

Safflower Oil in Alkyd Resins and Treated Oils¹

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DURING the last 20 years the treatment of the vegetable oils with substances such as phthalic anhydride, maleic anhydride, and other chemicals has resulted in improved and diversified surface coatings. For example, since about 1927 alkyd resins have steadily replaced oils and hard resin varnishes in enamels. Soybean oils treated with maleic anhydride and polyalcohols were substituted for some of the linseed oil in outside paints. It is claimed that linseed oil treated with maleic anhydride-pentaerythritol effectively replaces tung oil in varnishes.

Even though the processing of oils has been varied, it is surprising to note the absence of new types of oils on the commercial market. Linseed, soya, tung, and recently dehydrated castor oils are still the chief tools of the trade, with minor roles for coconut, raw castor, perilla, oiticica, and tall oil.

Safflower oil is a welcome addition to our list of raw materials. It is interesting because it can be produced in the United States and can be sold at prices agreeing with the paint makers' cost standards. Added to these two factors of utmost importance are others, such as similarity in processing techniques for other oils, good durability of films, and better color retention than linseed and perhaps soya films. These call for a fair evaluation of the oil.

India and other far eastern nations cultured safflower seeds for generations (1). With plenty of soybean oil for alkyds and linseed oil for outside house paints, little interest in safflower oil was aroused in America. However when enterprising farmers began to grow safflower in Colorado, California, and Nebraska and the oil was offered at a price competitive with soya, only the lack of availability in tank car lots caused consternation among paint manufacturers.

The growth of soybeans on the West Coast remains uneconomical because they do not grow well in that area. To supply West Coast alkyd resin producers the oil must be shipped from the Midwest. It is no wonder then that resin producers are eager to stimulate safflower growth in the Central and Imperial Valleys of California, considering only the saving in freight (2). The cultivation of the safflower plant adapts well to areas of high summer temperatures, either with dry land farming practices or with ditch irrigation.

In this paper we shall discuss our work with safflower oil in processing a long oil alkyd, a short oil alkyd, and a maleic-pentaerythritol combination. Although we used bleached oil in the reported work, it was observed that unbleached oil gave similar products with respect to processing, color, and drying.

Two sources of the safflower oil gave the following analyses, which are compared to linseed and soybean oils. These analyses of the safflower oil can be questioned as other sources have reported that examinations of a number of varieties of safflower oil have

shown that less than 0.1% of linolenic acid is present.

TABLE I
Fatty Acids Content of Safflower, Soybean, and Linseed Oils

Fatty Acids	Safflower 1 (3)	Safflower 2 (4)	Soybean (5)	Linseed (5)
Linoleic.....	72.0	72.3	51.2	19.5
Linolenic.....	1.0	1.7	5.4	50.8
Oleic.....	20.0	19.3	30.2	20.1
Saturated acids.....	7.0	6.7	13.2	9.6

Referring to the unsaturated acid content of the analyses in Table I, one would conclude that linseed dries fastest, safflower somewhat slower, and soya very slowly. Similarly, according to some rules for color retention, linolenic acid contributes to yellowing, hence linseed, soya, and safflower should be rated thus in the order of increasing color stability. Later we shall amplify this latter conclusion. The data presented are from preliminary investigations of safflower oil, and before concrete conclusions are drawn, additional work with a variety of resin formulations should be made.

Since fatty acids of safflower are commercially unavailable, alcoholysis or preparation of monoglycerides will be essential for alkyd resin processing. With soya, safflower, and linseed this is usually accomplished by heating approximately 80 parts of oil with 20 parts of glycerine or pentaerythritol at temperatures of 450-480°F. in the presence of reagent grade calcium hydroxide or litharge. Inert gas and efficient agitation insure good color and fast reaction. For example (1), 170 parts of oil were heated to 480°F., using blanket CO₂ and 600 peripheral feet per minute agitation. At 480° F. 19 parts of pentaerythritol, technical grade, and 0.0362 parts of reagent grade calcium hydroxide were charged. The pentaerythritol crusted around the top of the flask until the first stage of alcoholysis occurred, when it became soluble in the hot oil. Then 19 additional parts of pentaerythritol, technical, were added, and the oil mixture held at 480°F. for a clearness test in methanol (1-3).

These reaction times were observed:

TABLE II
Time for Alcoholysis of Soybean and Safflower Oil With Pentaerythritol

	First Stage	Second Stage (Alcoholysis Complete)
Soybean.....	24 minutes	43 minutes
Safflower.....	15 minutes	30 minutes

In another type of alcoholysis reaction (example 2) 94.5 parts of oil, 23.6 parts of glycerine, and 0.054 parts of reagent grade calcium hydroxide were heated to 450°F. and held at this temperature for a methanol alcohol test of 4 to 1. For comparative purposes litharge (0.1% lead based on the glycerine) was included with a linseed oil run.

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TABLE III
Time for Alcoholysis of Soybean, Safflower, and
Linseed Oil With Glycerine

Soybean Ca(OH) ₂	15 minutes
Safflower Ca(OH) ₂	6 minutes
Linseed Ca(OH) ₂	13 minutes
Linseed (PbO).....	25 minutes

In both examples it was determined that safflower converted to monoglycerides more rapidly than either soybean or linseed oil.

A common alkyd resin for architectural finishes contains approximately 63% oil, 25% phthalic anhydride, and 12% pentaerythritol. To produce this resin 70.5 parts of phthalic anhydride are added to the alcoholysis product of example (1). After processing continued for 10 minutes at 480°F., 0.78 cc. of the triphenyl phosphite were charged to effect removal of the haze due to calcium phthalate formed in the resin. The data below represents reaction rates at 480°F., agitation 600 peripheral feet per minute, and carbon dioxide sweep at 0.04 cu. ft. a minute per gallon of solids:

TABLE IV
Reaction Rates of 63% Safflower and Soya Alkyds

	60 min.		120 min.	
	Safflower	Soya	Safflower	Soya
Viscosity (70% solids in mineral spirits).....	Q	Q	T	S-T
Acid Number (solids).....	19	19	9.2	7.4
	180 min.		260 min.	
	Safflower	Soya	Safflower	Soya
Viscosity (70% solids in mineral spirits).....	U-V	U-V	W	W
Acid Number (solids).....	3.9	3.3	3.3	3.1

One can conclude that no apparent difference exists in reaction rates of the processing of long oil alkyds of either soya or safflower. The difference in color was a Gardner value of 3 for safflower and 4 for soya. Each resin, reduced to 50% solids with mineral spirits, received 0.5% Pb, 0.05% Co, or 0.05% Co as driers, and were aged 36 hours. Drying tests certainly strengthen the conclusion that safflower alkyds dry faster than soya alkyds.

TABLE V
Drying Times of 63% Modified Alkyd Resins

Alkyd	Series 1 (.5% Pb, .05% Co)		Series 2 (.05% Co)	
	Set-to-touch	Tack Free	Set-to-touch	Tack Free
Safflower	123 minutes	173 minutes	128 minutes	193 minutes
Soybean	143 minutes	273 minutes	173 minutes	310 minutes

In the preparation of short oil alkyds, excess glycerine is useful in holding body of the cook to make possible alkyds of low acid values. Benzoic acid, or Benthall, a technical grade of benzoic acid, also accomplishes this useful purpose, with less disadvantage in respect to water resistance than would be encountered with the excess glycerine. Safflower oil was compared to soybean and linseed oils in a series of alkyds with the following raw materials:

Oil (soya, safflower or linseed).....	33.0%
Glycerine (98%).....	21.8
Phthalic anhydride.....	39.4
Benthall (technical Benzoic Acid).....	5.8
	100.0%

Previously, in example (2), alcoholysis with glycerine was discussed. This example applied to the above batch. After an alcoholysis test of 4 parts methanol to 1 part hot oil, the balance of the glycerine, phthalic anhydride, and Benthall was charged. Processing conditions consisted of agitation at 600 peripheral feet per minute and carbon dioxide sweep at the rate of 0.04 cubic feet per minute per gallon of resin. Temperature was held at 430°F. After the batch was held at 430°F. for 10 minutes, 0.221 parts of triphenyl phosphite per 100 parts of raw material were charged. This represents 25 times the weight of the calcium metal used in the alcoholysis catalyst. Products of excellent clarity, without filtration, and improved color result from the use of triphenyl phosphite. Reaction rates for processing at 430°F. are tabulated below:

TABLE VI
Reaction Rates of 33% Safflower, Soya, and
Linseed Alkyds

Alkyd	Time (Min.)	Acid No.	Viscosity (46% Solids in Xylene)	Color
Safflower.....	150	9	T-U	3
Soya.....	120	15	V	5
Linseed.....	110	17	T	5-6

The comparison between the soya and linseed could be expected, but it could not be predicted that such a short oil alkyd containing safflower would process to an acid value of 9. Further checks with oils from other sources are indicated. The color of the safflower alkyd was excellent. Upon examining the hardness of films of this short alkyd baked on glass plates at 300°F. for one-half hour, the following Sward Hardness readings were made:

TABLE VII
Sward Hardness of 33% Alkyds Baked 300°F.
for One-Half Hour

Linseed.....	42
Safflower.....	37
Soybean.....	33

Drying tests made with 0.5% Pb and 0.05% Co reaffirms the conclusion that safflower alkyds dry faster than soybean and slower than linseed resins. No particular difficulty was encountered with pigment wettability when a 50-50 TiO₂, rutile-resin solids enamel was milled. These enamels were baked on steel plates and examined for gloss and yellowing characteristics. Of course, the linseed oil enamel yellowed considerably. One would find it difficult however to choose between a film of the safflower and the soya enamel for better original gloss and whiteness. Examination of the films after baking 4 hours at 300°F. emphasized that there is little to choose between these oils when desiring excellent alkyds for color and gloss retention.

Moore suggests that yellowing of films is caused not only by linolenic acid content of oils but by linoleic as well (6). Linolenic is rated five times as heavily as the linoleic. The degree of yellowing can be measured by tri-stimulus readings on a Hunter Multi-Purpose Reflectometer with the usual green, blue, and amber filters and by using the following equation:

$$Y = A(L_1 + 5L_2) + B$$

Y = Degree of yellowing

L_1 = Linoleic acid as fraction of total

L_2 = Linolenic acid as fraction of total

A = Constant for the amber filter

B = Constant for the blue filter

Substituting the appropriate values as given in the typical fatty acid analyses of safflower and soybean oil, Table I, for soybean oil, $Y = A(.782) + B$, safflower No. 1, $Y = A(.770) + B$, safflower No. 2, $Y = A(.808) + B$, and for linseed, $Y = A(2.74) + B$. Theoretically, safflower should be as good as soya for the non-yellowing paints. Examination of the baked films after storage in a dark place for six months supports the conclusion that safflower alkyds yellow almost as much as soya resins.

TABLE VIII
Properties of Maleic Treated Oils

	Soybean Maleic Oil	Safflower Maleic Oil
Acid Number.....	7	8
Viscosity (100% Solids).....	J	K
Color.....	8	8

Clocker has described the reaction of drying and semidrying oils with maleic anhydride and pentaerythritol (7). For example, soybean oil can be reacted with 3 to 7% maleic anhydride, and esterified with pentaerythritol to produce an oil which performs like linseed in drying and durability properties. This oil displays better non-yellowing properties than linseed.

To determine whether safflower will react with maleic anhydride, 200 parts of the oil were processed with 10 parts of maleic anhydride for one hour at 480°F. Pentaerythritol, technical, 6.7 parts, were added and processing continued at 520°F. for one hour.

Agitation and inert gas continued throughout the entire reaction at rates previously indicated for the long oil alkyd batch. The similarity of the treated oils is evident from a study of viscosity, acid number, and color.

As with soybean maleic oils, safflower maleic oils have improved drying qualities. The oils were treated with 0.5% Pb and 0.05% Co, aged overnight, and films, .003 inch thick wet, were drawn on tin plates. Drying times were as follows:

TABLE IX
Drying Times of Maleated Oils

	Set-to-touch	6 Hours
Soya Maleic Oil.....	4 1/2 hours	Heavy tack
Safflower Maleic Oil.....	2 3/4 hours	Slight tack

To generalize, safflower oil can replace soybean oil in alkyd resin formulations or maleic oils. Alcoholysis rates are usually faster with safflower oil than with soybean or linseed oils. Reaction rate curves of time versus viscosity or acid number for alkyd resin processing will be quite similar for soya and safflower oils. Although the color of the alkyd from safflower will be better than from soya, color retention of films are about equal. Safflower oil alkyds and treated oils dry considerably faster than similar soya alkyds.

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REFERENCES

1. U. S. Dept. of Agriculture Circ. No. 366, Aug., 1935.
2. Amer. Paint J., 22, 44, Aug. 8, 1938, p. 7.
3. Private Comm., Petroleum Specialties Co., St. Louis, Mo.
4. Private Comm., Pacific Coast Chemical Co., San Francisco, Calif.
5. Laboratory Letters, Spencer Kellogg and Sons Inc., Buffalo, N. Y.
6. Paper presented at ACS meeting, Division of Paint, Varnish and Plastics Chemistry, Detroit, April, 1950.
7. U. S. Patent 2,188,882-890.

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Correlation of Vegetable Oil-Hexane Solution Vapor Pressures

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EQUIPMENT for desolventizing vegetable oil miscellas obtained by extraction with hydrocarbon solvents has been commonly over-designed. The absence of information on the performance of packed or tray stripping columns for this purpose and of equilibrium relationships for hydrocarbon-oil solutions have contributed to evident uncertainty in design. Even with previous knowledge of plant practice and experimentally determined vapor pressure data for oil solutions the situation is not greatly improved. Such information may have been obtained with a hydrocarbon solvent of unique specifications not necessarily characteristic of all commercial solvents or all shipments from the same source.

In order to eliminate the variable of solvent composition or specifications a method has been developed by which the vapor pressure characteristics of various commercial hydrocarbon solvents, or fractions of them, in oil solutions can be obtained from known data for one hydrocarbon solvent. The result is a

generalized set of data which can be used to compute vapor-liquid equilibria and enable operating conditions in desolventizing equipment to be altered to achieve optimum performance with different hydrocarbon solvents. The only information required, in addition to vapor pressure data for one solvent-oil system, is the normal bubble point of the solvent or solvent fraction. The method is developed in this paper and justified by the use of experimental vapor pressure data on commercial hexane and heptane solutions of soybean oil.

Viscosity, density, heat of solution (3), and vapor pressure data (8) indicate that solutions of hexane and soybean oil are not normal or ideal solutions. The actual pressure of hexane over soybean oil solutions is less than that calculated for an ideal solution; i.e., $p/PX < 1$ where p is the pressure over the solution, P is the vapor pressure of the pure solvent, and X is concentration. The difference, described as a negative deviation from ideal solution, is assumed