INTRODUCTION

Water-thinnable coatings are generally defined as those involving the incorporation of water in the vehicle portion of the system. It may be partially or completely replace the organic solvents.present. The first paints used were water-thinned, and according to the Encyclopaedia Britannica[1], the Ancient Egyptians decorated the walls with painting excuted in distemper 2000 to 3000 year. B.C. white wash developed into bonding portland cement paints and into casein paints are the oldest types of water-thinnable paints[2].

According to the above definition, emulsion and water-soluble paint systems are included. The former was developed in 1948 while the other developed in 1955. Water-thinnable paints may be considered the greatest and bravest step found in industrial finishes taking into consideration the economic point of view[3].

The adaptation of water type paints to industrial applications has been slower than in the trade sale field[4]. Industrial type finishes are defined as finishes applied on the production line to various products such as automobiles, appliances, furniture, building materials, drums, ...etc. In most instances these are baking-type finishes. They have been many articles published on the use of water base paints in industrial applications[5-24].

The properties, curing mechanism, storage stability, application and formulation of various thermoactive water-soluble synthetic resins were discussed by Riese in 1966[25].

Many of the problems associated with water-thinned finishes are common to both emulsion and solution resins and typical of these are the need for oil-free surfaces and the allowance that must be made for the slower evaporation rate of water during the flash-off period and in the stove. The major characteristic problems of the two approaches are given below.[26]:

i- With all emulsion systems, the pigment invariably has to change phase during the drying process where it passes from the water to the resin phase. This makes it difficult or impossible to produce high gloss finishes at high pigment volume concentration. Furthermore, to produce gloss and film performance in emulsion systems, it is essential that all colloids and wetting agents used in the emulsion preparation and in the pigment dispersion stage are compatible with the resin phase after stoving and are then water insoluble. This limitation is a very real one;so emulsion systems are generally rated to be more suitable for primers.

ii- The presence of emulsifying agents in emulsions usually leads to trouble with foaming.

iii- The characteristic film formation in emulsions on non-absorbent surfaces, is by coagulation on the surface so that, in stoving, water in lower layers has difficulty in escaping. Thin film application and high pigmentation can be partial solution.

iv- If a high degree of solubility is induced in the system, high solids content and good build are obtained, but difficulty in eliminating water-soluble components during stoving are found, while if water solubility is reduced to obtain good water resistance in the final film then low solids, low build solutions or low molecular weigt resins result that require more heat conversion to provide satisfactory films.

<u>The advantages of water soluble resins are</u>:

i- <u>Fire risk</u>: One of the most important advantages of the use of water soluble coating systems is the lack of fire risk. Some criticism has been made of these systems that an alcoholic solvents should sometimes be included to bring out their maximum advantages. Tests have been carried out on a large scale, and showed that when the water content of the diluent is over 75 percent, it is quite impossible to ignite the constituents of the paint, even those containing the more volatile alcoholic solvents.

ii- Toxicity: Apparantly the toxicity of water-thinned coatings is less than that of the conventional types curently used while this is of no great consequence in normal good industrial practice, it is probable that increasing attention will be paid to this aspect with regard to atmospheric pollution.

iii- Surface preparation: While the need for clean surface is to some extent a disadvantage of water-based systems, it probably only acts to encourage the proper cleaning of surfaces which is desirable in any paint system.

iv- Cost:- The immediate interest of water in stoving finishes might be thought to be the use of water to replace expensive solvents and thereby to give cost advantages in the selling price of the paint. If alcoholic solvents, particularly the higher boiling ones, are necessary to modify the coating properties, this advantage may disappear completely, but in many cases the water-based system is less expensive when comparison is made on the basis of the cost per unit volume applied paint. The cost advantage may come from the elimination of the solvents used by the paint consumer. It may also come from collection of overspray in water washed spray booth, or it may come from savings on cleaning solvent or in the drying of objects prior to painting, or from the elimination of expensive storage facilities.

v- Wider range of application: The water-soluble resins in the first instance have been developed for conventional application techniques such as spraying, dipping, or flow coating. However, a new application technique has raised much interest; namely electrodeposition[5, 27-29].

In the electrodeposition process, the metal being coated is the anode, and the resin and pigments are being carried to it by the electric current. At the anode, the particles are discharged by the current and the liquid forced away from the deposited coating by the current. The coating resin is converted from a water-soluble form to a water-insoluble form. This method will deposit a uniform coating in inaccessible areas, rough surface, and hidden joints and crevices[30].

Broadly speaking, there are two methods of exploiting electrodeposition. One is to apply the primer by electrodeposition, then finish with conventional technique. The other is to use electrodeposition to apply a single coat which varies from matt to high gloss. Application of primers by electrodeposition is already an established practice in the automotive industry; and it is evident that single coat electrodeposition will become popular for finshing steel furniture and similar products.

The disadvantages of water soluble systems are summarized into the following problems which are not capable of easy solution[26]:

i- Water-based solutions need higher heat input for evaporation and since understoving of water-soluble resins results in a very severe loss of film properties, the combined effect is that stoving schedules are longer than with conventional solvent-based systems.

ii- The cleaning of surfaces with a high degree of efficiency will always be necessary in the case of gloss finishes, and almost is essential in the more highly pigmented paints.

iii- The only mechanism of obtaining water-solubility and finally water-insolubility that has achieved any real success depends on the use of an acid-containing polymer and a nitrogenous base. Inevitably, with elimination of some of the base during stoving, acid groups on the polymer are available for alkaline attack and there are no immediate prospects of improving substantially the alkali resistance of water-soluble coatings.

iv- In the pigmentation of water-soluble resins only those which are neutral and substantially insoluble in water are satisfactory. Strongly basic pigments and those containing appreciable quantities of water-soluble salts, are generally unsatisfactory in that they effect the stability of the paint on storage, or decrease the water resistance of the film. Pigments which are strongly hydrophilic, such as china clays, may delay the evaporation of water from the paint film and therefore should be used with care. A partial list of satisfactory and unsatisfactory pigments is given in Table 1.

Table 1: Suitable and Unsuitable Pigments for Water-Soluble Binders.

Suitable Pigments		Unsuitable Pigments
Titanium dioxide	Stronium-chromate	Zinc oxide
Antimony oxide	Hansa yellow	White lead
Lithopone	Chrome green	Basic lead sulphate
Zinc sulphide	Phthalocyanine-blue	Calcium silicate
Calcium carbonate	Prussian blue	Calcium plumbate
Barium sulphate	Ultramarine blue	Zinc chromate
Mica	Helio red	Red lead
Talc	Lithol red	
China clay	Iron oxide	
Lead silco-chromate	Carbon black	
Lead chromate		

v- In highly pigmented gloss finishes there is often a tendency for pinholes and ciss marks to appear during the stoving operation.Fry[31] has ascribed this to critical surface tension. Ciss marks may appear in the stoving operation and this is probably due to the formation of micelles of water-insoluble resin during the curing stage. It has been found that very small quantities of thixotropic pigment, such as bentonite or finely divided clays or calcium carbonate, will prevent this occurance, but care must be taken to maintain a satisfactory gloss.

Formulation of aqueous coatings:

The formulation of a water-soluble paint needs special care. Addition of certain ingredients are necessary to insure stability in the container, proper application characteristics, and satisfactory film properties. Marten[32] gave a water-soluble type formula as shown in Table 2:

Table 2: Water Soluble Formulation

Ingredient	Percent	Ingredient	Percent
Opaque pigment	20.0	Defomer*	0.001
Extender pigment	10.0	pH buffer*	0.1
Pigment dispersent*	0.1	Fungicide*	0.02
Resin	20.0	Wetting agents	0.1
Preservative*	0.2	Water	49.4
Antirust agent	0.1		100.0%

* Optional in some formulas.

Methods used to water-solubilize polymers:

The polymer to be water-solubilised must not only be sufficiently hydrophilic to be soluble in bulk, but also be capable of producing coherent and water-insoluble films on air drying or stoving.

The most convenient method is to introduce in the polymer chain, carboxyl groups which can be neutralised with a base;to solubilise the polymer as a salt, as illustrated below:

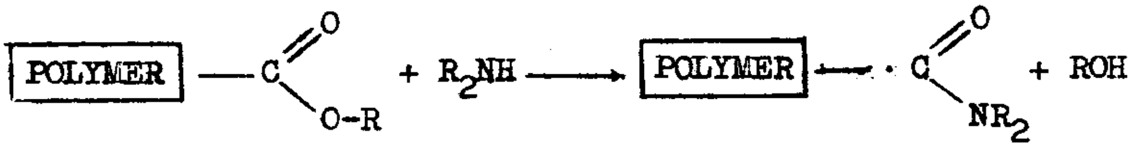
$$\boxed{\text{POLYMER}} \text{ --- } COOH + R_3N \longrightarrow \boxed{\text{POLYMER}} \text{ --- } COONHR_3$$

The inclusion of hydrophilic groups, for example, hydroxyl, in the polymer chain, will aid solubility and will provide sites for subsequent curing of the film by chemical reaction. Relatively low molecular weight polymers (20,000) are used to aid water solubility and to keep solution viscosity to minium.

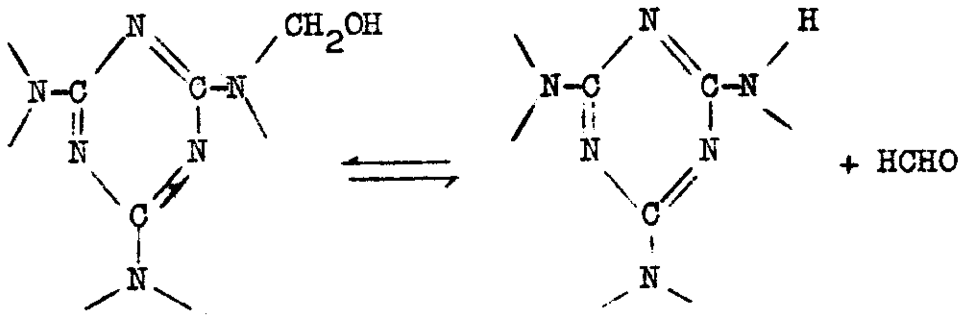
The choice of the neutralizing base for a polymer system is very important and critical, since it may affect polymer properties as solution storage stability, viscosity, curing rate, degree of water solubility, film durability and cost. The generaly characterstics of the neutralizing base are:

a- must be volatile,
b- relatively cheap,
c- not highly objectionable odours, and
d- must not chemically attack the polymer system.

Thus tertiary amines are generally preferred to other bases as they are less likely to attack chemically the polymer system through amminolysis:



and/or depolymerization of for example, a melamine/formaldehyd condensate.



$$HCHO + R_2NH \longrightarrow R_2NCH_2OH$$

Generally 90-100 percent acid groups neutralization will give optimum results for solution viscosity and storage stability.

The addition of water miscible organic solvents in small amounts (e.g. glycol, ethers, alcohols, etc) to water-soluble polymer solution usually controls solvent release and flow properties of the polymer and reduces the solution viscosity.

The chemistry of water-soluble thermoactive synthetic resins was discussed by Riese[34] in 1966. The most common resins which can be water solubilized are:

1- Oils:

The most convenient method of water-solubilization of unsaturated oils is by reaction with acid or anhydride dienophiles, usually maleic anhydride[35]. Other acid or anhydride dienophiles have been used and these include acrylic[36] and crotonic acids[37].

The most interesting feature of maleic oils is that one has a simple process for adding acidic groups in the middle of the oil molecule. These groups make the oil useful as a grinding medium as well as give the oil compatibility with ethyl and nitrocellulose. The acidic groups may be reacted with a variety of substances such as alkalis, polyhydric alcohols, and basic dyes to make the oil useful in water paints, textile size, cotton printing, adhesives, or as resins. The most important three uses of maleic oils are:

i- as water vehicle,

ii- improving the drying and heat bodying properties of non-conjugated fatty drying oils, and

iii- the preparation of resins.

The drying oils are commerically maleinized to increase their reactivity[38]. The product obtained by reacting maleic anhydride with a suitable glyceride is known as the adduct. Linseed, soybean, or other oils are heated with 2-10 percent of maleic anhydride for several hours at a temperature of 200-300°C. The reaction product is generally neutralized with glycerol or pentaerythritol. This treatment does not appreciably increase the air drying characteristices but improves the bodying properties, colour, and the water resistance of the dried films[39]. Maleinized oils may be stoved at elevated temperature and cross-linked through their unsaturation or by reaction with amino or phenol/formaldehyde condensates.

Essentially, their chemical behaviour and properties are those of conventional drying oils[41].

<u>Drying</u>: Normal systems of the maleinized oil types, i.e. those containing 2-10 percent maleic anahydride, are reactive toward atmospheric oxygen and will cure by oxidation/polymerization reaction at stoving temperatures of about 120°C in presence of metal driers to give hard, tough and glossy films. The drying process involves polymerization initiation, peroxide formation, peroxide decomposition and cross-linking[42].

It was found that even a simple maleinized linseed oil film stoved for 45 minutes at about 120°C gave a reasonable good performance as one or two-coat system on mild steel. Better performance rating, however, can be obtained by using linseed/tung oil mixtures; and tung oil with cyclopentadiene, which was then maleinized to give an ammonia-soluble product, gave very promising results. The drying time may be shortened by the addition of water-soluble driers which are usually cobalt, lead or manganese salts of acetic acid.

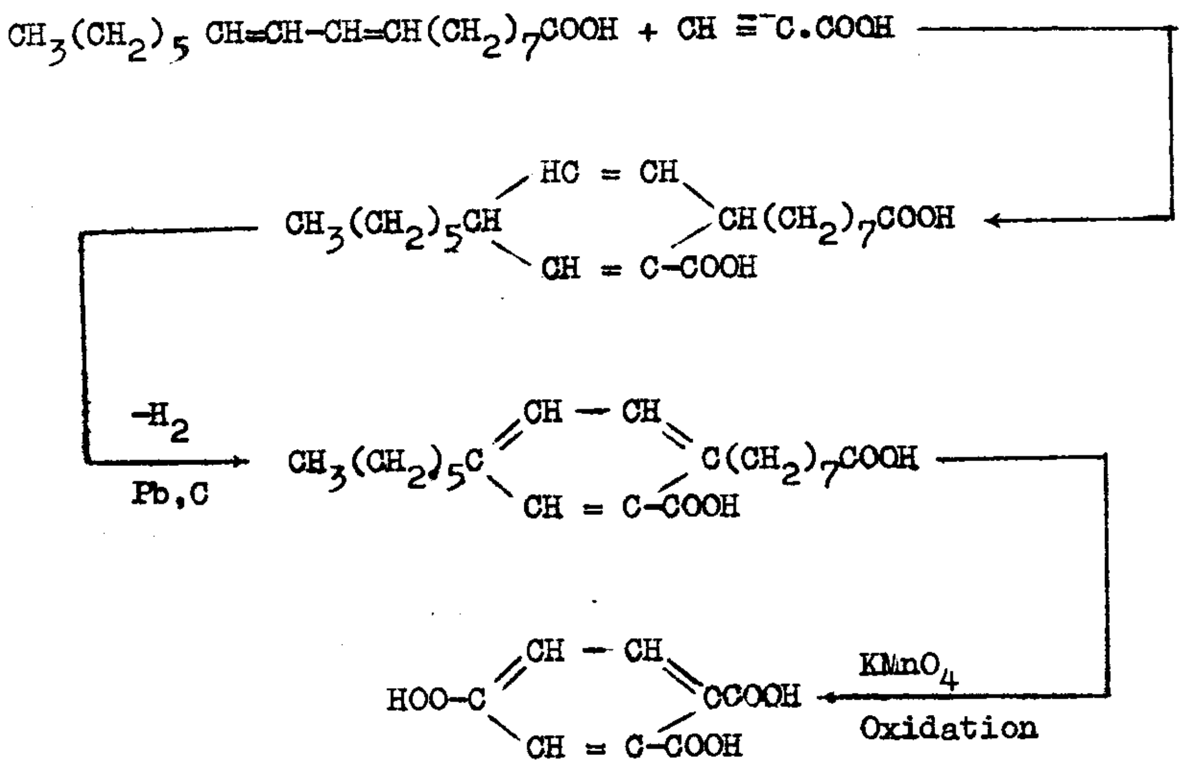
Preparation: The general method for the preparation of a water-soluble oil is to react the drying oil with just sufficient maleic anhydride to render the product soluble in dilute ammonium hydroxide, or other volatile base, thereby allowing a high proportion of the original reactivity of the drying oil to be retained in the product for the building of coherent and water resistant polymeric structure during the subsequent drying process, whether air drying or stoving[43].

Reaction Mechanism:

Structurally, maleic and fumaric acid are versatile chemicals for synthetic purposes. They contain an ethylenic bond that is activated by the adjacent carboxyl groups; in addition, they undergo reactions typical of anhydrides and acids[44]. In other words, maleic anhydride has a total potential functionality of four and can be reacted by an addition and/or a condensation mechanism[45,58].

i- Reaction between maleic Anhydride and conjugated fatty oils:

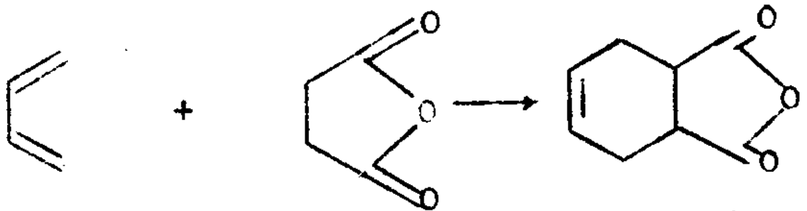
The reaction of the hydrocarbon chain of fatty acids were reviewed by Harwood[46]. He discribed the reactions of poly-unsaturated acids which are conjugated or capable of undergoing conjugation readily, with a variety of dienophiles. For the most part the adducts were not characterized; mixtures of products containing a six membered ring are assumed. In one instance the six membered ring was proved by the sequence of reactions shown below:



Trimellitic acid

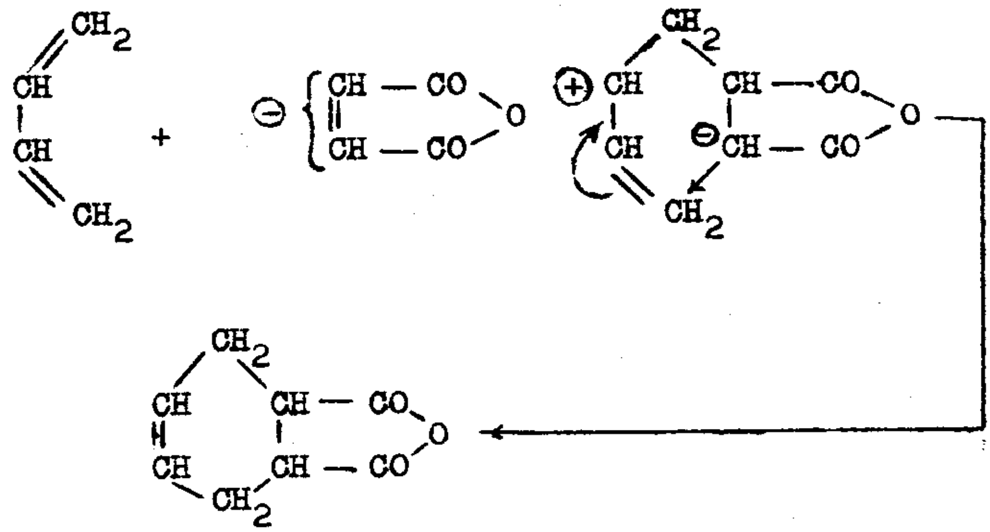
For oils containing conjugated unsaturated (wood oil and dehydrated castor oil) addition of maleic anhydrids proceeds smoothly at relatively low temperatures (80°C) through a Diels-Alder addition[48,49].

The Diels-Alder cyclo-addition is the main reaction in the addition of maleic anhydride to the group 9. 11-linolyl of dehydrated castor oil as shown below[50]

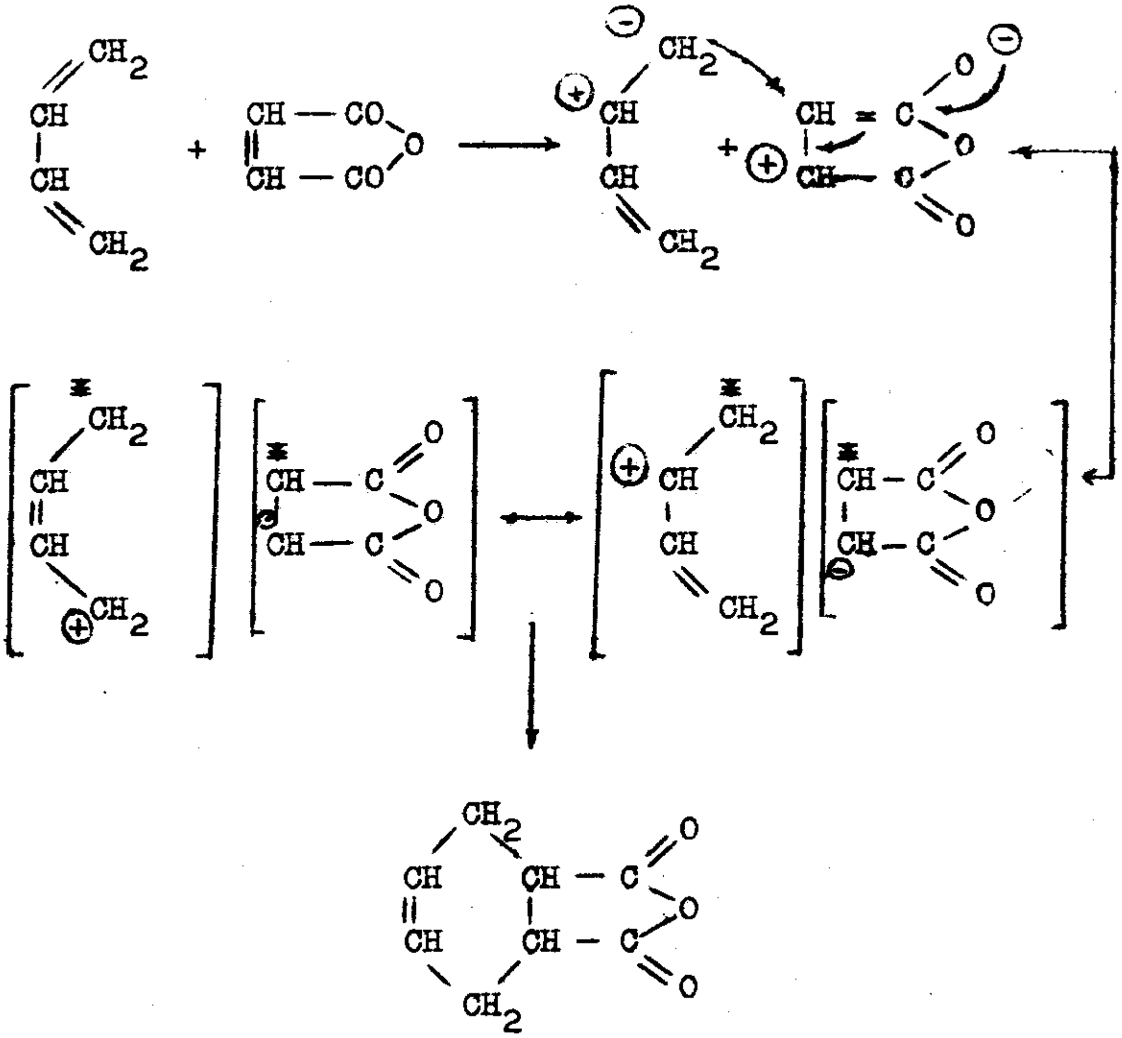


No reaction mechanism has yet been established for these Diels-Alder additions.

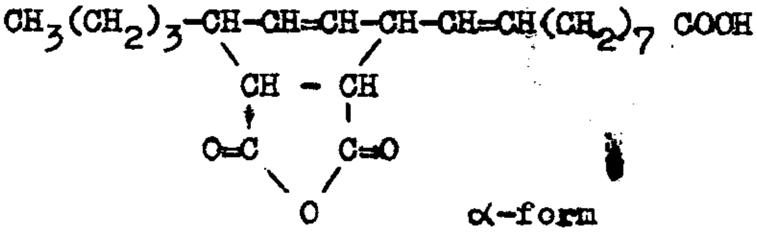
Price[129] suggested the following mechanism:



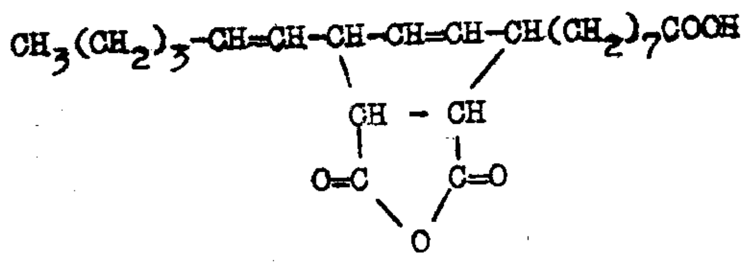
The following postulation was given by Weiss[51] in 1942.



Rudd[52], Morrell, Marks and Samueles[53] have shown that the addition products have the following formula:



α-form

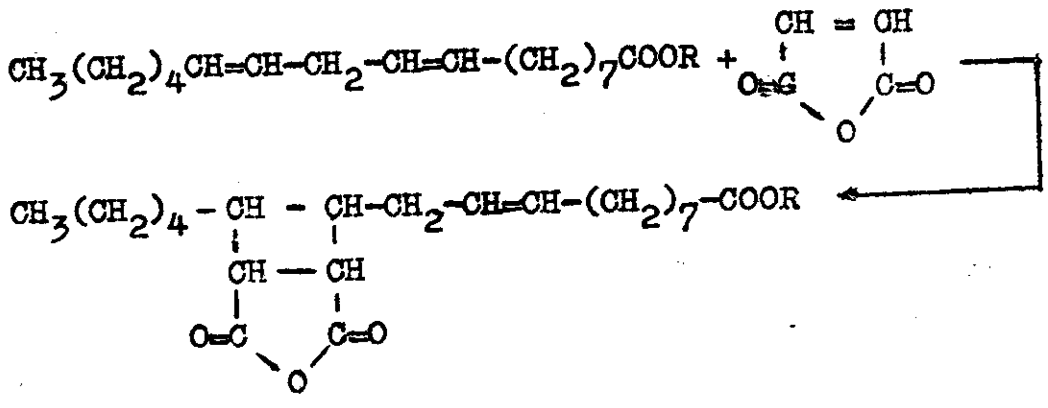


β - form

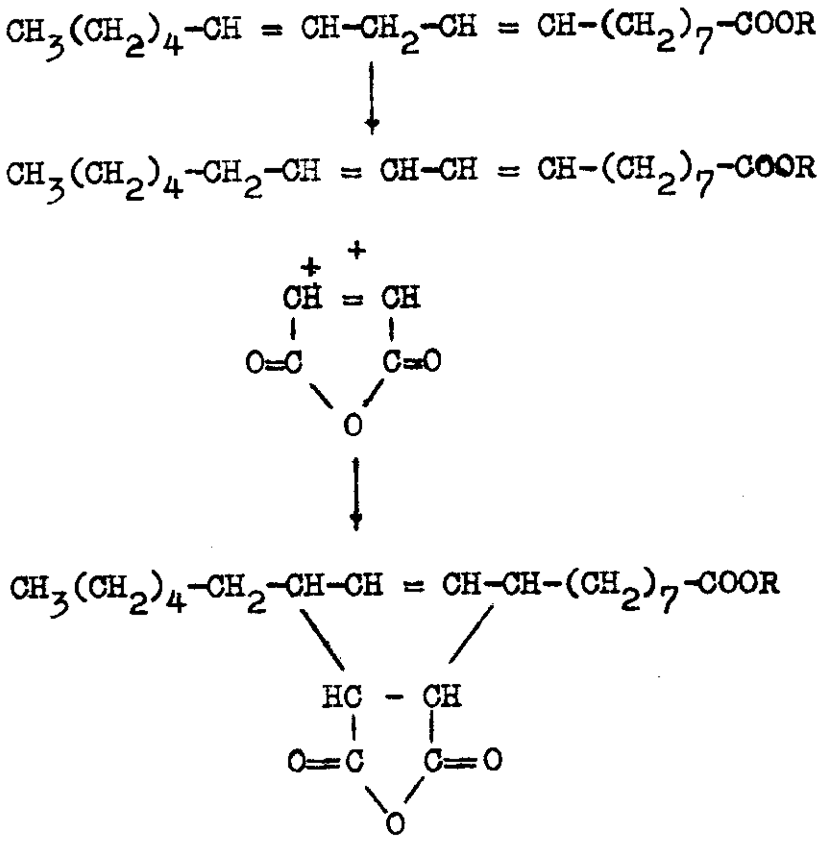
ii- Reactions between Maleic Anhydride and Non-Conjugated Fatty Oils:

The reaction between maleic anhydride and non-conjugated fatty acids or their derivatives or oils, in which the double bonds are separated by methylene groups, occurs at 200-250°C which is relatively high as compared with the temperature required for the reaction of conjugated fatty acid (80°C). The reaction of maleic anhydride with non-conjugated fatty acids and oils has been mentioned tentatively in the literature and the products are more complex and have not been precisely characterized[54].

Cloker[108] originally assumed that the reaction proceeded in accordance with the following equation:

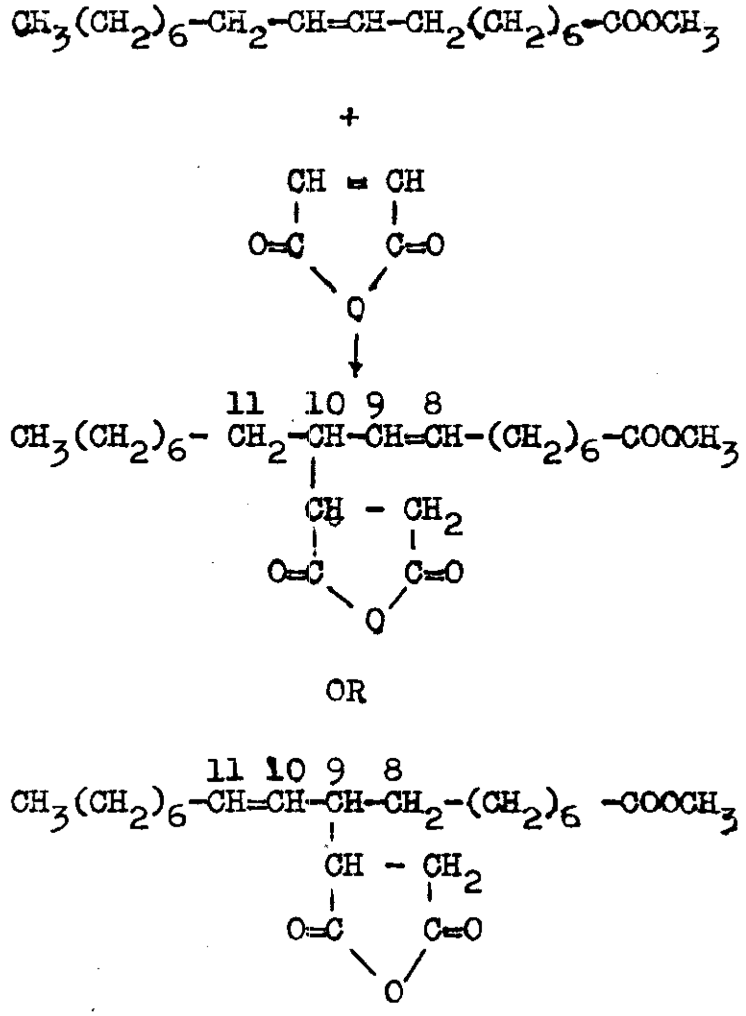


while this explains the resulting properties of the oil, the reaction does not seem plausible because of the assumption of a butane ring which is difficult to form in this manner. The addition reaction proceeds at an appreciable rate at 200°C, it is doubtful if such conjugation can be completely explain the reaction mechanism.[57]



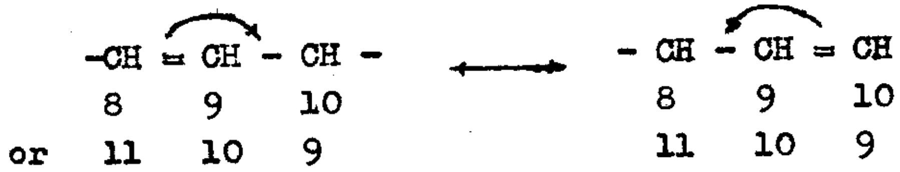
The most acceptable mechanism for the addition of maleic anhydride without affecting the unsaturation of the fatty component appeared to be the formation of a substituted succinic anhydride by reaction of maleic anhydride at an carbon atom, or at a double bonded carbon atom.

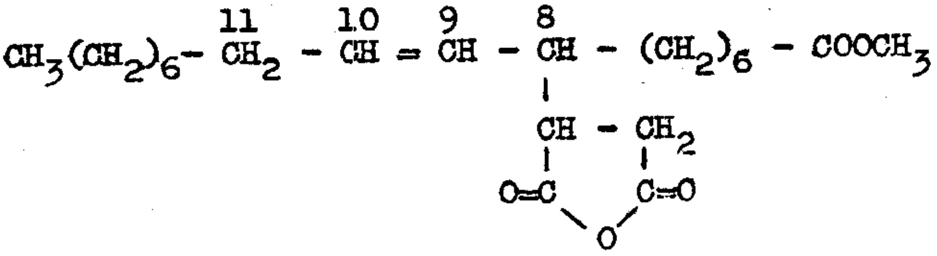
Ross et.al.[55] has shown that at a temperature of 200°C methyl oleate and maleic anhydride give rise to an isomeric mixture of addition products of substituted succinic anhydride formed by the attachment of the maleic residue to C_9 or C_{10} and the remaining double bond shifting to the C_{10} - C_{11} or C_9 - C_8 position respectively.



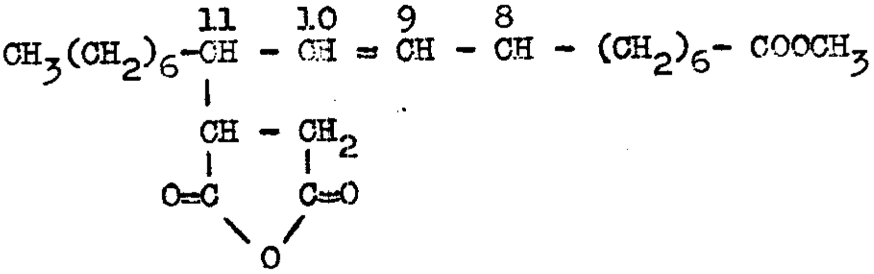
Bickford *et.al.*[56] showed that the addition of maleic anhydride may also occur at the 8 and 11 positions in methyl oleate without alteration in the position of the double bond.

The intermediate free radical is proposed to account for the observed results. The radical is believed to originate at the 8- or 11-position adjacent to the double bond leading to a resonance hydride which is equally susceptible to reaction at either of two position (8 and 10; 9 and 10):



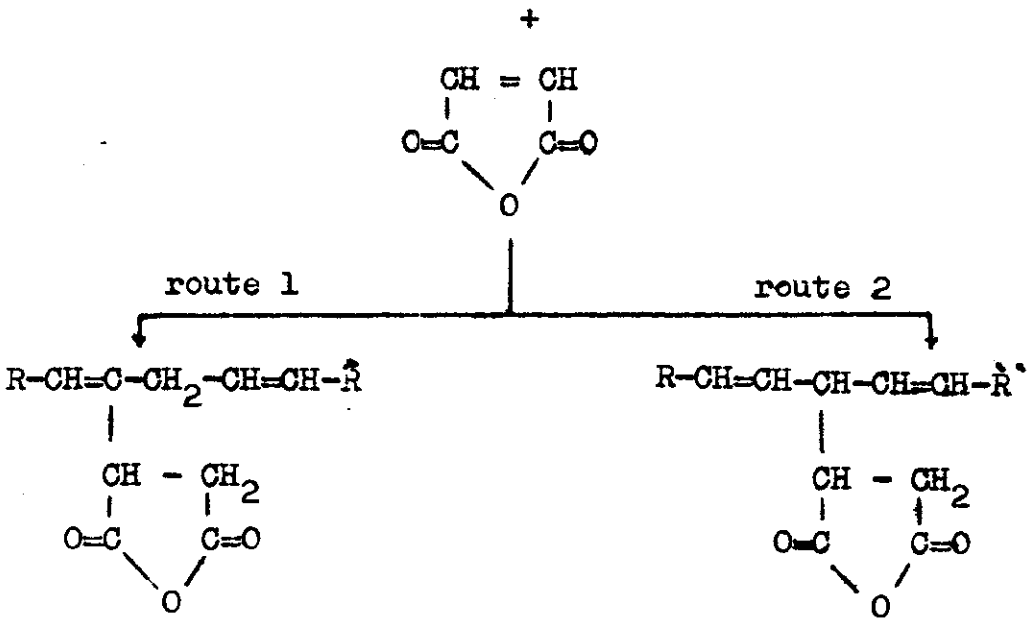


OR



Bolley[57] proposed the following two routes for the retention of unsaturation in case of linoleic ester:

$CH_3(CH_2)_4-CH=CH-CH_2-CH=CH-(CH_2)_7-COOR$

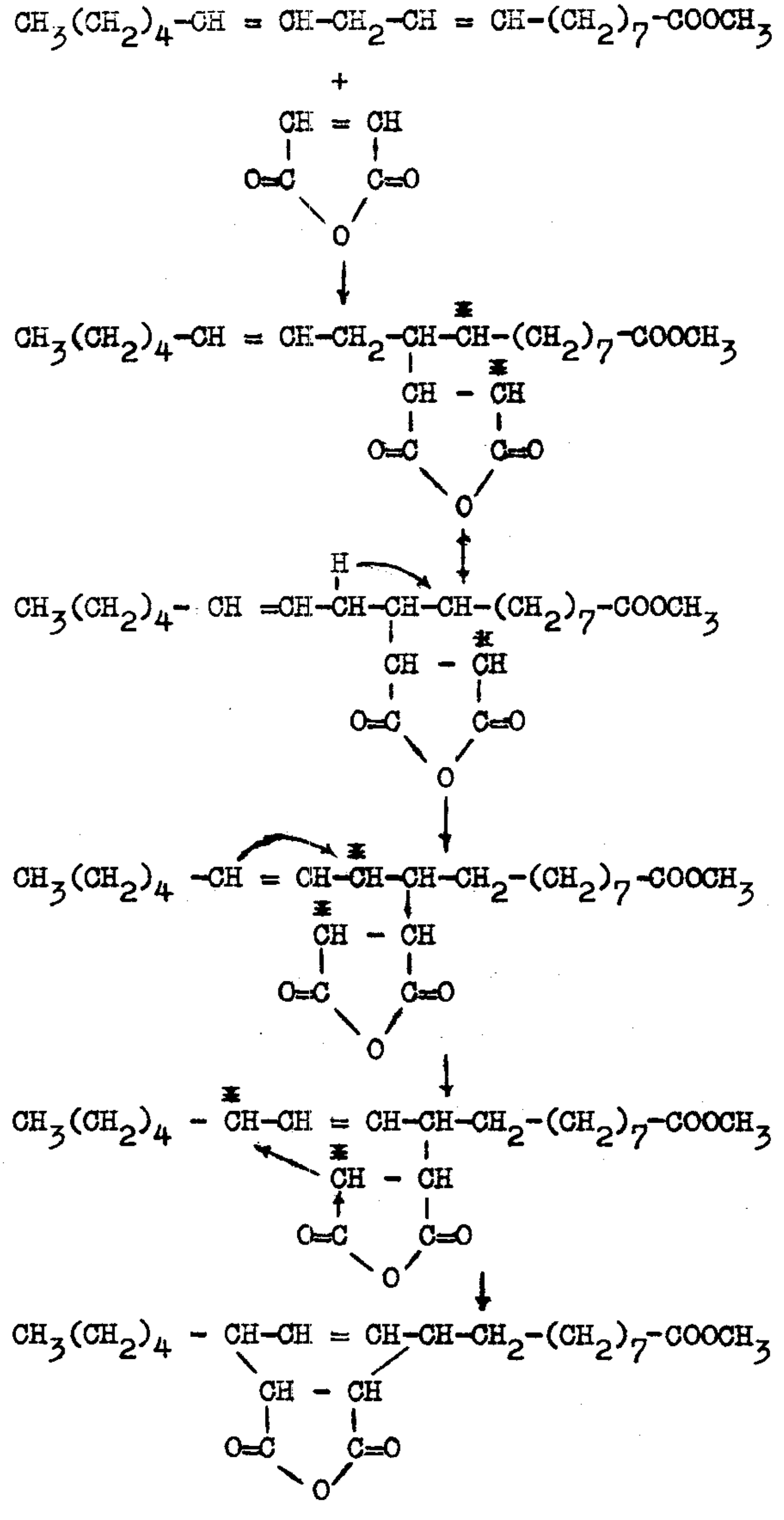


I II

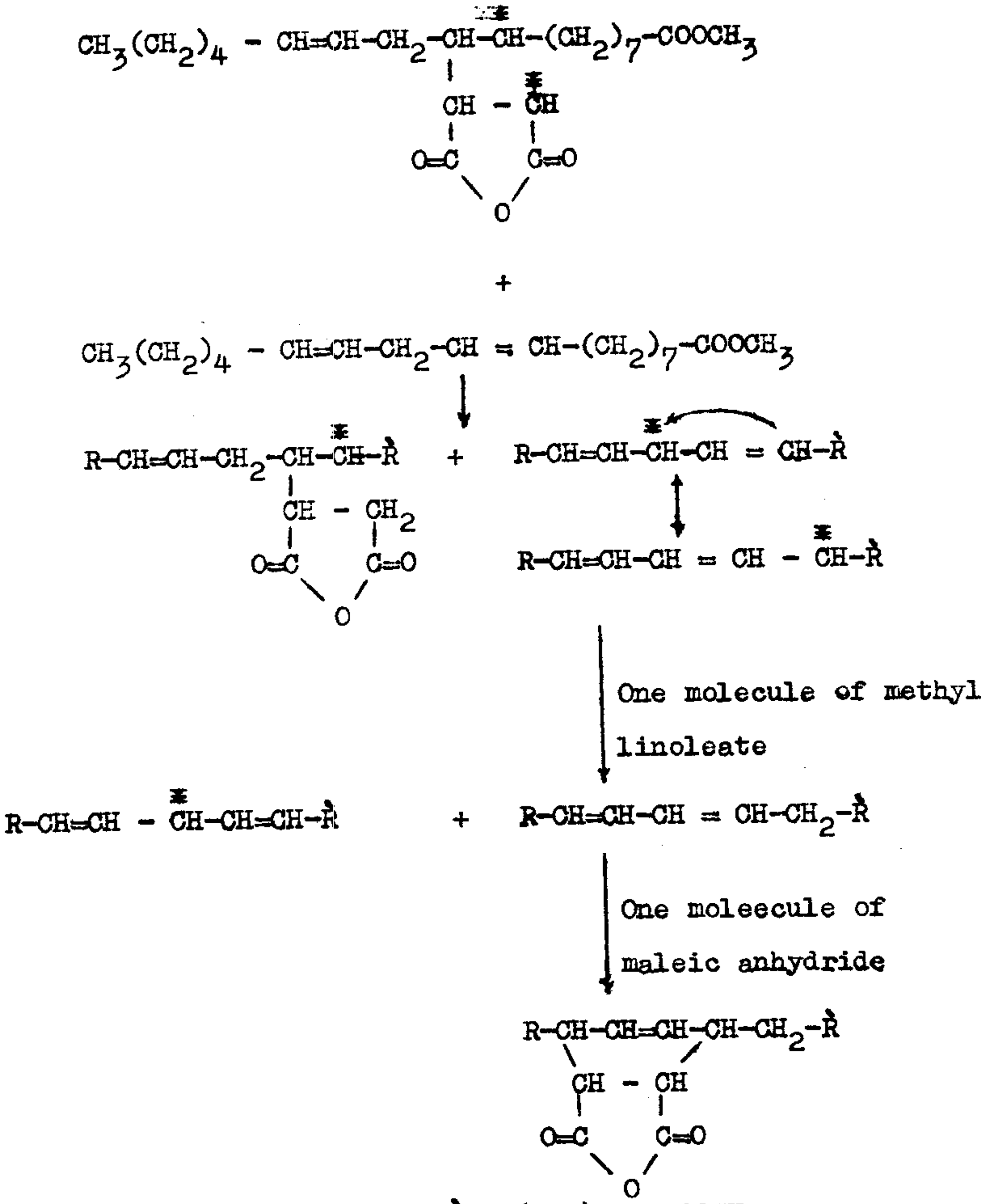
where $R = CH_3(CH_2)_4-$ and $\grave{R} = -(CH_2)_7-COOR$

He believed that the second route, which involves a hydrogen shift from the methylene group, more nearly fits the theory of chemical reactions.

Plimmer[54] suggested that the reaction may occur at a non-conjugated double bond according to the following scheme:

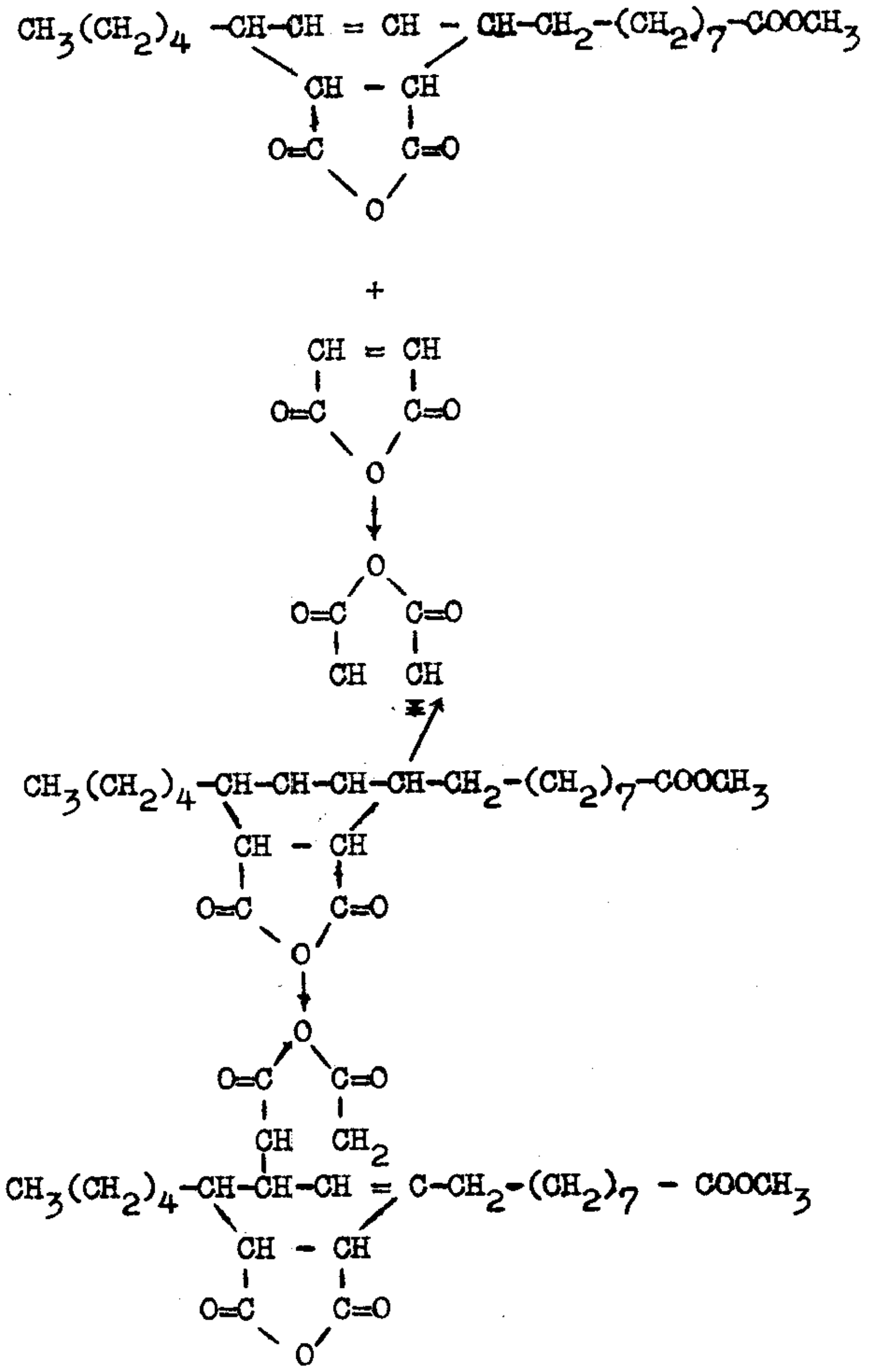


Plimmer also suggested that the reaction may involves a chain mechanism of the following type:



where $R = CH_3(CH_2)_4-$ and $\grave{R} = (CH_2)_7 - COOCH_3$

The intrusion of a second molecule of maleic anhydride probably occurs by addition to a doubly-bonded carbon atom and displacement of the double bond as follows:



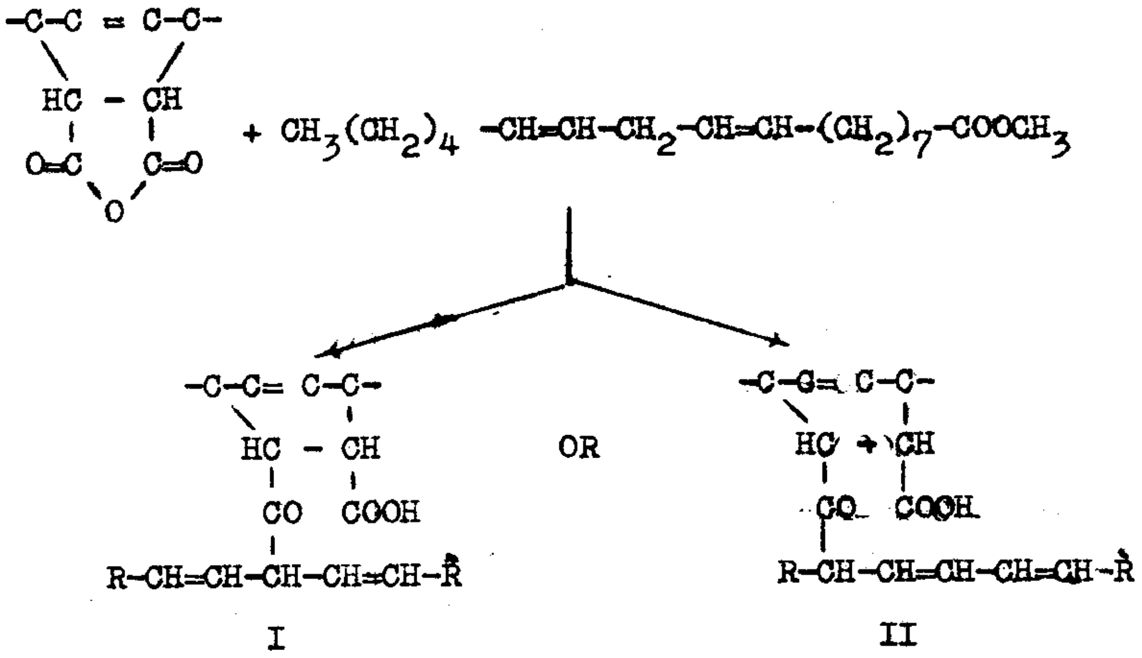
Loss of Acidity During Maleinization:

One of the most important and interesting feature but least understood properties of the reaction products (adducts) obtained from the reaction of maleic anhydride with drying oils are that such adducts have lower acid and saponification values than the theoretical ones. This loss of acidity during the maleinization is very important both fundamentally and economically;since it might require the use of a high proportion of maleic anhydride to insure its solubility, thus the reactivity of the oil being unduely reduced.

Bevan[132] had remarked on the considerable departure from the theoretical acid value obtained in the reaction of maleic anhydride with linseed oil and certain non-drying oils. In many cases, quoted "acid values were less than 50% of theoretical, the temperature employed being 220°C, and the time of the reaction usually five hours".

Bickford *et.al.*[58] showed that the reaction products of maleic anhydride with methyl oleate and methyl linoleate had acid and saponification values15-20 percent lower than the theoretical values,and suggested the combination of maleic anhydride through the carboxyl groups.

To explain the loss of the acid groups, Plimmer[54] suggested that one or more of the adducts must be involved in further reactions. He suggested that, in the case of methyl linoleate, these reactions yield structures such as those indicated in the following scheme:

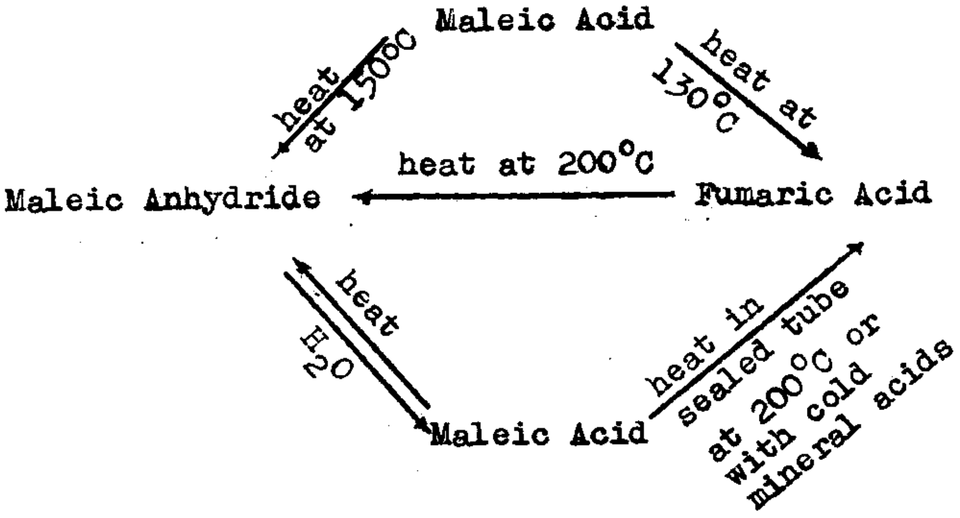


Where R = $CH_3(CH_2)_4$ - and $\mathring{R}$ = -$(CH_2)_7$ - $COOCH_3$

Brett[43], who discussed the loss of acidity between C_{18} conjugated esters and maleic anhydride, concluded that it involved essentially two factors-one associated with resistance of the adduct to hydrolysis and the other with loss of potential acid groups by chemical reaction.

The use of fumaric acid to modify linseed oil did not appear to offer any significant advantage over maleic anhydride in terms of acid and saponification values. This can be attributed to the conversion of fumaric acid to maleic anhydride under the influence of the experimental conditions.

The conversion cycle is shown below[59]:



2-<u>Alkyd Resins</u>:

A variety of oil-modified polyester, for air drying and stoving finishes, have appeared in the literature over the past years[60,61]. In general, water-soluble alkyds can be obtained by stopping the polyesterification reaction at a suitably high acid number followed by neutralization with ammonia or other volatile water-dilutable organic amines. The neutralized resin can be further thinned with water to the desired solid content.

The water soluble alkyds can be modified with various other resins to impart some of the desirable characteristics of these resins.

(a) <u>Oil-Modified Alkyd Resins</u>:

Waldie[62] produced water dispersible pigmented alkyd resin by saponifying an oil or fatty acid by adding a pigment suspended in water, and precipitating the pigment coat with the oil acids by acidification. The precipitate was separated and added to a reaction product of glycerol and phthalic anhydride which has been prepared separately.

Armitage[63] prepared water-soluble alkyd resins by heating to the esterifying temperature, a reaction mixture of polyoxy alkylene glycol, a polybasic carboxylic acid, a polyhydric alcohol other than the polyoxy alkylene glycol, and a drying oil or its fatty acids to effect complete esterification. The product is a clear, viscous resin with an acid number of 16. Emulsion paints prepared with the resin show high gloss.

Ronald[64] studied the preparation of water-soluble base paint with good storage stability. The paint was prepared from a polyhydric alcohol, a polycarboxylic acid, a drying oil or fatty acid, and lithium hydroxide added at a concentration of not more than 90% of the theoretical requirment.

A water soluble alkyd resin[65] was prepared by the reaction of polycarboxylic acids or their anhydrides with:

(1) esters of aliphatic monocarboxylic acids contg. $\geq$ 2 free OH-groups or 1 epoxy group in the alcohol protion and having the carboxyl group attached directly to a tertiary or quaternary C, and

(2) polyhydroxy compounds.

Schroeder[66] prepared water-dispersible oleoresinous coating based on vehicles made by reaction of maleic anhydride with a triglyceride oil or resin modified oil. These vehicles were made water-dispersible or even water-soluble by reaction with alkalis, ammonia or amines. A water-soluble vehicle that was comparable in performance to a coconut alkyd was made by preparing a polyester prepolymer from TMA, neopentyl glycol, and adipic acid. A white enamel made with this vehicle and a melamine resin was claimed to have better impact resistance, abrasion resistance, and colour retention than a coconut alkyd-melamine enamel.

Alkyd resins[67] were prepared by reacting (a) polycarboxylic acids or their anhydrides with (b) esters of monocarboxylic acids, the alcohol parts of which contain $\geq$ 2 OH groups or an epoxy group the acid part of which has the carboxylic group directly bound to a tertiary or quaternary

C atom. The total number of moles that can take part in the reaction should be 1.0-1.2 times the number of the total number of OH groups in the reaction mixture.

Kraff and Weisfeld[68] prepared a water-based alkyd resin from a medium oil/pentaerythritol/ethylene glycol/PA mixture.

Bruggeman[69] formulated water-soluble alkyds and enamels. Two examples of promising systems are presented: an alkyd system which attempts a balance to optimize all the variables, and an alkyd copolymer system which dries very quickly. The former was based on TMA, trimethylol ethane, and safflower oil. The latter was based on a short oil length safflower TMA alkyd modified by copolymerization with a combination of vinyl-toluene, CH_2: Me CO_2 Me, and CH_2: CMe CO_2H. Because of its fast drying, this system leaves some latitude to enhance other properties.

Crawford[70] <u>et</u>.<u>al</u>. prepared water-soluble alkyd resins by heating a mixture of polyhydric alcohols and Deils-Alder adduct at 170-80° until an acid value of 50-100 mg KOH/g was obtained.

Hay et.al.[71], prepared water-soluble alkyd resins by replacing TMA in an esterification mixture with 2,2,6,6, tetrakis (β-carboxyethyl) cyclohexanone or with a mixture of phthalic acid or anhydride and 2,2,6,6, tetrakis (β-carboxyethyl) cyclohexanone. Resins prepared from this cyclohexanone derivative give more compatible products of great hardness in shorter esterification times than when using TMA.

An Austrain Patent[72] indicated that water-thinnable alkyd resins with acid number at least 30 and -OH value 120 were neutralized and then combined with mainly volatile, polar compounds having at least one free -OH group and at least one hydrophilic ether group, optionally in the presence of solvent.

A process[73] for producing water-soluble film forming alkyd resins comprised neutralizing an alkyd resin with an amino alcohol. The resin was formed by the reaction of a polycarboxylic acid or anhydride, e.g. PA, with a N-free poly-hydric alcohol, e.g. glcerol. It contained sufficient free carboxyl groups to have an acid number between 25 and 100. The amino alcohol may be, e.g. 2-amino-1,3-propanediol.

A British Patent[74] indicated that water-soluble alkyd resins may be prepared from a polyol, a polycarboxylic acid, and a polymethylol alkanoic acid. Then, dimethylol propionic acid, neopentyl glycol, and PA were heated together and adipic acid added. The mixturs was neutralized with aqueous NH_4OH and hexakis (methoxy methyl) melamine was added. Films, baked 30 minutes at 150°, were glossy, smooth, hard and flexible.

Modified alkyd resins[75] useful for water-base paints were prepared from a drying or a non-drying oil, a polyhydric alcohol, polyehylene glycol, a non-oxidizing monobasic fatty acid, and a dicarboxylic acid or anhydride. The components were allowed to react at 175-290° to an acid number of 5-30, and the reaction product was neutralized and dispersed in an aqueous medium.

Domide and Manin[76] prepared water-soluble alkyd resins from a mixture of fatty acids of vegetable oils (oxidized with 15-23 wt.% 30% H_2O_2 at 120-40°), PA and pentaerythritol. The acid number of the resin was 100-150 mg KOH/g. Ammonia (25%) was added to pH 7-8 and the mixture was diluted with water to give a resin of viscosity 40 sec.

Belyaeva <u>et</u>.<u>al</u>.[77] produced a water-soluble alkyd resin; linseed oil or cottonseed oil was transesterified at 245 - 50° with pentaerythritol in the presence of NaOH or Na_2CO_3 as catalyst. The resulting ester was esterified with phthalic anhydride at 180°. The resin thus prepared was dissolved in 2:1 BuOH-iso PrOH mixture and the solution was neutralized with Et_3N.

Nieuwehhuis and Visser[78] prepared water-soluble resins from pentaerythritol, PA, adipic acid, and glycidyl esters of C_{9-11} branched chain fatty acids. The relation of the water solubility and stability of aqueous solutions of these polymers with respect to the formulation parameters was studied. These alkyd resins were combined with melamine-HCHO resins and were also applied electrophoretically.

A French Patent[79] described the preparation of water-soluble alkyd resins. Thus propane-1,2,3-tri-carboxylic-acid was boiled with an alcohol to give a monoester, which was condensed with a polyol and a fatty acid to give an alkyd resins used in the preparation of paints and enamels.

Yoshitom et.al.[80] prepared alkyd paints from linseed oil fatty acid, PA and pentaerythritol. The alkyd resin was modified with maleic anhydride and the resin dissolved in iso-PrOH, brought to pH 7.3 with aqueous Me_3N and diluted with H_2O to give 50% resin solution. Similarly an alkyd resin from soybean fatty acid, PA and trimethylol propane was modified with adipic to acid number 66 and neutralized with aqueous Me_3N.

Charles and Miston[81] described the preparation of a water-soluble alkyd resin. Thus cyclopentane tetracarboxylic acid was esterified with an equimolar amount of hexyl-alcohol, condensed with the condensation product of tri-methylol propane and linseed oil fatty acids or/and pelargonic acid, and made alkaline with Et$_3$N to give alkyd resins. The resins were useful, after thermal cross-linking, as coating of excellent mechanical properties and salt spray resistance.

Graver and Sedgwick[82] described the preparation of alkyd resins using a sulfonic acid catalyst. Thus the adduct of a drying oil and a dicarboxylic acid or anhydride prepared in the presence of an alkyl sulfonic acid catalyst, was heated with a lower alkanol or diol to give a water-dilutable thermosetting resin suitable for use in electrocoating application.

Maeda *et*.*al*.[83] prepared water-soluble alkyd resins by adding 2,2,6,6,β-tetrakis carboxy-ethyl cyclohexanone or its tetramethyl ester to mixtures of polybasic acids, polyhydric alcohols, and drying or nondrying oils.

(b) Alkyds Modified with Monomers:

Armitage[84] prepared water-dispersible alkyds by cooking at 200°C in the presence of small amounts of xylene. The resin formulation consisted of linseed acids, pentaerythritol, polyethylene glycol (150°C), PA and styrene. Advantages of this type of resin were: high gloss, fast air-drying, good hardness and good water resistance. Defects were: poor flow and levelling, and less hiding power than other alkyds.

Chadha and Gupta[85] described the preparation of water-dispersible alkyds suitable for severeclimatic conditions. The composition of the alkyd and the molar ratio were approximately similar to that used by Armitage[84].

Ichinomiya and Yamushita[86] indicated that graft copolymerization of alkyd resins of acid number $\angle 30$ with acrylic acid/or methacrylic acid, together with their esters, and subsequent treatment with amines or NH_3 produced water-soluble alkyd resin graft copolymers. These resins gave water-proof films by heating with amino plasts.

Ghisolfi *et.al.*[87] prepared alkyd resins with emulsifying power by the condensation of fatty acids with phthalic anhydride, polyethylene glycol and a polyalcohol. Later, they modified[88] the alkyd resins by adding polyvinylacetate; the ratio of the alkyd resin to polyvinylacetate was 1:1. This vehicle was more compatible with Pb pigments than the alkyd resins alone.

Vinylated alkyd resins (acid number $>$ 40 and containing free OH groups of -OH equivalent 100-200) reacted with NH_3 or a water soluble organic base. The resins were prepared from PA, pentaerythritol, glycerol, trimethylolethane, trimethylol propane, propylene glycol or neopentyl glycol. They were then vinylated by (1) a mixture of 10-35% by wt. (based on the reaction product) vinyl monomer, such as styrene, and 5-20% by wt. α,β-unsaturated acid, such as methacrylic acid or acrylic acid, in the presence of di-tert- Bu-peroxide (catalyst), or (2) vinylated oils prepared from linseed oil, dehydrated castor oil, soybean oil, sunflower oil, safflower oil, codliver oil crude castor oil or their mixtures.[89]

Zimmerman, et.al.[90] prepared alkyd resins useful for metal coatings by treating a polyol and fatty acid with a copolymer (no. av. mol. wt. $<$ 10,000) containing α-methylstyrene and/or styrene and 10-20/wt. % maleic anhydride.

A British Patent[91] indicated that water-thinnable compositions containing alkyd resins modified with ethylenically unsaturated monomers were useful for surface coatings. Thus a mixture containing Me-methacrylate, Et-acrylate, methacrylic acid, Bz_2O_2 was heated to yield a copolymer. A mixture containing castor oil and glycerol was heated in presence of Pb naphthenate to 225°C for 1 hour, then the copolymer was added to the cooled mixture. PA, TMA and glycerol were added and heated to 210°C to remove water. The mixture was kept at 210°C until the acid value reached 50. The resin was thinned in a water N-N-dimethyl aminoethanol mixture.

(c) Epoxy alkyd resins:

Epoxy modified alkyd resins infinitely water-dilutable and film forming were prepared[92] as follows: to stoichiometric mixture of a polyol and a dibasic acid was added fatty oil containing C_{6-26} saturated fatty acids or their esters. The mixture was heated until the acid number dropped to 70-90. Tetrachlorophthalic anhydride was added and the mixture reheated until the acid number was < 120. A glycol ether solvent and C_{8-26} epoxidized fatty ester were then added.

The condensation product of a C_{10-24} unsaturated fatty acid with 5-25% (based on the wt. of fatty acid) itaconic or fumaric acid were made to react[93] with an epoxy resin at a temperature which prevents the COOH-OH reaction until the acid number of the product was 1/3-1/2 of the initial value. The ester was then made-soluble in water by the addition of an amino compound such as NH_3, Et_2NH, or diethanolamine.

Wachholtz and Krof[94] prepared aqueous dispersions containing a water-dispersible modified drying or semidrying oil vehicle with-COOH groups partially neutralized with nitrogen base and 0.01-3 wt.% of a water soluble drier. They wereuseful as rapid drying vehicles. Thus linseed fatty acids were esterified by treatment with a bisphenol-A-epichlorohydrin epoxy resin, modified by treatment with maleic anhydride, and dissolved in NH_3.

Phillips and Casshie[95] prepared water-dispersible epoxy modified alkyd resins. Thus a glycidyl polyether of a dihydric-phenol was treated with a monocarboxylic fatty acid to give a partial ester, which was treated with a polyhydric alcohol and an OH-substituted acid-containing product. This product was partially neutralized and treated with NH_3 tto give a water-dispersible epoxy modified alkyd resin. Their dried films are durable and show water, alkali and acid resistances.

Gueldenpfennig and Rolf[96] described the preparation of water-dilutable epoxy resin esters. Thus a mixture of dehydrated castor oil fatty acids, rosin acids and maleic anhydride was heated under an inert atomosphere. The product obtained was heated with epoxide resin, prepared by treating bisphenol A with epichlorohydrin in the presence of alkali, (mol. wt., 470). The resin was neutralized with NH_4OH after having added 20% $HOCH_2-CH_2OEt$, until the pH of 20% solution was 7.8-9. This resin was deposited on metal by electrophoresis.

(d) Phenolic Modified Alkyd Resnis:-

Honel[97] obtained a product composed of a water-soluble phenol -HCHO condensation product and an alkyd resin.

A British Patent[98] described water-soluble compositions prepared by heating maleic anhydride with linseed oil and an oil-soluble alkyl phenolic resin (prepared from p-tert-butyl phenol and HCHO) at 230° for 50 minutes. The viscous resin formed was dissolved in isopropanol and 28% aqueous NH_3 at 60-80°. Cobalt and lead naphthenates were used as driers. The paint, baked at 150° for 30 minutes, gave a hard, transparent and water-proof films.

(e) Alkyd-Amino Resin Combination:

An American Patent[99] indicates that an aqueous dispersion of salt of a condensation product was prepared from 20-30 parts by weight xylene-soluble butylated poly-

(hydroxy methyl) melamine with 40-65 parts alkyd resin having an average molecular weight of 2000-10,000 and an acid number of 3-7. Water soluble alkyd resins[100] have been prepared from TMA, a glycol, e.g. propylene or neopentylene glycol and a dibasic acid, e.g. adipic acid. These cured on stoving at 204°C, and with the addition of catalyst (e.g. p-toluene sulphonic acid) at 176°C; blending such alkyds with water-soluble amino resin systems, curing at 120° could be obtained.

Purcell[101] described the preparation of water-soluble polyester resins that did not give off fumes or increase in acid number when baked at 120-155°. These polyester resins (acid number 25-100) were neutralized with an amino alcohol.

Wilkinson[102] prepared an alkyd suitable for industrial stoving from TMA (3 moles), neopentyl or propylene glycol (7 moles) and adipic acid (1 mole) cooked to an acid number of about 50 and solubilised in water with amine. Heat and chemical resistances and physical properties were good. Stoving temperature could be lowered to 155°C by incorporating an amino resin, e.g. hexamethoxy methyl-melamine.

Jan and Seneker[103] produced aqueous dispersions of amino alkyd resins. Thus a water-dispersed amino resin was mixed with a water-dispersed alkyd resin in the presence of a basic agent to give the system a pH of 7-9 and 20-80% solids:

The alkyd resin was composed of safflower oil, glycerol, isophthalic acid and the methoxy derivative of polyethylene glycol and p-tert butyl benzoic acid. The amino resin was composed of Resimene 878, a 50% solids butylated methylol melamine resin, dissolved in a mixture of 35% BuOH and 15% Bu cellosolve.

An oil modified polyester[104] condensate with an acid number 20-35 could be made water-soluble by the use of certain amines. Coatings obtained from aminoplast compositions comprising these salts had good resistance to alkaline materials and improved gloss. Lauric acid, propylene glycol, pentaerythritol, PA and xylene were heated to 200-300° under nitrogen blanket. The heating was continued until the acid number was 32.5. A mixture of this polyester and of a (dimethoxy-methyl) tri-methylol melamine could be pigmented and thinned with water to spraying viscosity.

Lohs[105] prepared water-soluble alkyd-melamine resin lacquers having excellent water stability, good viscosity behavior on dilution with water, storage stability, pigment absorption power, hardness, elasticity, and thermostability. They were composed of plasticizing alkyd resin containing OH and COOH groups, highly basic nitrogen compound that forms a soluble soap in water with the alkyd resin, a thermosetting water-soluble Me ether of melamine-HCHO condensate,

H_2O, and H_2O miscible organic solvent.

In general, the theoretical foundations of formulating alkyds compiled by Patton are also employed for water-soluble alkyds. Alkyds can be formulated by one of the four following methods:

1- F_{av} , an average over-all functionality for the alkyd composition.

2- P , the probability of branch to branch connection between reacting molecules at gelation.

3- AN , the acid number of the alkyd composition at its gel point.

4- M_{av} , the average molecular weight of the alkyd at gelation.

Two basic equations are used for all four formulation methods. The first equation sets the sum of all equivalents taking part in the alkyd reaction equal to unity:

$$1 = A_1 + A_2 + A_3 \quad \cdots\cdots\cdots + B_1 + B_2 + B_3 + B_4 + \ldots \quad (1)$$

The second equation sets the ratio of all B groups to all A groups equal to R:

$$R = \frac{(B_1 + B_2 + B_3 + \ldots)}{(A_1 + A_2 + A_3 + \ldots)}$$

These two equations give a common ground for all the four systems; it is the derivation of the third basic equation which is radically different for each system and which serves to differentiate among them:

1- F_{av} , $P_{\text{gel point}} = K/F_{av} = K\, m_o/2e_B$

2- P , $P = P^2 \int \frac{A^2}{R}$

3- AN , $AN(w)/56.100 = \left(\frac{A_2}{2}\right) + \left(\frac{A_1}{8}\right) - \left(\frac{B_3}{3}\right)$

4- M_{av} , $m_{AN} = \frac{W}{M_{av}} = \left(\frac{B_x}{x}\right) - \left(\frac{A_2}{2}\right) + \left[\frac{W(AN)}{56,100}\right]$

During the course of investigation, use was made of the expressions of F_{av}, P and the alkyd constant K. These expressions provide a general guidance for alkyd formulations, but the subsequent adjustments were performed to meet cooking and properties requirments.

The F_{av} formulation system is straight forward and simple and universally applicable to all alkyd compositions. The probability P of branch to branch connection is relatively simple for many cases and generally applicable to many alkyd compositions of three to four components.

The alkyd constant $K(m_o/e_A)$ is the ratio of the total number of molecules to the total acid equivalents and is equal to unity in any properly formulated alkyds. This alkyd constant is slightly higher than unity in practical formulations to ensure a safty measure during processing and storage.

An excess of hydroxyl groups or equivalents (R) refers to the excess of the hydroxyl groups over the carboxylic group for any of the alkyd components. Thus:

$$R = \frac{\text{total } e_B}{\text{total } e_A}$$

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

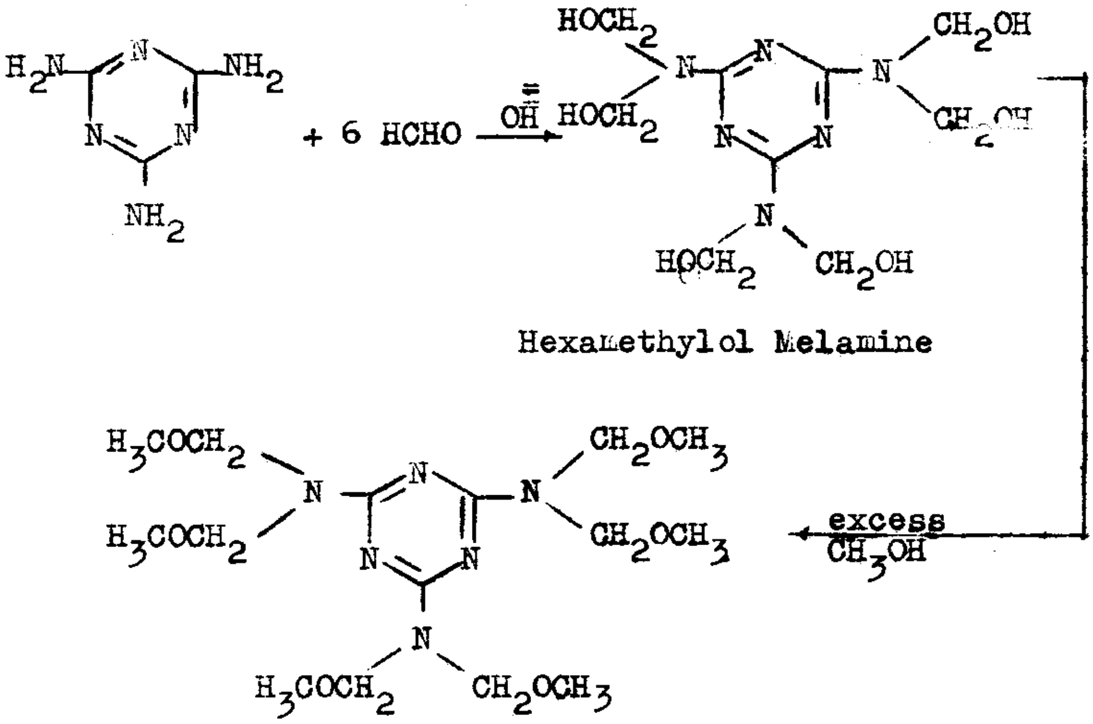
$$\% \text{ excess -OH groups} = 100\ (R-1)$$

Alkyds are conventionally formulated with an excess of hydroxyl equivalents except for very long oil alkyds, in which stoichiometric equivalent preparations are frequently used.

Oil content or percentage oil-length refers to the oil portion of an alkyd and is equal to the weight of any fatty acid in the alkyd taken together with the weight to polyol needed to completely esterify this fatty acid (minus the weight of the evolved water of esterification), expressed as a percentage of the total solid content of the finished alkyd.

(3) Amino-Formaldehyde Condensates:

Gams, Widmer and Fisch[106] were prepared hexakis (methoxy-methyl) melamine (HMM) as follows:



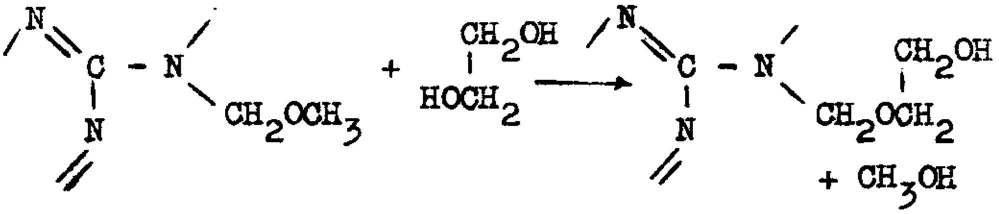
Hexakis (methoxy-methyl) melamine

HMM is a white crystalline solid which is not freely soluble in water but readly dissolve in water containing 5 percent ethanol.

The partially N-methylolated and partially N-methoxy-methylated water-soluble melamine polymers, blended with water-soluble polymer systems, tend to have poor storage stability[107]. HMM, a completely N-methoxy-methylated derivative is stable under similar storage conditions[107].

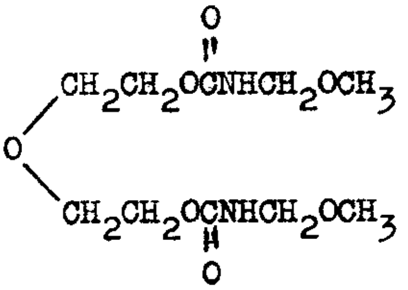
Tetrakis (methoxy-methyl) benzognanamine has been used to give systems with better storage stability and superior interfacial gloss than obtained from HMM[107]. It is more hydrophobic, expensive and forms coatings that are less durable with respect to gloss retention than HMM[33]. N,N'-bis (methoxymethyl) urea is also used[109] but is not as an effective crosslinking agent as the higher functional HMM.

Transetherification of amino curing agents with glycols is used to improve their water solubility characteristics[131]. For example HMM reacted with ethylene glycol gives a water-soluble product:

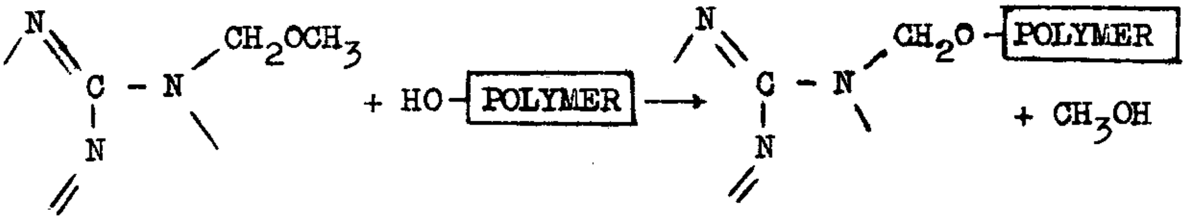


However this reaction reduces the relative functionality of HMM by replacing the reactive methoxy with the less reactive hydroxyl group. Water solubility is also increased by for example, replacing N,N'-bis (methoxy-methyl) urea with

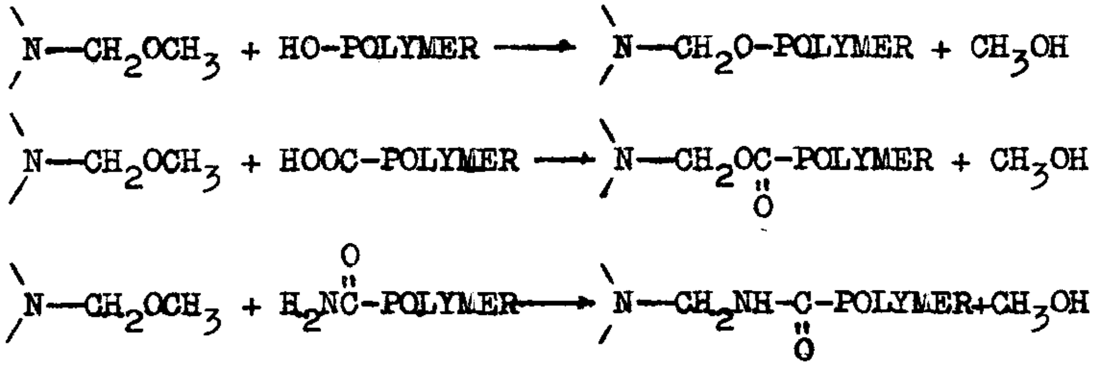
N,N'-bis(methoxy-methyl) diethylene glycol dicarbamate[110] but this is rather an expensive alternative.



The relatively high hydrophilic nature of these curing agent is used to improve the water solubility of polymers, as whole, by a transetherification reaction:



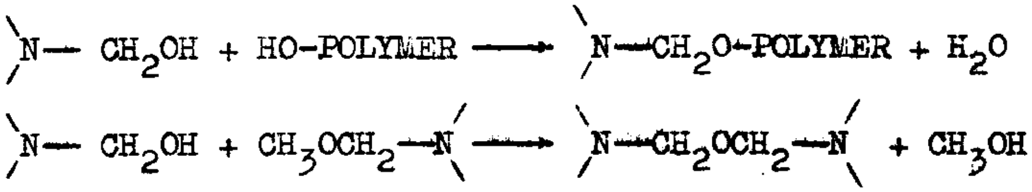
Amino-formeldehyde condensates undergo cross-linking reactions when they are heated under acid conditions:



$$>N{-}CH_2OCH_3 + HO{-}POLYMER \longrightarrow\ >N{-}CH_2O{-}POLYMER + CH_3OH$$

$$>N{-}CH_2OCH_3 + HOOC{-}POLYMER \longrightarrow\ >N{-}CH_2O\underset{\overset{\|}{O}}{C}{-}POLYMER + CH_3OH$$

$$>N{-}CH_2OCH_3 + H_2N\overset{\overset{O}{\|}}{C}{-}POLYMER \longrightarrow\ >N{-}CH_2NH{-}\underset{\overset{\|}{O}}{C}{-}POLYMER + CH_3OH$$



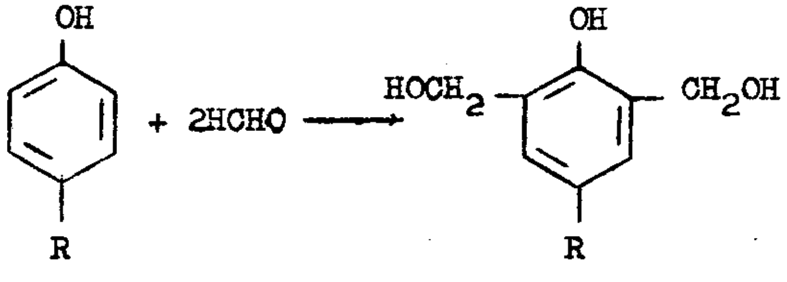
$$>N-CH_2OH + HO\text{-}POLYMER \longrightarrow >N-CH_2O\text{-}POLYMER + H_2O$$

$$>N-CH_2OH + CH_3OCH_2-N< \longrightarrow >N-CH_2OCH_2-N< + CH_3OH$$

Strong acids, e.g. amine salt of para-toluene sulphonic acids[111], may be added to water-soluble polymer or HMM blends to increase their rate of cureing.The acid catalyst is contained potentially in most water-soluble polymers as the amine salt.

(4) Phenol-Formaldehyde Condensates:

Modified phenolic alcohols with little or no condensation are generally used. To obtain water-soluble products, the functionality of phenol is reduced by blocking off the ortho or para positions. Reaction of substituted phenols with formaldehyde occurs at 30-60°C under alkaline conditions.

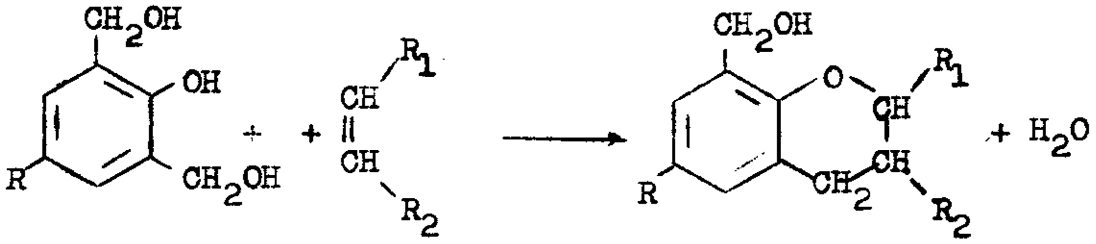


R may be, for example, methyl to give products which are water-soluble[112], tert-butyl to give products with reduced water solubility but improve film flow properties[113] or carboxyl to improve storage stability properties[114].

Crosslinking reactions are:

$$\text{---}\ CH_2OH + HOCH_2 - \xrightarrow[< 100^{\circ}C]{H^+} -CH_2OCH_2 - + H_2O$$

$$\text{---}\ CH_2OH + HOCH_2 - \xrightarrow[> 100^{\circ}C]{H^+} -CH_2\text{---} + HCHO + H_2O$$



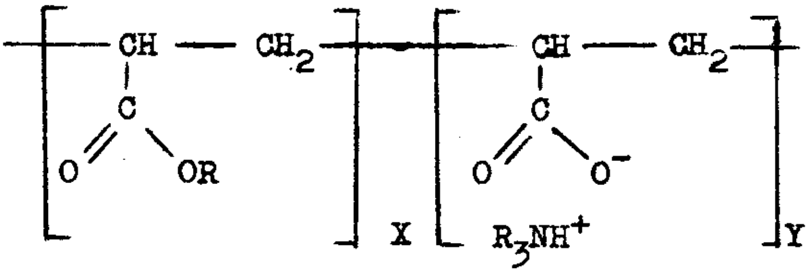
This last reaction may be used to attach phenolic alcohols to a polymer system by using the unsaturation of, for example drying oils and so improves their water solubility. Unfortunately, phenol - formaldehyde systems require high stoving temperatures and give darker coloured coatings than those obtained from amino-formaldehyde systems[115].

(5) Water-Soluble Vinyl Systems:

The well-known high durability of organic solvent-soluble acrylic thermoplastics[116] and thermosetting[117] systems has prompted much effort in an attempt to produce water dilutable acrylic systems. The acrylic emulsion thermoplastic and thermostting systems have, by far, received the largest share of attention in patents and other literature[118].

The best known types are styrene-butadiene emulsions[119], thermosetting acrylic emulsions[120] and polyvinyl acetate emulsions[121]. The properties of these systems are well known and consequently need no elaporate repetition.

Water-soluble thermosetting acrylic polymers are known, their[118] water-solubility is obtained by the inclusion of hydrophilic groups (for e.g. hydroxyl, carboxyl, ether, amide and methylol amide) coupled with relatively low molecular weights. Generally, water-soluble thermosetting acrylic polymers are prepared by acid/acrylate ester copolymerization[122] in a water miscible solvent and then acid neutralization with an organic amine.



Water soluble acrylic systems that are required to cure at room temperature to water insoluble films rely on cross-linking reactions such as ionic or co-ordination bonding and/or catalytic oxidation of residual unsaturation..

(6)Epoxy Resins:

Epoxy resins are described for the condensation products of polyaryl epoxy ethane compounds and their derivatives and are terminated by epoxy groups. These resins contain only carbon to carbon and ether linkages and when cross-linked through the hydroxyl and epoxy groups, by means of a cross-linking or curing agents, they yield products of exteremely chemical resistance. This would be expected for this type of linkages of high stability when compared with those present in alkyd resins.

Epoxy resins itself has not been described in the field of water-soluble resins. They are not included because of their high functionality and consequently are not able to reach the water-soluble stage before curing of the final film. The industrial water-soluble resins may be classified as solubilized polymers of drying oils, alkyds and acrylates[123].

However, water-soluble epoxy resins were prepared by reacting the epoxy groups with acids and neutralization of the acids with suitable amines. A water-based paint with high nonvolatile content based on a polyamide-epoxy system has been announced. Cashew nut shell liquid was solubilized by reaction with maleic anhydride followed by reaction with isopropanol, ethylene glycol monobutyl ether, dimethyl amino propanol and water[124, 125]. As has been mentioned before epoxy resins are characterized by the presence of epoxy groups with or without hydroxyl groups depending on their molecular weight. There-fore their application in surface coating may be conveniently divided into the following modifications.

Esterification[126]:

The epoxy resins are essintially polyhydric alcohols and therefcre are capable of forming esters with carboxylic acids. Therefore, they may be esterified with unsaturated acids to produce superior air drying varnishes. The esters of epoxy resins may also be used in combination with amino resins in wide range of outstanding stoving enamels. This is one of the ways of utilising them in coatings;where the resins are used to form esters in which the epoxy end groups have no particular significance and are esterified along with the hydroxyl groups. Whilst any type of epoxy resin may be esterified, the type of fatty acid used imposes some limitations. Experience has shown that for optimum film properties, it is usually desirable to use the highest molecular weight resin possible. However, the high functionality of the high molecular weight grades makes control of the reaction very difficult, and the final ester is characterised by high viscosity and low compatibility with other resins.

The choice of acid or acids, to make epoxy resin esters, greatly affects the qualities of the product. Fatty acids derived from linseed, castor, dehydrated castor, tall, soybean and coconut oils and those of abietic acid are commonly used for the manufacture of epoxy resin esters. In general, the choice of the acid is governed by similar considerations to those which apply in the case of alkyd resins.

Complete esterification of the epoxy resins is not usually attempted owing to the difficulty of obtaining sufficiently low acid values. The case is similar to the manufacture of alkyd resins, where a small excess of the polyol is normally used. In most cases the degree of esterification of epoxy resins varies between 30% and 90% of the theoretical value. There are different methods of describing the epoxy esters and the most important one is that based on the oil-length of the esters, depending upon the degree of esterification as shown in the following table:

Equivalent of Resin	Equivalent of Fatty Acid	Oil-length
1.0	0.3 - 0.5	Short
1.0	0.5 - 0.7	Medium
1.0	0.7 - 0.9	Long

Choice of "Oil-length" is largely determined by the method of application,method of drying and performance required. For instance,long-oil esters of drying oil fatty acids such as linseed oil are used for air drying vehicles. The medium and short-oil esters are quick drying, suitable for spray application as well as stoving applications.

Also the choice of oil-length greatly affect to some extent the solubility characteristics e.g. the long-oil esters require aromatic hydrocarbon solvents.

Table 3 may be taken as a guide for the type of solvent required.

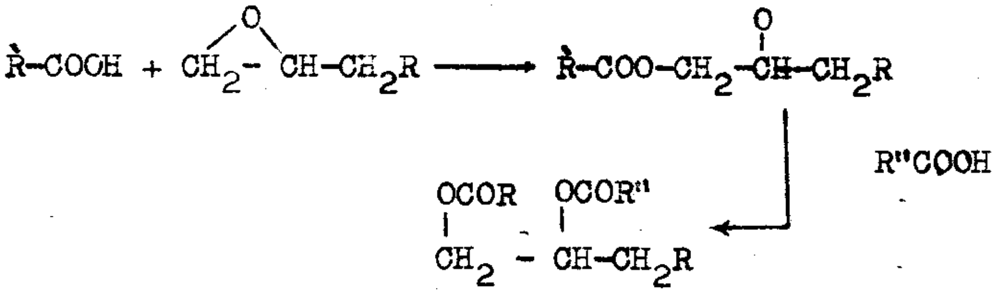
Table 3: Characteristics of Various Oil-length Epoxy Esters

Oil-length	Percent Esterification	Type of solvent
Short	30 - 50	Toluene or xylene
Medium	50 - 70	White spirit (80%)
Long	70 - 90	White spirit

The chemistry involved in the esterification of epoxy resins has been described in many papers and includes the following types of reactions:

1- <u>Carboxyl/ epoxy esterification</u>[127]:

The reactions which occur when epoxy resins are heated in presence of monocarboxylic acids are represented by the following series of equations[126]:



In this case the epoxy group is considered to be equivalent to two hydroxyl groups. The esterification is carried out, quite simply, by heating the reactants together in an inert atmosphere, usually at temperatures around 260°C. When esterification is carried out with drying oil fatty acids , such as those of linseed or dehydrated castor oil, air drying varnishes are obtained while those of non-drying oils (castor or coconut oils) lead to non-drying varnishes.

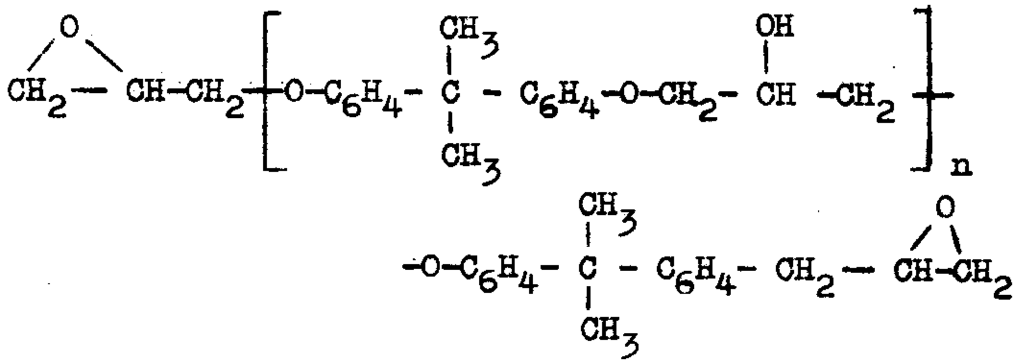
Theoretically any type of epoxy resins can be esterified but, in general, epoxy resins of molecular weight ranges between 600 to 1400 are the most suitable for the manufacture of epoxy ester varnishes. Higher molecular weight epoxy resins (higher than 1400) possess too high functionality to enable them to be used satisfactory to make esters and gelling is likely to occur before a sufficiently low acid value can be obtained.

The effect of acid value on the performance of the epoxy ester is important and has been determined over the range 1 to 15 mg KOH. There is no appreciable difference in the performance between esters of acid values of 1 and 5 mg KOH. At acid values above 5 mg KOH, a difference in performance begins to be noticeable and becomes marked over 10 mg KOH. Esters of high acid value show the following tendencies:-

a) Slower rate of drying.
b) Lower chemical and water resistances, and
c) Greater tendency to "pikle" on recoating.

2- Carboxyl/hydroxyl esterification[126]:

In general, epoxy resins may be represented by the following general formula:

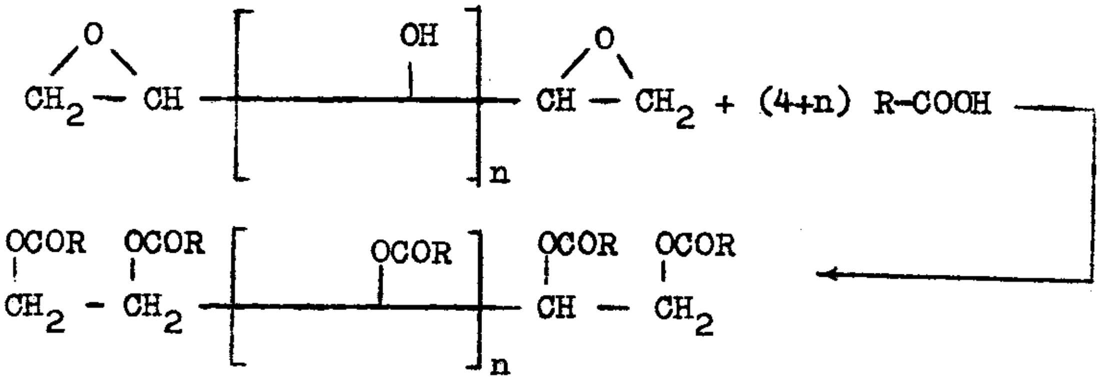


By increasing the number of the repeated units (n) in the general formula, will of course, lead to an increase in the molecular weight and in the softening point as indicated in the following table:

Table 4: Characteristics of Epoxy Resins

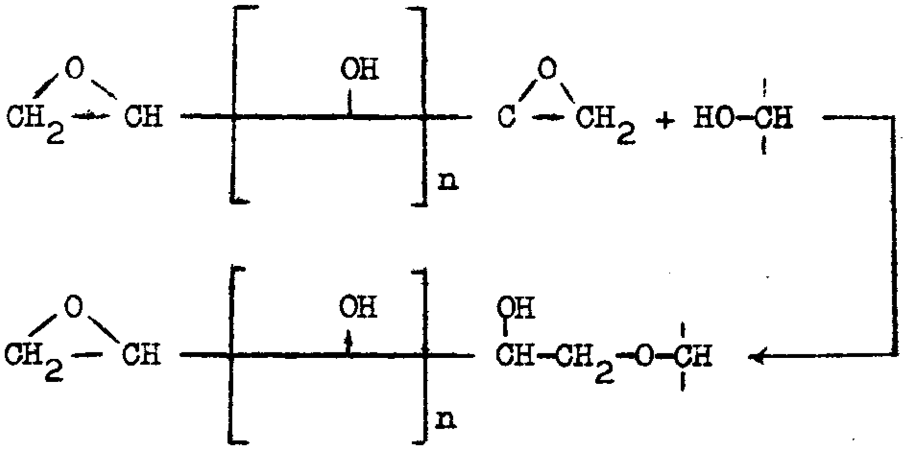
Number of "n"	Molecular Weight	Softening Point	Epoxy Equivalent	Hydroxy Equivalent
0.0	340-370	Liquid	0.5	0.00
2.0	900	64-71	0.2	0.32
3-7	1,400	95-105	0.1	0.34
9.0	2,900	125-132	0.05	0.36
12.0	3,750	145-155	0.03	0.4

In case of esterifying high molecular weight epoxy resins containing the hydroxyl groups, the following reaction takes place in addition to the carboxyl epoxy esterification reaction.



(3) Epoxy/hydroxyl etherification[126]:

Another type of reaction which is involved, besides the esterification, is the etherification of the epoxy groups with the hydroxyl groups. The reaction proceeds as follows:



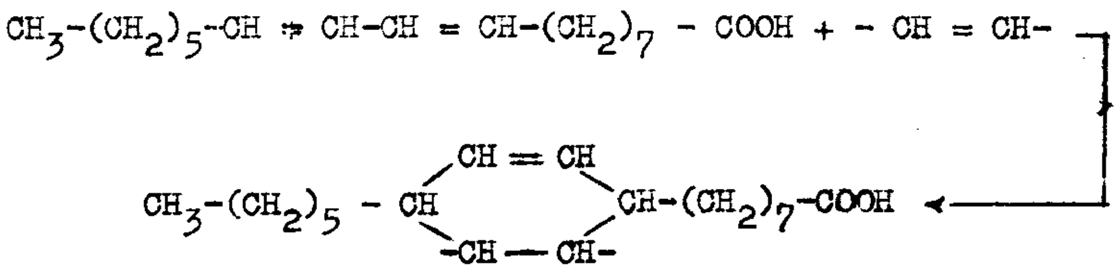
Disappearance of epoxy groups in this way means that for short-oil esters less fatty acid is able to react additively, and consequently more has to esterify with hydroxyl groups with the liberation of water. This etherification reaction leads to higher molecular weight branched structure and hence higher ester viscosities. In presence of alkaline material, such as sodium carbonate or sodium salt of fatty acids, the dissociation of the fatty acids is promoted and the carboxylated ions formed react more rapidly with epoxy groups.

The esterification of epoxy resins has been applied widely as a mean for reducing the functionality of the resins. For example, the formation of epoxy resin/phthalic alkyds can be produced on an industrial scale and involves the formation of a partial ester of the epoxy resin with the fatty acids desired, through both the epoxy and the hydroxyl groups of the resin. The resultant product has a hydroxyl functionality between 1 and 4. Such an opoxy rosin partial ester is then introduced as a polyhydric alcohol in the formation of phthalic alkyd resins.

These modified resin alkyds exhibit the combined desirable properties of both epoxy resin esters and conventional alkyds and open the way to improve the phthalic alkyds for surface coating formulations[128].

(4) Reactions associated with the unsaturated fatty chain centres of the acid.[54]

These reactions are mainly concerned with the addition reactions between the olefinic centres of the fatty acids present. Fatty acids contain conjugated centres are capable of undergoing addition reaction with other unsaturated fatty chains through the Diels-Alder type[49,130]. The following example illustrates the addition of 9,11-linoleic acid of hydrated caster oil to a double bond:



The reaction proceeds smoothly with the formation of six-membered ring.

In case a non-conjugated fatty acids, isomerisation of the isolated (or non-conjugated system) to conjugated type under the influence of the experimental conditions occured prior to the addition reaction. This view was postulated by Bolley [57]. Thus taking 9,12-linoleic acid present in the linseed oil, the following reaction can be illustrated:

$CH_3-(CH_2)_4-CH=CH-CH_2-CH=CH-(CH_2)_7\ COOH$

9, 12-linoleic acid

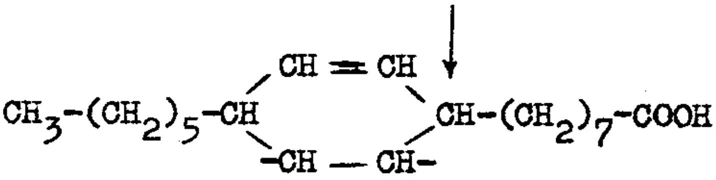
$\downarrow$ isomerisation

$CH_3(CH_2)_4-CH_2-CH=CH-CH = CH-(CH_2)_7\ COOH$

9, 11-linoleic acid

+

$-CH = CH-$



It should be noted that both types lead to a dimer fatty acid.

Systems of this type offer many attractive advantages.

1- Cure can be effected at room temperature by using highly reactive amines such as ethylene diamine or diethylene triamine.

2- Films cured at room temperature posses excellent solvent and chemical resistance, are hard, flexible and have good adhesion.

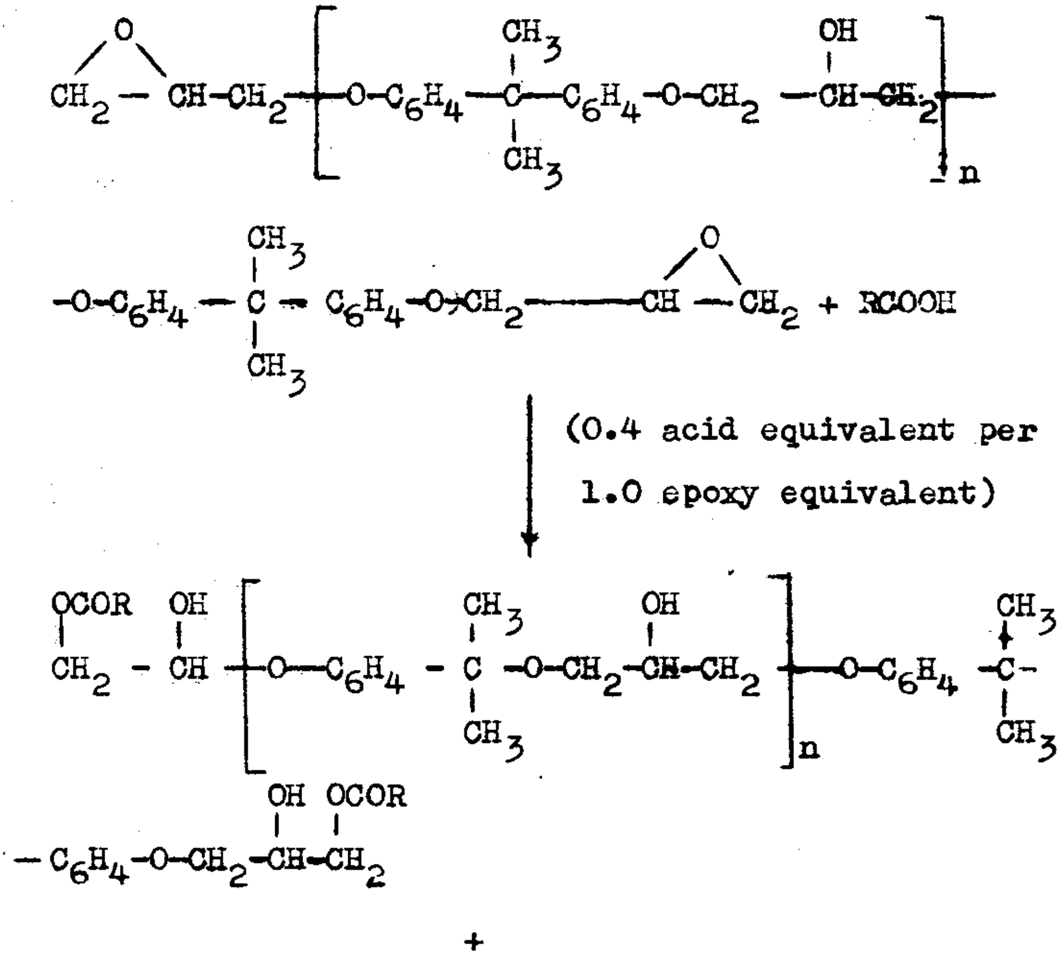
3- Initial "set up" is very rapid and films up to 5 mils dry thickness can be laid down in one coat on vertical surface with-out sagging.

4- Films can be forced dried at low temperatures or stoved in very short time.

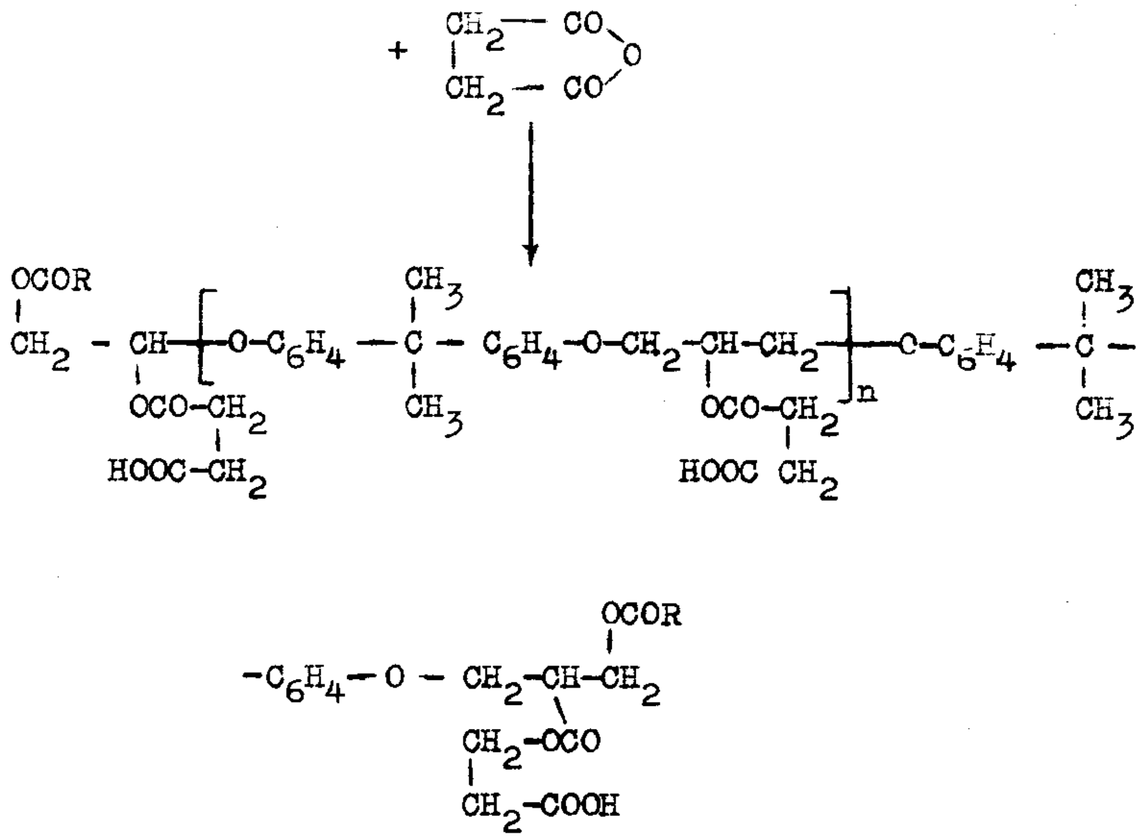
Epoxy resins of molecular weight in the region of 1,000 have been found to give the best all round results taking into account all factors, such as solid content, rate of cure and final film properties.

Lately in 1968, Westerenen <u>et.al</u>.[127] published an article on the water-soluble epoxy resin esters. Their work is mainly concerned with the preparation of short-oil epoxy resin esters followed by reaction with cyclic monoanhydrides to form the corresponding half-esters. These half esters are completely water-thinnable after addition of certain amounts of coupling solvents and neutralization with amines. Also they concluded that the half-ester technique is a promising lead in the development of aqueous epoxy ester systems to be applied by electro-deposition.

The concept of the formation of water-soluble half-ester epoxy resin can be represented by the following series of equations:



(0.4 acid equivalent per 1.0 epoxy equivalent)



The resultant resin contains sufficient hydrophilic groups to ensure its water-solubility upon neutralization with a volatile base.

Water-soluble synthetic resins containing epoxy resins are obtained by the condensation of the resin with heat reactive components at elevated temperature followed by treatment with polycarboxylic acid or anhydride. After the addition of a base, water-soluble synthetic resins suitable as binders for pigmented or unpigmented coating materials are obtained[134,135].

In 1961, a British Patent described the production of a water-soluble epoxy modified alkyd resin was claimed. An example of this type is formed by heating an unmodified epoxy resin with linseed fatty acids at 220°C until an acid value of 85 mg KOH is reached. Then, tris (hydroxy methyl) ethane is added, followed by addition of phthalic anhydride at 215°C until an acid value of 58 is obtained. The product is then cooled to 90° and neutralized by dimethylaminethanol solution with continuous stirring to pH 9(136,137).

A water-base resins are prepared by the partial esterification of epoxy resins, ethylene propylene oxide or glycerol with oleic, linoleic or linolenic acid. The produced partial ester is then subjected to malenization with maleic anhydride which reacts with the remaining hydroxyl groups of the parent resin(138).

Spalding[139] produced water-soluble epoxy esters for coatings by condensing the itaconic or fumaric adduct of C_{10}-C_{24} unsaturated fatty acid with epoxy resins (epoxy equivalent 1000) at temperatures which prevent the carboxyl/hydroxyl reactions. The product obtained is used for various aqueous coating formulations and metal primers[140].

A British Patent reported the formation of water-soluble coatings from acidic epoxy esters. Such resins are prepared by reacting the epoxy resin with various drying fatty acids such as D.C.O., L.O. or soybean oil fatty acids to give an epoxy ester which reacts with fumaric acid or maleic anhydride till an acid value 30-100 is reached. The adduct is dissolved in ethyleneglycol monobutyl ether or any similar solvent and then neutralized with triethylamine and diluted with more water. These resins are excellent base media for the formulation of stoving primer paints and similar coating compositions. Because of their high water solubility such formulations are useful in electrophoretic processes. The resin coatings have good alkali and detergent resistance[141].

Van Westrenen _et.al_. in 1967 studied the preparation of water-thinnable epoxy resin esters. These binders are characterised by good pH stability and show good hardness, impact strength, appearance and salt-spray resistance. The resin formation involved the use of stanous octoate as catalyst[142].

A similar water-dilutable epoxy resin esters of improved film performance are obtained by:

1- Formation of partial esters containing free hydroxyl and epoxy groups by esterification of the resin with mono carboxylic acid mixtures.

2- Reacting the partical esters with poly-basic carboxylic acid to give epoxy resin esters containing free carboxlic and hydroxyl groups.

3- Neutralization of the product with ammonia or strong organic nitrogenous base in presence of water[143].

A Japan Patent reported the preparation of water-soluble epoxy resins suitable for electro-deposition coatings. It involves the polycondensation of the cis and trans epoxy succinic acid or their alkyl derivatives with polhydric alcohols in a manner similar to those of alkyd resins[144].

Baranov et.al. in 1972 reported the addition of α-isopropyl β-isobutyl acrylic acid during the condensation of epoxy resins with fatty mono acids of oils, polyacids, polyols and acid anhydrides leads to the formation of water-soluble bright weather resistant epoxy oligmers[145].

Recently, Jeffery et.al. in 1972 and Zuzmichev in 1973 prepared a water-thinnable binders by the treatment of maleated oils with oligoepoxy esters[146,147].

Modified epoxy resins which can be formulated as water-dilutable coatings are described by Marcel in 1974. These coatings exhibit good flexibility and impact resistance[148].

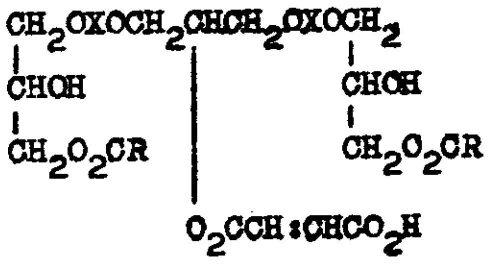
Various water-soluble coating formulation based on epoxy or modified epoxy resins were described for application by electrodeposition[133,149-155].

Fast-drying water-soluble epoxy resins coating compositions are prepared by mixing the epoxy resin with silicon tetracetate and a hardening agent[156].

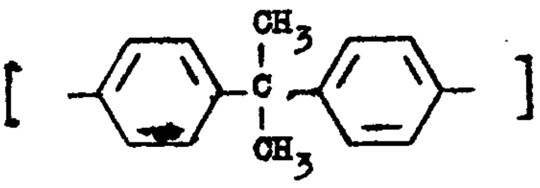
Water-soluble epoxy or modified epoxy resins in combination with other water soluble resins are also mention. Thus a water-dilutable resin is prepared by mixing partially esterfied epoxy resin with phenolic or aminoplast resins followed by neutralization with amines.[157]. An example of this type of water-soluble formulation involves the partial esterification of epoxy resin with linseed oil fatty acids followed by dilution with ethylene glycol and water. The product is treated with triethylamine, to increase the pH to 8 and then a resol type of phenolic resin is added. Similar products were also reported and revealed from patents[158-160].

Japan patent was reported the use of acrylic resins as modifying agents for epoxy resins. The product obtained can be applied to steel surfaces and hardned by heating. They show good adhesion to the substrate and also show excellent water and solvent resistance[161].

Bajoras et.al. in 1972 reported the preparation of water-soluble adducts of epoxy esters of ricinoleic acid. The esterification process was conducted in presence of sodium benzoate as catalyst. The ester formed was subjected to malenization at 135°C and the adduct was dissolved in butyl cellosolve. A water-soluble vehicle is obtained upon neutralization with ammonia or triethylamine. These coating compositions were successfully applied over aluminium, nickel, steel and phosphatized steel by electrodeposition technique. The following structure represents the skeleton of the prepared adduct[162].



where X represents



and R-COOH represents ricinoleic acid:

$$\left[CH_3(CH_2)_5\underset{OH}{CH}-CH_2-CH{=}CH-(CH_2)_7-COOH \right]$$

A German Patent in 1973 reported the preparation of soluble resins for use in paint. They are based on the reaction of epoxy resins or modified suitable phenol-epoxy resin with free fatty acids and acrylic acid in presence of catalyst. The product is then neutralized and electrophoretically coated over steel plate to give a corrosion resistant film after curing[163].