

Synthetic Drying Oils and Vehicles from Unsaturated Acids and Synthetic Polyols

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SOME NATURAL vegetable oils like linseed oil possess a high degree of unsaturation and have been used in tremendous quantities in coatings because of their ability to dry to useful solid films. On the other hand, the semi-drying oils like soybean oil possess only a moderate degree of unsaturation and dry very poorly or not at all. Polymer theory and the concept of functionality as advanced by Carothers (9) and extended by Bradley (4), Kienle (30), and others provide the explanation that linseed oil dries more rapidly because it has a greater number of reactive sites in the molecule. The number of reactive sites in a molecule is termed its functionality. When the functionality of an oil is sufficiently high so that large, 3-dimensional molecules are formed by interaction among molecules of oil, the liquid oil becomes solid. This formation of very large molecules by a succession of chemical combinations is often called polymerization. The functionality of soybean oil is not sufficiently large to permit the extent of polymerization necessary to yield useful dried films.

The functionality of oil theoretically could be increased by increasing the number of double bond reaction sites in the molecule. Although this is not easily feasible in the case of soybean oil, this is accomplished readily in the preparation of dehydrated castor oil from castor oil by dehydration. Another approach to increase the functionality and hence the drying ability and usefulness of vegetable oils comprises the hydrolysis into glycerol and fatty acids, which in turn are esterified by polyols of functionality greater than three. The esters formed by reaction of unsaturated fatty acids with polyols are called synthetic drying oils and constitute the subject of this paper.

Polyols containing from about three to six hydroxyl groups in the molecule have been investigated quite extensively for possible use in synthetic drying oils and other vehicles. The straight esters of these polyols find little commercial use at the present time because of economic and technical factors. There is, for example, little economic incentive to re-esterify soybean fatty acids with pentaerythritol to achieve drying properties approximating linseed oil because linseed oil is plentiful and cheap, at least in this country. On the technical side, soybean and other oils can be converted conveniently into products of substantially improved drying rate by use of dibasic acids and polyols to form alkyds. Also these oils can be modified by facile reaction with maleic anhydride whereby maleated oils of high reactivity are formed. Oils modified by dibasic acids in these ways are very versatile industrial products and are sold in large volume, but they are not within the scope of this paper. Nevertheless the straight synthetic oils are of theoretical and historical interest and worthy of consideration. Furthermore economic conditions and technical requirements change rapidly and differ considerably throughout the world, and products not now in use may become industrially important.

On the other hand, there are polyols which do form commercially important synthetic drying oils when esterified by the straight unsaturated fatty acids. These polyols usually have relatively high molecular weight of 500 or more and contain six or more hydroxyl groups per molecule. They are resinous in nature and hence frequently are called resinous polyols. The synthetic drying oils derived from these polyols dry rapidly and form hard films. Because they resemble varnishes and alkyds in properties and require no further modification with hard resins to form desirable films, they usually are called synthetic vehicles rather than synthetic drying oils. These polyols have high equivalent or combining weight and may be considered to have a built-in resin component in the molecule.

The fatty acids which are used in the preparation of synthetic oils and vehicles for coatings recently have been described by Hamilton and Wittcoff (26). The principal unsaturated fatty acids used in coatings (with approximate Wijs iodine numbers in parentheses) include soybean (120-135), cottonseed (100), linseed (155-180) and dehydrated castor (140-160). Tung, safflower, and other oils also may be employed, frequently in the form of their methyl esters. An acid mixture of importance is tall oil. Although tall oil contains 35-50% of rosin acids, distilled grades contain as little as 1% or less of rosin acids and have iodine values of about 130. Other monobasic acids, such as rosin and *p*-tert-butylbenzoic acid, also may be used in the preparation of the synthetic oils and vehicles.

The Polyols of Low Functionality

A great variety of polyols have been converted into unsaturated esters for possible use in synthetic oils, but for the sake of brevity an attempt has been made to discuss mainly or only those of practical or special theoretical interest. A general review of polyols was published in 1953 (41).

Polyols containing three hydroxyl groups per molecule find use in coatings mainly in the form of alkyds. Besides glycerol, other common triols suitable for alkyd use include trimethylolpropane (28, 31), trimethylolpropane (10), and 1,2,6-hexanetriol (54).

Pentaerythritol has wide commercial use, particularly in alkyds. The straight drying oil esters were found by Burrell (7) to dry more rapidly and yield harder films than the corresponding glycerol esters. The rapid esterification of pentaerythritol may be ascribed to the fact that all of its hydroxyl groups are primary. The excellent heat stability of the esters results from the stable chemical structure wherein the carbon atom adjacent to the carbon atoms holding the hydroxyl groups contains no hydrogen atom. Ordinarily the decomposition of esters occurs with the elimination of carboxylic acid and the generation of a double bond in the polyol, but this is not possible in the case of pentaerythritol esters. Dipentaery-

thritol and higher polymers of pentaerythritol also were investigated (8).

Diglycerol, which also contains four hydroxyl groups, was found to yield esters which possessed good thermal stability and dried about like pentaerythritol esters but formed softer films (38).

Sorbitol has six hydroxyl groups, but inner ether formation permits the combination of a maximum of about four of these with fatty acids (6). The esters tend to discolor and decompose fairly readily when cooked at high temperatures. Usually sorbitol is used in combination with other polyols in esters.



Sorbitol

Witteoff (59) utilized 2,2,6,6-tetramethylolcyclohexanol in synthetic drying oils. Lead stearate was an effective esterification catalyst. The esters dried somewhat faster and were harder than corresponding pentaerythritol esters.

Other polyols which have been investigated include inositol (21) and methyl alpha-D-glucoside (22).

In general, as the functionality of the polyol increases, the derived synthetic oils dry faster and yield films of greater hardness and integrity. Also with increasing functionality of the polyol, the derived esters body more rapidly to a given viscosity when heated. However the structure of the polyol, aside from its functionality, also has an influence upon ester properties. The rate of esterification is greater when primary alcohols rather than secondary alcohols are present in the polyol. Typical data on some of the synthetic oils made from a fatty acid of iodine number about 130 are shown in Table I (39). Comparisons of various polyols in tall oil esters and maleated tall oil esters also have been made (39, 56).

TABLE I
Properties of Synthetic Drying Oils Derived from Polyols
of Low Functionality (39)

	Glycerol	Diglycerol	Pentaerythritol	TMC
Iodine number, Wijs.....	113	110	117	114
Acid number, mg. KOH/g.....	9.9	11.9	6.4	11.0
Viscosity, Gardner-Holdt.....	A1-A	B-C	E	I
Bodily time, 275°C., to reach viscosity of I, hrs.....	15	5	3.5	0
Drying time ^a				
Set touch, hrs.....	18	6.5	7	6
Lint-free, hrs.....		8.5	8.5	7
Pencil hardness after 72 hrs.....	<6B			
Immersion tests, films		5B	4B	3B
72 hrs. old				
1% Soap, minutes to initial failure.....	30	120	180	120
Hot water, minutes to initial failure.....	5	5	5	5
Cold water, minutes to initial failure.....	5	15	20	15

^a All film tests reported here were run on films made from oils of equal viscosity (Gardner-Holdt I) in the presence of 0.2% calcium and 0.02% cobalt.

The Resinous Polyols

The resinous polyols yield useful vehicles when esterified with drying oil acids unmodified by dibasic acids. By far the most important resinous polyols are the epoxy resins; these will be discussed in some detail in a later section.

Polyvinyl alcohol is an important commercial resinous polyol which has many industrial applications in adhesives, cloth, moldings, emulsions, and other products. It cannot be esterified under ordinary conditions, but Rheineck (43) has prepared esters directly

from fatty acids by using large quantities of phenol as a mutual solvent. Eckey (20) has prepared esters of polyvinyl alcohol by an ester interchange between low molecular weight polyvinyl acetate (probably at least 40 units) and the methyl esters of fatty acids. These esters are distinctive because of the great number of ester groups in the molecule. A third method of preparation of the fatty acid esters of polyvinyl alcohol was carried out by Harrison and Wheeler (27); they polymerized vinyl fatty acid esters directly, but only very poor conversions were obtained. It does not appear that commercial use is made of synthetic oils from polyvinyl alcohol at the present time.

Phenolic resins form the basis for some ester vehicles. The direct esterification of phenolic hydroxyl groups as reported by Aelony (2) is of interest in this connection, and esters of phenol-formaldehyde resins have been made (3, 36).

Other resinous polyols based on phenol-formaldehyde resins are condensation products of novolac resins with ethylene oxide, propylene oxide, and styrene oxide (14). A product of this nature which has received some commercial attention in the past is an alkylene oxide adduct of a phenol-formaldehyde resin; it is called Dow Resin 622 (15, 16). It is a hard brittle resin with an equivalent weight of 152, a minimum softening point of 57°C., and a Gardner color of 5-6 as a 50% solution. Esterification proceeded very quickly at 240°C. even when as much as 90% of the theoretical quantity of fatty acid was used. The esters had good solubility in aliphatic hydrocarbons. Film tests were reported on esters wherein 50% of the available hydroxyl groups were esterified by various fatty acids (15, 16). Drying rate and hardness were somewhat inferior to epoxy esters. Further tests, presumably on baked films, indicated that the esters had good alkali- and abrasion-resistance. The polyol also was converted into alkyds of various types.

Esters of the novolac-alkylene oxide condensate were compared in air-dried films with epoxy esters and other vehicles by Tess and Mueller (52) (Table II). Both the novolac-oxide esters and the epoxy esters dried rapidly, but the epoxy ester had much better hardness and water- and alkali-resistance in long linseed and short dehydrated castor esters.

Polyallyl alcohol has been made in a variety of ways (1). Products range from viscous liquids to frangible solids, depending upon method of preparation and molecular weight. They contain from 5 to 20 hydroxyl groups per molecule, and all hydroxyl groups are primary. Polyallyl alcohol is not now commercially available but has been the subject of considerable investigation in the past. Cox, Jerabek, and Konen (12) studied three grades of polyallyl alcohol in the form of unsaturated drying esters in a variety of applications. Polyallyl alcohol was found to be an excellent upgrader of glyceride oils; the mixed glycerol-polyallyl alcohol esters of soybean fatty acids containing a total of 10-15% polyallyl alcohol were superior to linseed oil in film properties. Complete soybean and linseed esters containing 21-25% polyol gave good quality 30-gal. varnishes containing pentaerythritol ester gum as the resin component. A mixed soybean-rosin ester was equivalent to a medium oil-length castor alkyd as a baking enamel vehicle. Polyallyl alcohol also was investigated in tall oil esters (39, 56).

TABLE II
Typical Bulk and Air-Dried Film Properties of Some Synthetic Vehicles from Fatty Acid Esters of Resinous Polyols* (52)

Polyol	Epoxy ^b	Styrene-Allyl Alcohol ^c	Novolac-Alkylene Oxide ^d	Alkyd	Epoxy	Styrene-Allyl Alcohol	Novolac-Alkylene Oxide	Alkyd
Type fatty acid.....	D.C.O.	D.C.O.	D.C.O.	D.C.O.	linseed	linseed	linseed	linseed
% Fatty acid, wt.....	40	42	40	40	56.5	48.5	58.7	50
Equivalents acid per hydroxyl.....	0.42	0.58	0.36	0.80	0.80	0.70
Solution properties								
% Solids.....	40	50	29	40	45	64	60	38
Viscosity, Gardner-Holdt.....	E-F	E-F	E-F	C	E-F	E-F	E-F	E-F
Color, Gardner.....	4-5	2	5	2-3	3	4-5	7	5
Solvent.....	xylene	ms	ms	xylene	ms	ms	ms	ms
Acid number, mg. KOH/g., solids.....	5.6	4.0	1.0	9.6	7.5	6.0	1.0	5.0
Cotton-free, hours.....	0.7	1.5	3.4	4.0	2	2	2	4
Sward hardness, 1 week.....	21	16	11	13	15	14	7	14
Flexibility, 1/8-inch mandrel.....	OK	OK	OK	OK	OK	OK	OK	OK
Impact, 31 inch-pounds.....	OK	OK	OK	OK	OK	OK	OK	OK
Cold water, 24 hours, haze.....	VS	S	M	H	NE	M	M-H	S
Boiling water, 15 minutes, haze.....	S	S	blisters	H	NE	S	H	NE
Xylene, 15 minutes, softening.....	VS	lift	VS	M	VS	lift	VS	soft
Alkali, 3% NaOH.....	NE 4 days	soft @ 4 days	wrinkles @ 4 hrs.	dis. @ 2 hrs.	NE 4 hrs.	hazy @ 4 hrs.	blisters @ 4 hrs.	dis. @ 15 mins.

Abbreviations: D.C.O.=dehydrated castor oil; V=very; S=slight; M=moderate; H=heavy; NE=no effect; ms=mineral spirits; dis.=disintegrated.

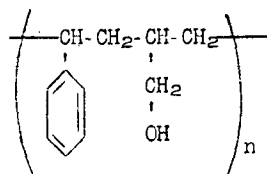
* Film tests on esters containing 0.05% cobalt. Drying time on films 1 mil in dry thickness; water and alkali tests on films 2 days old.

^b Epon 1004, Shell Chemical Corporation.

^c Resinous Polyol X-450, Shell Chemical Corporation.

^d Dow Resin 622, Dow Chemical Company.

An outgrowth of considerable investigation of polyallyl alcohol and modifications thereof at the Shell Development Company is the production of a new commercially available copolymer of allyl alcohol and styrene designated by the name Resinous Polyol X-450 (48). The product is a hard, almost colorless solid with a combining weight of 222 and average molecular weight of about 1,150. It contains about 5.2 hydroxyl groups per molecule, and because these are all primary, esterification rate with fatty acids is very rapid.



Styrene-Allyl Alcohol Copolymer

A distinctive feature of the drying oil esters of styrene-allyl alcohol is the good solubility and low viscosity in hydrocarbon solvents. Even short esters are soluble in mineral spirits whereas comparable alkyds require xylene. Esters containing 50% soya fatty acids (80% of theoretical) have 65% solids at application viscosity (E-F, Gardner-Holdt) whereas alkyds and epoxy esters at equal fatty acid content and viscosity have non-volatile content of around 40%. The high solubility is also manifested in low viscosity of esters in straight aliphatic odorless thinners where solids of 60% have been obtained at application viscosity, and solubility is complete at solids as low as 5%.

In general, films of the styrene-allyl alcohol ester have been characterized by excellent color, good color-stability, good drying-rate, fair mar-resistance, excellent alkali-resistance, good water-resistance, and fair solvent-resistance. Short esters have been found to be not as flexible as epoxy esters and alkyds. Outdoor weather-resistance has been found to be very good; enamels have been found to chalk and lose gloss somewhat more rapidly than alkyds but less than that of epoxy esters.

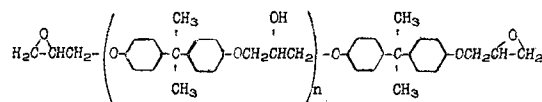
The low viscosity of esters of styrene-allyl alcohol has been helpful in the preparation of styrenated products which possessed very high styrene content

(two-thirds) and extremely fast drying-rate. In another type of application the short lauric esters in combination with melamine resin gave outstanding detergent-resistance in white enamels.

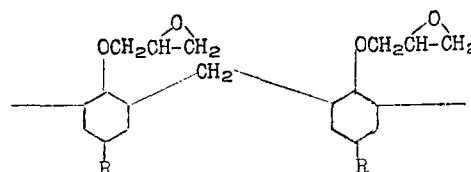
Although this copolymer has several uses without modification with fatty acids, this is outside the scope of this paper. Some properties of the esters in comparison with other vehicles are shown in Table II (48, 52).

Epoxy Resins as Polyhydric Alcohols

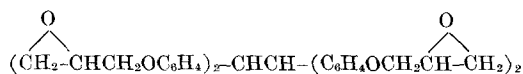
The most important resinous polyols for synthetic vehicle preparation are the epoxy resins derived from the condensation of epichlorohydrin with 2,2-bis(p-hydroxyphenyl)propane which is commonly called bisphenol A. Greenlee (25) has described the preparation and properties of these resins in numerous patents. The idealized structure of these resins may be represented as follows:



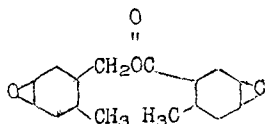
Particularly in the higher-molecular-weight resins, the epoxy concentration is somewhat less than this formula indicates, probably mainly because of the hydration of epoxy groups. The molecular weight depends upon the ratio of reactants. Epoxy resins which are glycidyl ethers of aliphatic polyols also are available, but these have little use in the form of esters. Novolacs prepared from alkylated phenol and formaldehyde have been treated with epichlorohydrin whereby polyglycidyl ethers have been formed (32); these resins are commercially available and have the general structure as follows:



Another type of epoxy resin has the following idealized structure (46):



Still other epoxy resins are based on cyclohexene derivatives; a commercially available liquid resin has the following structure (42):



A useful list of commercially available epoxy resins has been assembled by Lee and Neville (33) in their recent book on epoxy resins. A total of 42 commercial resins produced by Carbide Plastics, Ciba Products, Dow Chemical, Jones-Dabney, and Shell Chemical are listed. More recent producers include American-Marietta, Borden Chemical, Food Machinery and Chemical, Koppers, and Reichhold Chemicals. Properties of some typical commercial epoxy resins based on bisphenol A are given in Table III.

TABLE III
Properties of Typical Epoxy Resins (47)

Resin name	Melting point, °C. Durrans	Color Gardner ^a	Viscosity, poises ^a	Epoxide equivalent ^b	Equivalent weight for esterification
Epon 828	liquid	8 max.	135-195	185-205	85
Epon 1001	65-75	4 max.	1.0-1.6	425-550	145
Epon 1004	95-105	4 max.	4.3-6.2	875-1025	175
Epon 1007	125-135	5 max.	17-27	1900-2450	200
Epon 1009	145-155	5 max.	36-100	2400-4000	220

^a Readings on solutions at 40% solids in butyl carbitol except for Epon 828 at 100% solids.

^b Grams of resin containing 1 gram-mole of epoxide.

The commercial epoxy resin esters are almost always based on solid resins. The liquid grades are used most often in such structural applications as laminates, pottings, and adhesives. The epoxy resins based on bisphenol A are the type usually used for ester preparation; the specific product most widely used is typified by EPON® Resin 1004 (Shell Chemical Corporation); this product has a combining weight of 175 and a number average-molecular-weight of about 1,400; the eight esterifiable groups consist of about 5.0 hydroxyl groups and 1.5 epoxy groups. In subsequent discussions this type of epoxy resin is the grade referred to unless other types are specified.

The volume of epoxy resins has expanded considerably since their introduction in 1950. It has been estimated that production of epoxy resins in 1957 in the United States was 40 million lbs. and consumption was 28 million pounds; in 1958 consumption was estimated at 28-30 million lbs. (11). The most widely used solid grades cost 54-56¢ per pound.

Techniques in the Esterification of Epoxy Resins

Although open kettles may be used to prepare epoxy esters, the products are darker and higher in viscosity compared to products made in closed kettles. In closed kettles an inert gas sparge is recommended to achieve the palest colors and avoid high viscosities. Lowest viscosities and color are achieved by use of azeotropic cooking where xylene or other proper solvent serves to remove water (19). Usually all ingredients are charged to the kettle at once, but sometimes the resin is added to preheated fatty acid to

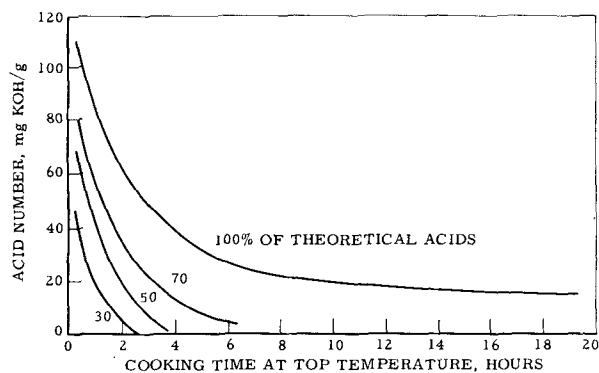


FIG. 1. Effect of oil length on esterification rate of an epoxy resin at 500°F. (47).

minimize overheating of a layer of epoxy resin with resultant charring or excessive viscosity. A temperature of 250°C. is appropriate for esterification with linseed fatty acids because the rate is quite rapid and dimerization of fatty acid chains is slight. It is sometimes desirable to use a lower temperature if more reactive acids, such as dehydrated castor, are used, and higher temperatures with less reactive acids of the soybean or tall oil types. Resin acids require a higher temperature of about 275°C. (527°F.) or even more. The effect of temperature is more critical with esters of long oil length because cooking times are longer and it is necessary to minimize excessive viscosity by fatty acid dimerization. Figures 1, 2, and 3 show the effect of oil length upon esterification time and the effect of various cooking temperatures upon esterification rate and viscosity (47).

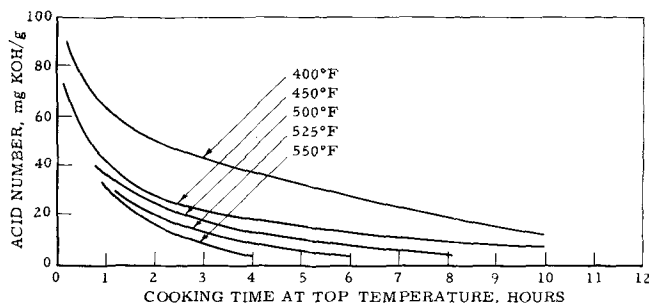


FIG. 2. Effect of temperature on esterification rate of an epoxy resin using 70% of the theoretical quantity of soybean acids (47).

In most esterifications of epoxy resins it has not been the practice nor has it been found necessary to add catalysts. However various bases and salts have been tried as catalysts, and reaction rates have been accelerated in some cases. Some investigators (34) concluded that the reaction between carboxyl and epoxy groups is accelerated by very small quantities of calcium oxide, zinc oxide, and other related products and that both faster esterifications and lower viscosities were achieved. Zinc resinate was found to increase the rate of reaction of epoxy resins with fatty acids containing some tung acids (24). The effect of triphenyl phosphite in the preparation of long linseed esters (80% of theoretical) has been reported by Martin, Loible, and Turner (34). With increasing concentration of triphenyl phosphite,

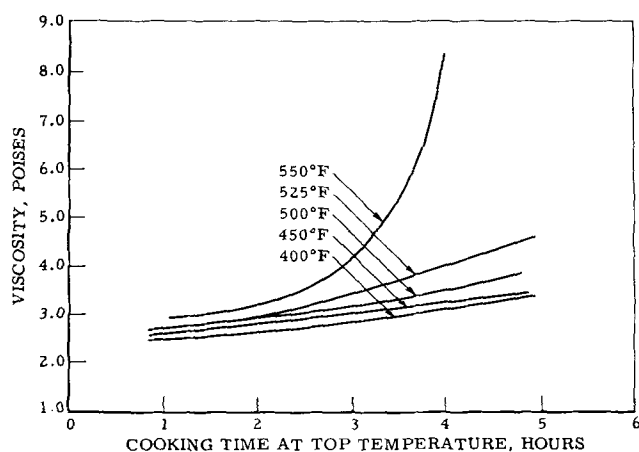


FIG. 3. Effect of temperature on viscosity during esterification of an epoxy resin using 70% of the theoretical quantity of soybean acids (47).

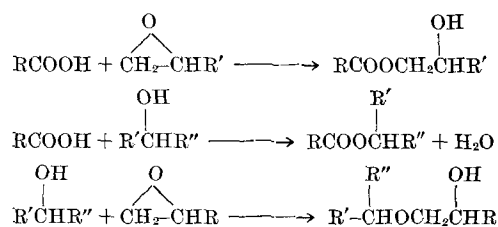
esterification rate was increased, colors were lighter, and viscosities were greater. Above 0.2% phosphite, esters increased in viscosity and developed haziness upon storage. Although 0.1% phosphite was considered safe, benefits were marginal.

It is possible to esterify the free hydroxyl groups of epoxy resins with only a slight attack on the epoxy groups by an alcoholysis reaction between the free hydroxyl groups and the methyl esters of fatty acids (13). The reaction can be accomplished by heating the reactants in the presence of small quantities of sodium methoxide while removing methanol. Homogeneous varnishes also have been made by cooking epoxy resins and drying oils at 580°F. (53). The chemical reactions involved appeared to be alcoholysis between the hydroxyl groups and the ester groups of the oils, also polymerization between epoxy groups and hydroxyl groups in resultant mono- or diglycerides or in the resin itself.

The epoxy resins also have been employed in alkyds (50), but this topic is not within the scope of this paper.

Chemical Reactions in the Esterification of Epoxy Resins

The principal reaction with which we are concerned in the preparation of synthetic oils is an esterification between a carboxylic acid group and an alcohol group. This is an equilibrium reaction, but high yields of the desired ester are obtained by removal of water. In the preparation of esters from epoxy resins there are three major reactions which must be considered; they are the carboxyl-epoxy, the carboxyl-hydroxyl, and the hydroxyl-epoxy reactions:



In each of the reactions involving the epoxy group two isomers may be formed; these are a secondary alcohol and a primary one, but the former will predominate as shown. In addition, hydration of the

epoxy group may occur, but when water is removed rapidly and efficiently, this is probably of small consequence as are other possible chemical reactions.

Ordinarily it is desirable to minimize the hydroxyl-epoxy reaction because of the attainment of excessive viscosity or even gelation, also because of the loss of esterifiable groups with accompanying difficulties in obtaining the desired degree of esterification.

These reactions have been investigated by Shechter and Wynstra (45), using model compounds of low molecular weight hence more tractable than the usual solid epoxy resins themselves. These investigators found that the uncatalyzed reaction at 200°C. of equivalent quantities of caprylic acid, dipropylene glycol, and the diglycidyl ether of 2,2-bis(p-hydroxyphenyl) propane resulted principally in interaction between epoxy and hydroxyl and also between acid and hydroxyl and to a much lesser extent between epoxy and acid. Fortunately in the practical esterification of epoxy resins the epoxy-hydroxyl reaction apparently is not as extensive as these results with model compounds would suggest. Differences in esterification temperature may be a factor. Steric hindrance also probably inhibits the reaction between epoxy and hydroxyl because both groups are present in large resin molecules.

Since the hydroxyl-epoxy reaction is the only major reaction which leads to loss of esterifiable potential, the sum of ester, hydroxyl, and epoxy content in the product should equal the sum of the original hydroxyl plus epoxy content if no hydroxyl-epoxy reaction occurred. Any difference between these two sums is a measure of the hydroxyl-epoxy reaction. The data of O'Neill and Cole (40) on the esterification of an epoxy resin, using 91% of the theoretical quantity of linseed acids, is reproduced in Table IV. The original

TABLE IV
Esterification of Epoxy Resin with Linseed Oil Fatty Acids at 260°C. by Solvent Process (40)

	Acid number	Epoxy number	Hydroxyl number	Water evolved
Calc. for mixture.....	117	25.5	67	%
Time at top temp., 260°C...			
0 hour.....	64	0	68	1.0
1 hour.....	27	0	37	2.3
2 hours.....	19	0	25	2.5
4 hours.....	11	0	20	2.6
6 hours.....	9	0	17	2.7

All analytical values are on the same basis and are expressed as mg. KOH per gram.

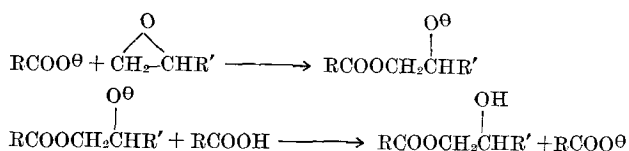
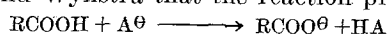
reactants had esterifiable groups equivalent to 118 mg. KOH/g. ($67 + 2 \times 25.5$); in the final product the total of ester value ($117 - 9 = 108$) and residual hydroxyl (17) is 125. Some error in analytical figures is inevitable and in this case may be accounted for partially by decarboxylation, but the approximate equality of these figures suggests that all the original esterifiable groups can be accounted for and the amount of hydroxyl-epoxy reaction is negligible. It can also be noted that all epoxy groups were destroyed long before completion of esterification. Some reaction between hydroxyl and epoxy can occur; this was shown when these investigators heated octadecyl alcohol with the diglycidyl ether of bisphenol-A for 9 hours at 240° and found 25% of the alcohol had reacted. By studying the reaction of stearic acid and the diglycidyl ether of Bisphenol-A, they concluded

that some esterification of hydroxyl groups occurs along with the esterification of epoxy groups by acid.

North (37) plotted the evolution of water against acid value in the preparation of a short oil ester. His data can be interpreted as indicating that esterification of hydroxyl groups occurs along with esterification of epoxy groups. Earhart and Montague (18) measured the quantity of water evolved when the usual grade of epoxy resin was esterified by various percentages of fatty acid. It was found that in esters which contain above 40% by weight of fatty acid (this is about 0.40 equivalent of acid per esterifiable group) the quantity of water obtained exceeded only very slightly the quantity of water expected if all the epoxy groups and part of the hydroxyl groups were esterified. These data show that little if any hydroxyl-epoxy reaction occurred at the common oil lengths under the conditions employed. It should be emphasized that excess water over the stated theoretical value indicates that esterification of hydroxyl groups occurred to a certain extent; it does not indicate that this excess is a measure of hydroxyl-epoxy reaction if residual epoxy groups exist in the ester. In very short esters residual epoxy groups may well be present; simple water-acidity plots therefore are of limited significance unless supplementary analytical data are obtained. It also is important that an allowance be made for the presence of water in raw materials.

It may be concluded that, in general, the hydroxyl-epoxy reaction is not a major reaction in epoxy resin esterifications. However, even if it occurs to a minor extent, it may have significant effects, such as greatly increased viscosity and difficulty in achieving low acid numbers, particularly at long oil lengths. Special esterification techniques can be expected to minimize the epoxy-hydroxyl reaction: hot layers of pure epoxy resin should be avoided by proper stirring; also resin may be added slowly to preheated fatty acids.

In the case of base-catalyzed esterifications of model epoxy compounds, it has been suggested by Schechter and Wynstra that the reaction proceeds as follows:



It was further shown that the reaction of phenols and alcohols also probably proceeds by the analogous formation of phenoxide and alkoxide ions. Although in a reaction of epoxy groups with only one of these groups the rate of reaction is alcohol > phenol > carboxyl, in a mixture of all of these groups the acid reacts first, then the phenol, and finally the alcohol because the strongest acid would be the first to form the intermediate anion. These results suggest that bases or salts may have beneficial catalytic effects by increasing esterification rate and extent and minimizing the hydroxyl-epoxy reaction. Such results have been reported, as has been mentioned earlier.

Properties of Esters of Epoxy Resins

In general, the epoxy esters are noted for excellent adhesion, flexibility, toughness, and chemical resistance. In some applications their use has been restricted by a relatively rapid loss of gloss of pig-

mented enamels upon outdoor exposure by chalking. In some formulations there is a tendency to yellowing. Maximum chemical resistance usually is attained by curing the straight resin by polyamines, polyamide resins, phenolic resins, urea-formaldehyde, and various other co-reactants. Excellent results also are achieved by the curing of short oil esters with urea and melamine resins. The properties of the esters are dependent upon the functionality of the resin; the usual grade contains eight esterifiable groups per molecule, as mentioned earlier. Epoxy resins containing only six esterifiable groups or as many as 15 are used to achieve special properties.

Just as alkyds may be made with various oil contents, so may epoxy resins be combined with various quantities of fatty acids. Usually 40% to 80% of the available esterifiable groups in the epoxy resin are esterified, and sometimes as low as 30% or as high as 90%. In the range of 30–50% esterification the esters may be called short oil; at 50–70%, medium oil; and at 70–90%, long oil esters. Terminology in epoxy resin esters is different from that in alkyds: an 80% epoxy soybean ester, for example, means that for each esterifiable group present in the epoxy resin molecule, 0.8 of an equivalent of fatty acid has been employed in the esterification reaction. A convenient and widely accepted terminology has been introduced by one supplier to designate the esters (47); in this system a letter is used to designate the type of fatty acid, and a number for the attempted degree of esterification. Thus L-8 indicates the linseed ester which has been esterified with 80% of the theoretical quantity of fatty acids; the actual composition in this case is comprised of 56.5% fatty acid and 43.5% resin.

A second terminology also has been widely used. In this system a 60% ester is defined as one which is prepared from 60 parts of fatty acid and 40 parts of resin. It is, of course, important to ascertain the system used in any given discussion. The calculation of ester compositions has been discussed (18).

As the percentage of fatty acid increases, there is an increase in the following ester properties: solvency in hydrocarbons, application solids at a given viscosity, brushing ease, color retention, and resistance to water. As the fatty acid content increases, there is a decrease in the following properties: viscosity at a given nonvolatile content, hardness, tack-free drying rate, and compatibility with urea and melamine resins. Alkali resistance is generally outstanding and is partly dependent upon acid number. Some typical properties of some epoxy esters are shown in Table II in comparison with some other vehicles.

Usually about 0.04% cobalt has been used for air-drying epoxy esters. Occasionally other drier combinations have been used. Glaser *et al.* (23) have found a combination of manganese and rare earth driers of some advantage. North (37) has shown that the use of 0.20% calcium with cobalt is beneficial, but some haze may develop. For baking systems he recommended the use of 0.02% manganese or 0.01% cobalt.

Applications of the epoxy esters have been described by Somerville (50) and others (47), but only a few examples will be mentioned. As reported by Howard, Radecke, and Scheibli (29) an epoxy ester system has proved to give excellent results in large-scale application in industrial maintenance enamels for use in oil refineries under moderately corrosive

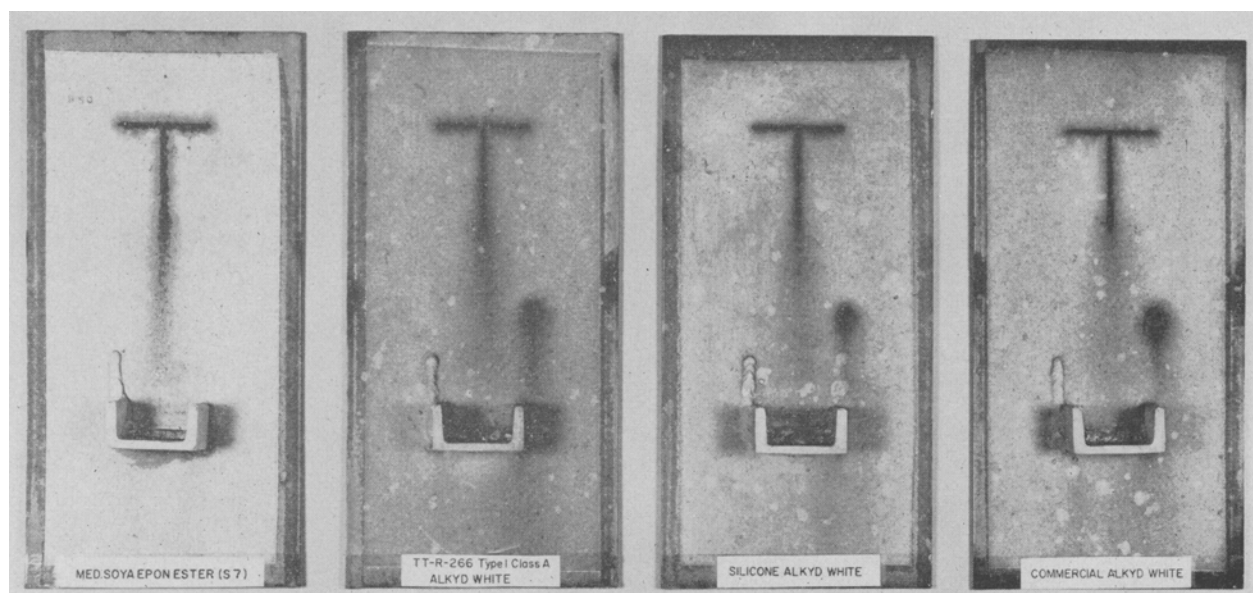


Fig. 4. White paints exposed for 26 months in a refinery atmosphere at 45° from the vertical (29).

conditions. The actual system used was comprised of a red lead primer made from a long linseed ester and white and gray topcoats from a medium long soybean ester. Exposure panels and extensive full-scale experience have shown that the epoxy esters were superior to alkyds and oleoresinous vehicles in protecting the steel surfaces from corrosion and also in giving a cleaner, more attractive appearance to painted tanks and equipment. The superior appearance of the epoxy ester finishes can be attributed mainly to the greater chalking rate of epoxy esters compared to alkyd resins; yet this chalking rate was so slight that only very slight decrease in film thickness could be noted in 5 years of exposure. Figure 4 illustrates the superior appearance of the epoxy ester coating.

Short dehydrated castor esters have been used in quality over-print varnishes which can withstand severe forming; this same ester has been employed to form excellent baked finishes in combination with melamine resin. The outstanding detergent-resistance of short soya or other esters combined with melamine resin makes them of prime use in wash-machine primers. Short to medium oil esters from soybean acids or tall oil make good vehicles for automobile primers, but they chalk too rapidly for use as topcoats for automobiles. A mixed linseed-rosin ester has been used as a high quality of floor varnish having superior abrasion-resistance, hardness, and drying

rate. An excellent spar varnish has been made by combining an epoxy ester with a tung-phenolic varnish (50). Some epoxy esters have been shown to have good outdoor durability as clear varnishes (53). Styrenated epoxy esters have been found to possess very rapid drying rate, good mar-resistance, and good weather-resistance (55). Epoxy ester coatings for use in the metal litho industry have been described (23). The properties of tall oil esters have been reported (56).

Stress-strain properties of free films of epoxy coatings have been investigated by Bradley (5), Mika (35), and Van Hoorn and Bruin (57). Among several systems studied. Mika investigated the stress-strain properties of a medium soybean epoxy ester in comparison to medium soybean and linseed alkyds, all of which were made from 50% by weight of fatty acids. His data are reproduced in Table V. It was found that the epoxy ester had the greatest tensile strength and elongation, originally and after oven-aging or exterior weathering, compared to both alkyds. Stress-strain properties of pigmented epoxy esters also were studied.

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TABLE V

Stress-Strain Properties of Alkyds and an Epoxy Ester (35)

	Epoxy soybean ester	Soybean alkyd	Linseed alkyd
Fatty acid content, %.....	49.3	50.0	50.0
Acid No., mg. KOH/g., 100% solids...	6.0	6.0	6.0
Sward hardness, 2 weeks.....	12	12	18
Film thickness, mils.....	1.9	2.0	1.8
Viscosity, Gardner-Holdt.....	P	Y	Z-1
Tensile strength, p.s.i.			
Original, 2 weeks old.....	2100	800	1050
After 12 hours at 100°C.....	4000	2250	2500
After 14 months weathering.....	6100	3400	3700
Elongation, %			
Original, 2 weeks old.....	132	108	94
After 12 hours at 100°C.....	96	66	52
After 14 months of weathering.....	42	34	16

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Isocyanate-Modified Drying Oils

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THE FIELD of isocyanate chemistry and urethane polymers has held the interest of paint formulators and resin chemists increasingly in recent years. Because of their extreme reactivity, isocyanates can be used in coatings in an almost unlimited number of ways. Recently Remington and Lorenz (1) have listed four distinct types of urethane-coatings systems. These are as follows.

1. A two-component system in which an isocyanate polyol adduct of low volatility is mixed with an hydroxyl-containing resin just prior to use. The polyhydroxy material might be a polyester, a polyether glycol, or castor oil. This is, of course, a two-package system, which has a limited pot life once the two components are mixed. It can be pigmented by dispersing the pigments in the polyhydroxy component. By varying the amount of hydroxyl groups and the amount of isocyanate available for cross-linking, the formulator can achieve a wide range of physical properties in the finished film. This system can be formulated to give outstanding chemical resistance.
2. A one-component system consisting of two ingredients, an isocyanate polyol adduct which has been "blocked" to make it nonreactive, and a polyhydroxy resin. Upon baking, this blocking agent (usually phenol) is driven off, and the isocyanate is available for cross-linking. This system is stable and can be pigmented. It must be cured by heat.
3. A one-component system consisting of an isocyanate-terminated polymer, which cures by reaction with atmospheric moisture. This system is stable as long as no moisture is present. It is extremely difficult to pigment since moisture-free pigments must be used. Once the package has been opened and air with some moisture enters the container, shelf life is limited. A variation of this system provides for the addition of an amine catalyst prior to use. This then becomes a two-package system.
4. The so-called oil-modified urethane system, or urethane oil. Here the isocyanate is reacted with a partial ester of a polyol with an unsaturated fatty acid or an alcoholysis product. If the amount of isocyanate used is stoichiometrically equivalent to the hydroxyls present, the

resulting resin is stable. This system cures by the conventional mechanism of polymerization through the unsaturation in the fatty acids. This is a stable system which can be pigmented and handled in much the same manner as conventional-coatings resins.

These so-called isocyanate-modified oils were among the first urethane materials to find any practical industrial applications. A development of pre-World War II German urethane chemistry, these urethane oils were used in war-time Germany as protective coatings and were reported in the BIOS and PB reports published shortly after the war as being closely related to alkyd resins in formulation and in properties. Since that time relatively little attention has been given to products of this type. In 1951 Robinson and Waters (2) described an extensive study of urethane oils, which closely followed the earlier German work. More recently Pansing (3) reported on similar products based on linseed oil and soybean oil. Apart from these contributions, little detailed information has appeared in the literature.

Chemistry

The isocyanate group will react with and add to any compound containing an active hydrogen. This would include water, alcohols, primary and secondary amines, carboxylic acid groups, hydrogens, or certain activated methylene groups, such as aceto-acetic ester or malonic ester, etc. The urethane reaction, of course, refers specifically to the reaction of the isocyanate group with alcohols.

When a polyisocyanate is reacted with a polyhydroxyl material, a urethane polymer is the result. As shown in Figure 1, when a di-isocyanate (*e.g.*, tolylene di-isocyanate) is reacted with either a partial ester of a polyol (*e.g.*, glycerine) and a drying