties of alkyd resins. Soya oil glycol monoesters have been prepared through the transesterification of soya bean oil with ethylene, diethylene, propylene and dipropylene glycols (34).

II- Fatty acid and oils:

The extent and type of unsaturation in the drying fatty acids has a strong effect on the properties of the finished alkyd. In general triene unsaturation contributes more drying rate, colour properties, and film hardness than diene unsaturation. Conjugated systems are slightly better than non-conjugated in the development of the initial drying. The mono unsaturated fatty acids have little drying tendency, while the saturated acids appear to inhibit drying performance. In general, it has been found that the oils or fatty acids with higher iodine value dry faster.The hardness of dry alkyd films at constant film thickness is proportional to the amount of glycerol phthalate and the amount of oil modification.

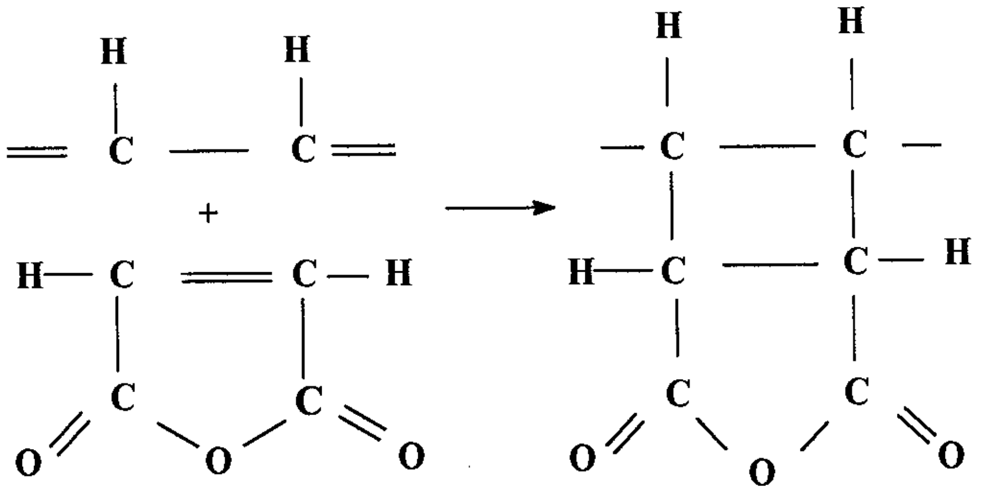
III- Poly basic acids:

Phthalic anhydride is the most important acid used in alkyd resins because of its low cost and the excellent properties that it imparts to alkyd resin polymers. Isophthalic acid (its meta isomer) has become more extensively used. Its alkyds have higher molecular weight, higher viscosity, better drying properties and give harder and more durable films with better heat and chemical stability. Isophthalic alkyds gel more rapidly than comparable O-phthalic alkyds. Both acids have the same functionality but intermolecular cyclization has been postulated as the reason of this behavior (35). Brown (36) has attributed these results to the etherification of polyol in case of isophthalic acid. Terephthalic acid (its para-isomer) has very poor solubility in alkyd ingredients, and very high melting point.

Other dibasic acids can also be used in alkyd preparations in limited amount, these include tetrahydrophthalic anhydride, hexahydro phthalic anhydride, tetra-chlorophtalic anhydride, maleic anhydride, fumaric acid and dimerized fatty acids.

Maleic and fumaric acids are used to replace part of the phthalic anhydride, these acids react with the unsaturation of the fatty acids, thus increasing the total functionality of the alkyd system and therefore increase the molecular weight of alkyd resins. The alkyd resins formed dry more rapidly and gives harder films with better alkali resistance and better exterior durability.

The following scheme shows the reaction of maleic anhydride with unsaturation of fatty acids (22):



Modification of alkyd resins:

The modified alkyd is the products obtained from the chemical modification during the preparation of alkyd by using another chemical or incorporate chemical agents other than those generally used. Alkyd may be modified with natural resin, phenolic resin, polyamide resin, vinyl resin and also melamine-formaldehyde resin to improve its physical, chemical and mechanical properties.

Rosin was originally included in alkyds as a modifier because of its low coast. However, it may also be added as many other mono basic acids such as benzoic acid, to enable oil length to be shortened without causing increased viscosity. Rosin itself contributes to faster dry and film hardness, but degrades, weathering performance, its use is now restricted to alkyds for primer applications (37).

Non-Phthalic alkyd was prepared from rosin-maleic adduct and maleopimaric acid by Shukla et al. (38). Using maleopimaric acid in alkyd preparation gives better alkali-resistance.

Also P-carboxyphenylmaleamic acid is used in the modification of alkyd resin to shorten the cooking time and producing polyester varnishes of superior properties (39).

Alkyd resins contaning linseed oil and tung oil were prepared by reacting vegetable oils, polyol and carboxylic acids, polyesterifing the product with phthalic anhydride in the presence of rosin acids and maleic anhydride.These alkyd resins have good drying properties, useful in manufacture of primers with good hardness(40,41).

Alkyd resins modified with phenolic compounds has been described and showed better solvent and alkali resistance (42).

Recently, solvent-type coatings based on alkyd/ polyesteramide resins have been described (43,46). These types of resins combine the useful properties of alkyd and polyamide resins.

When no fatty acids used in alkyd resins or when they are completely replaced by another type of acid, the product can be considered as "oil-free alkyd".The unsaturated polyesters (47) were modified by poly (ethyleneglycol) end groups in order to influence the solution behaviour in styrene and to modify mechanical properties of the crude resin.

Properties of alkyd resins:

The properties of alkyd resins depend on the nature and amount of the modified oil incorporated (48). Therefore they are conveniently classified according to the type of oil present in alkyds which can be classified into drying oil resin, semidrying oil resin, and nondrying oil resin. Also alkyd resin can be classified according to their oil length i.e. short oil-length, medium oil length, long oil length and very long oil-length resins.

Short oil alkyds generally require aromatic solvent, giving higher viscosity resin at lower solids. If formulated with drying or semi drying oils, have fair air dry, good adhesion, good durability, good gloss and gloss retention, fair to good colour retention, and rapid baking cycle.

The medium or long oil length of drying or semi-drying oils can air-dry oxidatively at room temperature. To form hard films, it must be stoved with crosslinking resin. Medium and short oil alkyds give hard films with good gloss retention and chemical resistance; they are less flexible than long alkyds and normally dried by stoving (48).

Polyeseter finishes (49), are very hard, tough, resist to solvent and resistant to moderately hot objects. This is extremely useful property for a furniture finish. Their adhesion to most surfaces are poor and the films are not flexible in the ordinary sense, unless soft sufficient flexibility to withstand to the expansion and extraction of the substrate as the humidity varies is obtained by spacing out the cross-links. This can be done by decreasing the proportion of unsaturated acid in the polyester resin or by using long chain, flexible saturated acid or alcohol. The mechanical standing and polishing properties of the finish will suffer if cross-linking is excessively reduced.

Unlike epoxy finishes, polyesters undergo appreciable volume shrinkage on hardening. This can cause loss of adhesion, pulling away from edges and other defects, upon outdoor exposure, the varnish (wax type) has good gloss retention, but tends to a fail by cracking, especially on expanding and contracting substrate (49).

Isophthalic acid used in alkyd resins and the formulation of these alkyd resins was discussed by Adams et al. (50) the performance of these coatings is presented and compared with coatings prepared from conventional alkyds.

Njoku et al. (51) prepared an alkyd resin from rubber seed oil and evaluated it as coating varnish. Okiemen et al. (52) measured the viscosity of the prepared alkyds in different solvent at oil content of 20, 30, 40, 50 and 60%.From these measurements they found that the di-methyl formamide is the best solvent for these type of alkyds.

Alkyds with different oil length have been prepared from rice germ oil by Naser et al. (53). The study showed that short rice germ alkyds were air drying, while medium and long rice germ alkyds dried only upon stoving at 90°c for three hours. Replacement a part of rice germ oil by drying oil (linseed oil) improved the drying characteristics and gave better film performance relative to those made from rice germ oil alone.

An alkyd resin coating prepared from sunflower fatty acids, pentaerythritol, phthalic anhydride, trimellitic anhydride, and trimethylolpropane, trimethyl-acrylate gave dry film thickness of 100-125μm. These air drying coating compounds are suitable for manual application (54).

Pascal Sabin, et al. prepared two sets of alkyd resins of variable oil lengths with the required properties for offset printing inks formulations, modified by sunflower and rapeseed oil, were synthetized according to "Monoglyceride" process. The influence of the acyl compostion of the modifying vegetable oil and of the oil content on alkyds properties was determined by detailed chemical and rheological characterization. Molecular structure, size, and molecular size distribution appeared to be linked to these two factors. A comparative study with two usual linseed oil modified alkyds led to determination of the more appropriate alkyds for applications in offset varnishes (55).

Abd El Ghaffar, et al. (56) prepared modified short and medium alkyd resins using perfluorinated urethane toluene isocynate. These modified resins incorporated in a set of paint formulations where the corrosion protection efficiencies were enhanced by the improvement in the hydrophobicity of these alkyds.

A modified alkyd varnish shows excellent properties in regard to drying time, adhesion, impact strength and water resistance obtained from synthesized medium oil alkyd resin using sorbitol and pentaerytritol instead of glycerol (57).

High solid air dry styrene modified alkyd resin with low free styrene residue content (≤ 0.7%) was prepared from castor oil, soya bean oil or linseed oil, polyol, polycarboxylic acid, styrene and additives. The resin can be diluted and its varnishes were evaluated as hammer paint (58).

Istratescu et al. (59) prepared alkyd resins from synthetic or vegetable-oil fatty acid and their manufacture for weather-resistant coatings. These alkyd resins contain 1-15% excess-OH groups at high molecular weight, 5-25% excess OH groups at medium molecular weight and 15-40% excess OH groups at low molecular weight, exhibit ability to wet pigments, and used for weather resistant coating.

Another modified alkyd resin with good corrosion and weather resistance was prepared by Yin et al. (60). This resin consisting of vegetable oils 30-60%, polyhydric alcohols 5-15%, poly basic acids 10-35% Dacron 10-45% and diluents 20 - 65%. A resin lacquer prepared from soya oil, pentaerythritol, phthalic anhydride and Dacron was mixed with pigments, tale, a diluent, and a drying agent, milled, and filtered to form a title paint.

Ostberg-Gunilla et al. (61) used the inversion technique to emulsify high viscosity alkyds by simple hydrophilic non-ionic and anionic surfactant.Fine dispersed stable emulsions were obtained by adding water to the akyd/emulsifier mixture at constant temperature. The influence of type and concentration of surfactant on the inversion properties and droplet size were studied.

Also Makarewicz- Edwin (62) studied the stability of linseed oil varnish and alkyd resin in water emulsions stabilized by nonionic surfactant. In case of alkyd resin the best emulsifiers can be used as nonionic surfactant, were ethylene and propylene oxides in addition to (nonyl) phenol and oxyethylene fatty alcohol. The stability can be improved by xylene and butanol addition as well as by increasing the resin concentration to 50% by weight.

Resin calculations (32):

Alkyd calculations are used to predict the finished formulation, theoretical and properties of the resin, the amount of reaction water liberated, the probable risk of gelation and the amount of cross linker required to cure the resin.

The calculations also often help when reformulating resin to modify certain properties and when using basic principle to formulate new resins. A prerequisite for using the formulations is a knowledge of the equivalent weight of each reactant.

The equivalent weight (E) of a material is its molecular weight (M), divided by its theoretical functionality (F), and can be directly calculated for known materials.

$$E = M/F \qquad \text{........................ (1)}$$

For materials of unknown mixed compositions, the equivalent weight can be calculated from the experimentally determined acid number (A.N.) or hydroxyl number (OH. N). The units of this number are (mg.KOH/gram of resin solid). This factor 56, 100 becomes the numerator in calculations 2,3.

$$\text{Acid Eq. wt.} = 56.100/\text{A.N} \qquad \text{..................(2)}$$

$$\text{Hydroxyl Eq. wt.} = 56.100/\text{OH.N} \qquad \text{............. (3)}$$

This basic reaction producing alkyd is the esterification reaction, which is ideally the reaction of an equivalent number of acid groups and hydroxyl groups, yielding a polyester and water.

Equation (4) gives the sum weight of water contributed by each source of carboxyl functionality. Each carboxyl equivalence yields one mole of water and each anhydride equivalence yields half mole of water.

$$\mathbf{H_2O\ off = 18\ (Eq.\ acid) + 9\ (Eq.\ anhydride)} \qquad \ldots\ldots\ldots\ldots(4)$$

The calculation of water evolved is useful tool for following the course of the esterification reaction as distillate is collected and to find the difference between charges weight and yield (Y).

$$\mathbf{Y = charge\ wt. - H_2O\ off\ (from\ eq.\ 4)} \qquad \ldots\ldots\ldots\ldots(5)$$

Table (2) indicates the approximate amount of excess hydroxyl equivalents that are needed to avoid gelation at low acid numbers in drying oil alkyds of verious oil contents. These empirical values have been calculated from experience in the preparation of large number of drying oil alkyds containing phthalic anhydride and a variety of different drying oils (26).

Table (2) Excess hydroxyl equivalents at various oil contents.

Fatty acid content of alkyd %	Corresponding oil content %	Hydroxyl equivalent in excess of the polyol needed to esterify the PA used	Approximate axcess OH equivalent content in the finished alkyd %
62	65	0	0
59 - 62	62 - 65	5	0 - 5
57 - 59	60 - 62	10	5 - 10
52.5 - 57	55 - 60	18	10 - 15
48 - 52.5	50 - 55	25	15 - 20
38 - 48	40 - 50	30	20 - 25
29 - 38	30 - 40	32	25 - 30

By using the data given in table (2) and the following equation, defining and determining the content of any ingredient in an alkyd composition and the various stoichiometric relationships, a method for calculation of alkyd composition that should approximate practical formulation has been developed :

$$\textit{Content as wt. of } X = \frac{\text{wt. of x charged to alkyd}}{\text{Theoretical wt. of finished alkyd}}$$

Where **X** represents any ingredient of the alkyd charge.

The amount of oil content required can be calculated by the following equation:

$$gm(oil\,required) = \frac{A}{100-A}\,(B+B_1+C-D) \qquad \text{........(6)}$$

Where:

A = % oil desired in final alkyd,

B = gm polyol needed to esterify dibasic acid,

B_1 = gm excess polyol,

C = gm dibasic acid,

D = gm water evolved from dibasic acid.

- Hydroxyl excess and formulation to avoid gelation:

The polyesterification occurs between poly functional carboxyl and hydroxyl-containing molecules, the result can be over-increasing chain length. Monomers that have three or more functional groups particularly contribute to rapid polymer growth.

For practical purpose, coating polymers must be limited in molecular size untie they are applied. Various alternatives are available for limiting the polyesterifiction reaction. Traditional resin based on drying oils contain mono functional fatty acids that act as chain terminator and effectively limit polymer growth to practical viscosity ranges.

At the other end of spectrum are totally synthetic or oil-free resins, based on di and trifunctional materials. Chain growth in such resins can be controlled by the use of an excess of polyol, which tends to produce relatively low molecular weight polymers that are hydroxyl terminated when all the acid groups are reacted.

An excess of hydroxyl groups or equivalents (R) refers to the excess of hydroxyl groups over the carboxylic groups for any of the alkyd components, thus,

$$R = \frac{Total\ \ e_B}{Total\ \ e_A} \qquad \text{.............(7)}$$

Where:

e_A and e_B are carboxylic and hydroxyl equivalents respectively. The percentage excess-OH equivalent is given by :

$$\textbf{\% excess - OH groups = 100 (R-1)} \qquad \text{........(8)}$$

Patton's gelation constant (63):

For an alkyd to be outstanding in performance, it must be processed to as high a molecular weight as possible, at the same time the molecular weight must not be allowed to become excessive, or the alkyd vehicle will get-out of control during processing (convert to an intractable gel) or exhibits an instability on self storge. Hence the alkyd formulator must at all times avoid the design of either small or large polymers (7).

The method for calculation, based on an average alkyd functionality, was of most universal applicability by using the concept of an alkyd constant "K". The derivation, as before, will be based on Carothers classical thorem (64) with the adaptation applying to specific case of alkyds. By the use of this alkyd constant, it is possible to routinely access the feasibility of preparing an untested alkyd, adjusts an improperly formulated alkyd to a corrected composition.

The completion of reaction at gel can be expressed as :

$$P_{gel\ point} = 2/f_{av} = 2\ m_o / e_o \qquad \text{.................(9)}$$

Where:

f_{av} = average functionality (stichiometric properties)

$P_{gel\ point}$ = extent completion of reaction at gel point.

m_o = number of moles at start reaction.

e_o = number of equivalents.

At this point, a different approach is taken into consideration. Equation (9) as written above covers the case in which the alkyd components are present in stichiometric properties, a case is not applied to alkyds formulated with excess hydroxyl groups.

The problem can be resolved by considering the total of those equivalents that have actually reacted when condensation reaction is 100% completed, that is when all the acid groups have been reacted. This total must of necessity equal twice the number of acid equivalent initially present in the alkyd composition (one hydroxyl group is reacted for acid group reacted).

As far as effective used of functional groups is concerned, only those that have react count. The hydroxyl groups present in excess remains unused and reduce the effective functionality of the molecules to which they are attached.

Hence for the case in which hydroxyl groups are present in excess, the effective number of equivalents for the alkyd composition is $2e_A$ (where e_A equals the total number of acid equivalents initially present in the alkyd mixture and not the actual number e_o). substituting this value of $2e_A$ for e_o in equation (9) gives equation 10.

$$P_{\text{gel point}}\ \textbf{(excess hydroxyl group present)} = \frac{m_o}{e_A} \qquad \dots\dots\dots\dots\dots\dots (10)$$

In general, an alkyd is formulated to reach a point just short of incipient gelation at 100 percent of reaction. This is equivalent to saying that at gelation (incipient). P should be equal 1.00 . The importance of equation (10) in the design and assessment of alkyd now becomes manifest, for it provides an alkyd to meet the condition of incipient gelation at P = 1.00 .

The ratio m_o/e_A is defined as an alkyd constant "K"

$$\mathbf{K = m_o/e_A}$$

It is now postulated that the ratio of total moles to total acid equivalents for any properly formulated alkyd is equal to unity. This is a theoretical constant. As will be shown, the alkyd constant of 1.00 will be slightly increased in practical formulations to ensure a measure of safety during processing and storage.

By comparing the computed $K = m_o/e_A$ for the proposed formulation against the working constant for that types of alkyd, the alkyd chemist is in position to judge whether the preparation of the alkyd resin is feasible.

Application of alkyd resins (65):

Alkyd resins are polyester-based materials that are normal modified with oil or fatty acids. These products may be further modified with a variety of other chemical materials. Various poly basic acid, polyhydric alcohol, oils, fatty acids and modified agents may be combined to produce alkyds with specifically designed properties. The precise combination of the ingredients used, together with the careful control of the reaction, influences the final properties of the alkyd produced, for this reason, many alkyds are available to the coating formulator. In considering the applications of alkyd resins, it is convenient to take them according to its oil length.

Short oil alkyds:

Short-oil alkyds may be divided into nondryng and drying types.The short drying alkyd resins contains linseed, soya or dehydrated castor oils. The linseed based alkyds are used in automotive refinishing enamels. The short-oil non drying alkyds contain coconut, hydrogenated coconut, castor or similar saturated fatty acids provide the best colour retention on baking, and improve gloss retention. It is used as plasticizer for cellulose nitrate. Resins of this type contribute the necessary properties of adhesion, flexibility, durability, and colour retention in furniture lacquers and other fast-drying industerial finishes. The nondrying alkyd amino resin backing enamels yield very hard, tough finishes for automobiles, refrigerotors, washing machines, and other metal-finishing.

Medium oil alkyds:

The medium oil alkyds are the most versatile of the alkyd family. In general, all round durability is better than their longer or shorter relations. The commonly used medium oil length alkyds are based on linseed oil. Alkyds of this types are extensively used in anticorrosive primers and in general maintenance printing applications.

Rosin and phenolic modifications are frequently made of medium oil length alkyds, to give them excellent hard drying properties, with improved resistance to abrasion, water and alkali. They are extensively used in maintenance paints, industrial primers and some marine primers.

Long oil alkyds:

Long oil length alkyds are almost prepared from drying and semidrying oils, with pentaerythritol as polyol. The most common oils used are linseed and semidrying oils, soya, safflower, sunflower and tall oil. All these resins are soluble in low odour aliphatic solvents, permitting excellent brushing properties with good flow characteristics and easy brush cleaning.

Their main use is in architecture and maintenance as brushing enamels, undercoats and also marine paints. The linseed oil gives the best drying properties, but is prone to yellowing away from direct sunlight, the main use, therefore, is restricted to primers and exterior finishing coat, and in dark colours.

Most architectural high gloss enamels for consumer market are formulated on long oil-soy-based. Safflower-oil based alkyds gives slightly better drying and non-yellowing properties, but more expensive than soya oil. Sunflower oil based alkyd has properties between those of a soya and sunflower.

Very long oil alkyd:

The use of very long oil length alkyds is restricted to the printing ink industry. Very long nondrying oil based alkyds find limited use as plasticizers, castor is the preferred oil. Since flexibility is the main requirement, straight chain dibasic acids are used in their formulation. Plasticizers of this type are mainly used with ethyl cellulose and nitro cellulose where they show excellent compatibility and retain flexibility at low temperature.