

to that of petroleum greases and will therefore be restricted to specialized applications. In other words, it is believed that synthetic greases will continue to supplement petroleum greases and will be employed primarily in those applications where extremes of temperature are encountered.

**Summary**

A brief review has been given of the principal types of lubricating greases and of the fatty materials used therein. No attempt has been made to include a discussion of all conditions which may affect grease

structure. However it has been indicated that various factors, as far as the grease itself is concerned, influence performance because they either affect the size and shape of the dispersed particles of the thickening agent, or affect the solubility relationship between the dispersed particles and the oil.

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## Applications of Fatty Acids and Derivatives in Alkyds and Other Polyester Coating Resins

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**I**N THE surface-coatings field, to which this paper is directed, fatty acids are used principally in the following types of products: alkyd resins, epoxy resin esters, *in-situ* varnishes, maleinized oils, and polyhydric alcohol esters.

While the fatty acids that are available commercially vary in composition, depending upon the oil from which they are derived, the coating chemist is primarily interested in the following key fatty acids:

Drying Types	Carbon Atoms	Non-Drying Types	Carbon Atoms
Clupanodonic . . . . .	22	Ricinoleic . . . . .	18
Arachidonic . . . . .	20	Lauric . . . . .	12
Eleaostearic . . . . .	18	Capric . . . . .	10
Licanic . . . . .	18	Pelargonic . . . . .	9
Linolenic . . . . .	18	Caprylic . . . . .	8
Linoleic <sup>a</sup> . . . . .	18		
Oleic . . . . .	18		

<sup>a</sup> and conjugated isomer.

The higher saturated fatty acids, such as myristic, palmitic, and stearic, are of little interest to the coating resin chemist except that they act as diluents in the oxidative type of fatty acids essential to the drying processes involved in effecting dried resinous films.

The fatty-acid derivatives of most interest to the coating chemist are as follows:

Name	Carbon Atoms	Carboxyls	Combining Weight
Dimer Acid.....	36	2	300
Soybean and Fish Oil F.A. Alcohols	18-22	0	.....
Sebacic Acid.....	10	2	101
Azelaic Acid.....	9	2	94
Pelargonic Acid.....	9	1	158

For the sake of completeness in tabulating the tools with which the surface-coating chemist works, the following are the more important oils from which fatty acids are (or may be) derived:

- |                          |             |
|--------------------------|-------------|
| Castor                   | Linseed     |
| Coconut                  | Safflower   |
| Corn                     | Soybean     |
| Cottonseed               | Sunflower   |
| Dehydrated Castor        | Tall Oil    |
| Fish (Menhaden, Sardine) | Walnut-Seed |

From a commercial viewpoint the fatty acids from cottonseed, soybean, and coconut oils are used in the greatest volume. Since cottonseed, corn, and soybean soapstocks are large-volume by-products of the food industry, fatty acids, with approximately 10 iodine value steps ranging from approximately 100 to 140, are available because of modern fractional distillation and crystallization techniques.

If it were not for the fatty acids available from these soapstocks, fatty acids would not be used in alkyds in competition with oils in view of the economic advantage of the latter.

The principal properties of the fatty acids which define their use in surface coatings are the iodine value, molecular weight and characteristic groups, and position and number of the unsaturated bonds.

The iodine value gives us an idea of the degree of unsaturation and a rough approximation of whether the particular fatty acid can be considered a drying or non-drying type for a particular application. Recently, the author has been applying the concept of functionality to the iodine value, along with the functionality of the dibasic acid, polyhydric alcohol, etc., involved. For example, if the basic polymer to which a fatty acid is attached is of low molecular weight, a high iodine value will be necessary in order to obtain acceptable drying speed. If the basic polymer is of higher molecular weight, a fatty acid of lower iodine value will suffice as long as the iodine value is due in great part to linoleic acid, which oxidizes sufficiently fast to effect cross-linking in a reasonable period of time.

The molecular weight of fatty acids is important only for differentiating the long chain drying acids



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from the short chain non-drying acids. The latter are mostly employed in alkyds and other esters which are used together with thermosetting resins to formulate baking-type coatings, or with nitrocellulose in wood lacquers.

Our interest in the relative positions of the unsaturated bonds is to differentiate conjugated double bonds from unconjugated double bonds. The conjugated double-bond types of fatty acids are more sensitive to heat and oxygen and effect faster bodying gas checking, and wrinkling.

What the modern coating-resin chemist really needs to know is the composition of the mixed fatty acids he is buying. While years ago it was enough to know that certain fatty acid types would sufficiently effect fast-drying alkyds if the iodine value were above a certain minimum, the modern coating-resin chemist is more concerned with the properties of the individual fatty acids (*e.g.*, that linolenic acid will effect more yellowing than linoleic) and therefore wants to know the composition in order to build into the coating resin the properties he desires and to exclude those properties he does not desire. For this reason we believe there is a trend toward specifying the fatty acids in the products for sale (1).

**D**IMER acids were born at the Northern Regional Research Laboratories during the early World War II days. Dimer acid is essentially a polymer of two molecules of linoleic acid and therefore is a dibasic acid. Its largest use to date is in the manufacture of polyamide resins although it has also been used to modify alkyds, rosin-maleic-polyhydric alcohol resins, and epoxy resins. As would be suspected, it imparts the properties of a bodied oil (*i.e.*, viscosity with flexibility) and can be used in prescribed amounts to satisfy the formulator of a tailor-made resin.

The unsaturated alcohols produced by the sodium reduction of the fatty acids in soybean or fish oils are recent additions to the tool-kit of a coating-resin chemist. Although the alcohols are monofunctional as far as the alcohol grouping is concerned, they are potentially polyfunctional via oxidation at the double bonds and therefore are indicated as modifiers (chain stoppers) in the medium to short-oil alkyds where they will serve to reduce the functionality of glycerol and pentaerythritol and allow a greater degree of esterification of phthalic anhydride and other dibasic acids.

Sebacic acid is well known in the coatings industry. It is made by a complicated oxidation reaction of ricinoleic acid, using sodium hydroxide. The high price of sebacic acid has retarded broad usage, but the low-temperature plasticizing and non-migrating properties of glycol-sebacates in polyvinyl chloride have justified their use in various formulations.

Azelaic acid has just been introduced to industry in increased commercial quantities. It is one of the products obtained when oleic acid is oxidatively split at the 9-10-carbon atom. Being a nine-carbon dibasic acid, its odd carbon configuration should effect plasticizing power equal to, if not greater than, sebacic acid.

Pelargonic acid, a nine-carbon monobasic acid, is the other acid obtained when oleic acid is split oxidatively. In view of its nine-carbon atom size, it can be used to modify short-oil alkyds of the type now pre-

pared from coconut fatty acids or the caprylic, capric, and lauric fractions.

Having discussed the major types of oils, fatty acids, and fatty-acid derivatives, let us consider how the fatty acids are visualized when formulated into alkyds and other resinous compounds. First, in order to evaluate the effect of fatty acids in a very complex resinous formula, it becomes necessary for a formulator to establish his own fundamental philosophy of how he will visualize the fatty acids in the final resinous formula. Most neophyte coating chemists start out on a molar basis, *e.g.*, in formulating a simple alkyd with one mole of glycerol, they might choose 1.25 moles of phthalic anhydride and 0.5 moles of fatty acids. While this system has its advantages in helping solve the stoichiometry of resin formulating, it leaves much to be desired in the way of following the effect of varying amounts of fatty acid in terms of film properties.

The alkyd industry is now fairly well standardized on a "percentage-oil-length" nomenclature basis although some of the polyhydric alcohols besides glycerol require the word "oil" to be put in quotation marks because oil in the sense of a triglyceride may not be involved.

The author's own philosophy on oil modification terminology for simple glycerol-phthalate resins was presented at the Symposium on Alkyd Resins in Chicago in 1948 (2).

For more complicated "oils," *i.e.*, fatty-acid esters of pentaerythritol, dipentaerythritol, etc., a simpler method of defining "oil" is as follows: 1 equivalent of fatty acids, plus 1 equivalent of polyhydric alcohol, minus 1 equivalent of  $H_2O$ , equals 1 equivalent of "oil."

**W**ITH this definition as a guide let us discuss a few of the applications of fatty acids to resinous coating materials.

*Synthetic Drying Oils.* During the war, when drying oils were in short supply, the chemist met the challenge by up-grading drying oils of lower iodine value and non-conjugated or lower conjugated fatty acids.

For example, the pentaerythritol ester of soybean fatty acids was used as a passable linseed-oil substitute. Other variations were to combine 2-6% maleic anhydride with fatty acids in order to add functionality and thus increase the viscosity of the resulting "oil." These maleinized oils were useful for building viscosity into varnishes in the absence of tung oil or linseed oil, or to serve in the capacity of bodied linseed oil.

Passable tung-oil substitutes were formulated by making pentaerythritol esters of dehydrated castor-oil fatty acids. While an oil of this type was minor in volume, it served as an example of building functionality into a synthetic drying oil.

*Varnishes.* The war years saw great changes in the composition and manufacture of varnishes. Since paint companies were allocated only so much oil based on previous consumption figures, they learned to stretch their supplies by employing the synthetic oils mentioned previously and by various *in-situ* methods of making varnishes from tall oil. A typical example of an *in-situ* tall oil varnish taken from the literature (3) of one of the tall oil producers is as follows: 86.8 parts, tall oil (32% rosin acids, 1.4% unsaponifiables,

66.6% fatty acids); 5.2 parts, maleic anhydride, and 14.3 parts, pure pentaerythritol to give a theoretical yield of 100 ester after a loss of 6.3 parts of water.

The instructions for cooking call for heating the tall oil and maleic anhydride to 400°F. (205°C.), holding for 1 hour, adding the pentaerythritol, and esterifying at 530°F. (277°C.) until an acid number of 10-15 is obtained, after which it is dissolved in mineral spirits to give a varnish with the following constants: viscosity (70% in mineral spirits) of T, acid value (solids) of 15, and color of 8-9.

The war provided the incentive to carry out development work on tall oil, and its use has now become firmly entrenched in our economy.

**Epoxy Resin Esters.** The condensation products of bis-phenol and epichlorohydrin are resinous materials which lend themselves to esterification with fatty acids. These resins are offered to the surface-coatings industry by the Jones-Dabney Company, Division of Devco and Raynolds under the trademark Epi-Res; the Shell Chemical Corporation under the trademark Epon; and the Bakelite Division of Union Carbide and Carbon Corporation as Bakelite Epoxy Resins.

Various proportions of fatty acids are indicated for esterification with these resins, but the proportions are generally 35-45%, depending on the equivalent weight of the epoxy resin to be esterified. Soybean, linseed, and dehydrated castor oil fatty acids are recommended for air drying and baking finishes.

The concept of oil-length in fatty acid epoxy resin esters has not been standardized, but one method is to calculate the fatty acids to triglycerides and express as "oil." However we hasten to add that the OH groups in epoxy resins bear no direct relation to those in glycerol since they are spaced at distant intervals as depicted by the formula. Another method of expressing the fatty acids as esters is to treat the epoxy resin as a polyhydric alcohol on an equivalent weight basis and calculate as a resinous ester.

The most remarkable property of the epoxy resin esters, as compared with alkyd resins, is the alkali resistance. It is probably a debatable subject, but our theory is that the alkali resistance is due in great part to the small proportion of conventional ester linkages, the relative absence of polar groups, and the protection afforded the ester groups by the bis-phenol skeleton. The speed of drying of a soybean fatty acid modified epoxy resin is easily understood on a polymeric and functionality basis, *i.e.*, the resinous skeleton to which the oxidizable fatty acid is attached is so much larger as compared to the glycerol-phthalate skeleton of an alkyd resin that a small amount of oxidation with subsequent cross-linking is sufficient to raise the molecular weight many-fold and satisfy the physical requirements of drying.

**Fatty Acids in Alkyds.** The greatest use of fatty acids in the surface-coatings field is in alkyds. We shall not go into the formulation of alkyds as such since many papers and patents exist in the literature.

Fundamentally speaking, the major properties and applications of alkyds as coating resins are dependent on, and dictated by, the properties of the fatty acids used to modify the basic polyesters composed of polyhydric alcohols and dibasic acids.

If one will literally boil down the key elements of an alkyd into the simple components that are easy for the mind to comprehend, the understanding of alkyds

will be relatively simple. The simplest statement of the composition of an alkyd on this basis is:

X	% "Oil"	{	Fatty Acid	}	-	H <sub>2</sub> O
			Polyhydric Alcohol			
Y	% Polyester	{	Dibasic Acid	}	-	H <sub>2</sub> O
			Polyhydric Alcohol			
Z	% Modifier <sup>a</sup>	{	Modifying Acid	}	-	H <sub>2</sub> O
			Polyhydric Alcohol			
100%						

<sup>a</sup> The modifier in some cases may be non-acidic.

We wish to emphasize that the composition should be visualized on an esterified basis.

With these basic statements as a premise, let us discuss the effect of the % oil. As a starter, the viscosity of an alkyd in a solvent will be inversely proportional to the % oil, *i.e.*, the lower the proportions of oil, the higher the viscosity, and *vice versa*.

In general, the drying (or apparent drying) time is directly proportional to the percentage of oil; drying rate is inversely proportional to oil length. However there is an anomaly which modifies this statement, and that point will be clarified later.

With this picture before us, we are now able to select fatty acids for formulating into alkyds based almost solely on the properties of the fatty acids available from the large array of types from which we can select.

**T**HE 14-, 16-, and 18-carbon saturated fatty acids have found little use in alkyds (in the pure state) and can be more or less discarded from our thinking. Stearic acid makes a waxy alkyd of no use as a conventional coating material.

The 8-12-carbon atom fatty acids have found use in the shorter oil length alkyds as film-forming ingredients in connection with urea and melamine resins to form the basis for some white appliance topcoat finishes.

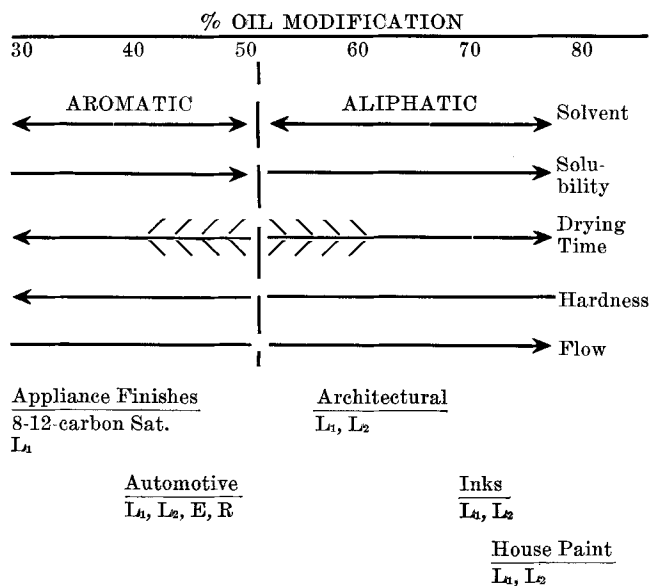
Oleic acid, used alone, has no major application in alkyd resins. It will oxidize and impart a low degree of cross-linking in an alkyd and therefore in some respects should be considered as a plasticizing fatty acid.

Linoleic acid is the workhorse of all the fatty acids. It gives fair speed of drying with minimum yellowing.

The 9-11 conjugated isomer of linoleic acid, obtained from dehydrated castor oil, imparts the ideal properties of great speed of dry with low yellowing. However, if used in excessive quantities, it will cause gas checking, and it is also subject to polymerization while esterifying. Since the percentage of the 9-11 acid present in dehydrated castor oil acids is only of the order of 30%, little trouble from gas checking and bodying is encountered under normal conditions.

Linolenic acid, the main constituent of linseed oil, is a relatively fast-drying fatty acid, but it has the disadvantage of effecting yellowing of alkyd resin films.

Eleaostearic acid and licanic acid, which are the main constituents of tung and oiticica oils, respectively, impart fast drying but are very heat-sensitive during esterification and are not used in large amounts in coating compounds, where gas checking or wrinkling cannot be tolerated. The gas checking



L<sub>1</sub> = Linoleic acid, L<sub>2</sub> = Linolenic acid,  
E = Eleaostearic or Licanic, R = Rosin.

and wrinkling properties are used to advantage however in wrinkle-finish coatings.

Arachidonic and clupanodonic acids, which are present in fish oils, impart great drying speed to alkyds and other resinous esters but have been found from experience to cause embrittlement of the resulting films. The degree of yellowing imparted is approximately of the same order as that of linolenic acid.

Ricinoleic acid is used in alkyd resins which are designed for use with amine resins and nitrocellulose since the OH group from ricinoleic acid effects greater compatibility and plasticizing power than other 18-carbon atom fatty acids. Ricinoleic acid must be esterified with care at temperatures below 250°C., or dehydration will occur and result in the types of acids occurring in dehydrated castor oil.

We have discussed the properties of the fatty acids as pure constituents. Although technology is striving to produce purer fatty acids at economical prices, we must rely presently on the economic mixtures which nature has given us in the whole oils or pay a premium for some of the excellent fractionated and segregated fatty acids now on the market. At the mo-

ment therefore we must choose various commercial grades of mixed fatty acids with the properties of the major constituent in mind and exclude from our choice (or minimize) the unwanted constituents. For example, if we had to choose between two fatty acids, with identical iodine values of 135, that were derived from cottonseed oil in one case and soybean oil in the other case, both of which contain linoleic acid, we would choose the one from cottonseed oil in order to minimize after-yellowing. This would accrue from the higher linolenic-acid content of the fatty acid from soybean oil.

Having considered the concept of "oil" length and the properties conveyed by the individual fatty acids in the various oils, we shall now focus the picture by way of a diagram, which indicates a) the effect of oil length on the more important properties of an alkyd, b) the types of fatty acids generally used in certain selected oil lengths, combined with c) the usage of alkyds as related to oil length.

Most of the facts depicted in the table are easily understood from the discussions in the earlier parts of this paper. However, as mentioned earlier, there is an anomaly connected with the general statement that the drying time of an alkyd is proportional to oil length. While the set-to-touch times of alkyd films increase progressively with oil length, as one would expect, the maximum speed of drying, as measured by polymerization, is obtained in the 50-55% oil-length range. A plausible explanation is that there are fewer statistical chances for fatty-acid groups to oxidize and cross-link with one another in short-oil alkyds than in long oil alkyds, in a given length of time.

For clarity it should be mentioned that larger volumes of alkyds are produced from oils than from fatty acids, by employing alcoholysis techniques with oils and polyhydric alcohols, followed by esterification with dibasic acids. However a basic understanding of alkyds is heavily dependent on the properties of the individual fatty acids. Whether one should use commercial fatty acids or oils in actual practice is a matter of economics and the properties required of the ultimate coating.

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