Safflower Oil Utilization in Surface Coatings[1]

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Abstract

The unique high linoleic acid content of 78% in safflower oil makes it especially suitable to the coatings industry. The high content of linoleic acid, low amount of saturated acids, and absence of linolenic acid constitutes an oil which forms fast-drying, nonyellowing films that have an excellent through dry and low wrinkling characteristics.

More safflower oil is utilized in the manufacture of alkyd resins than any other single nonedible use. The oil alcoholizes rapidly with polyols and heat-bleaches to very light colors in cooking the alkyd resins. These alkyds have the best combination of fast-drying and nonyellowing properties of any drying oil alkyd of equal oil content.

Heat-bodied safflower oil has uniform polymer structure as shown by its viscosity reduction curves. Heat-bodied and low viscosity safflower oils are used in exterior house paints. These paints show good through dry, low wrinkling and resistance to dew flatting.

Specialty uses for safflower oil include urethane resins, caulks and putties, linoleum and oil emulsion exterior house paints.

Introduction

Historically speaking, there is not too much to be found in the technical literature describing the first use of safflower oil in protective coatings. The literature is vague and safflower oil, when mentioned, is usually listed among other oils as alternatives or equivalents for any one given product. This is especially true in the patent literature.

Thurmond, Hempel and Marling (1) are possibly the first to have reported on the application of safflower oil in alkyd coating resins. Their exploratory work in 1951 established that safflower oil alkyd resins dried faster than their soybean oil counterparts and somewhat slower than linseed oil resins. But they retained excellent nonyellowing properties on film aging. Also, safflower oil was shown to be faster in alcoholysis than the other two oils, a distinct technical advantage.

The first contact the senior author had with safflower oil dates back to about 1935 or 1936. At that time the problem was to prepare an improved nonyellowing alkyd resin. A literature search with respect to oil composition showed that safflower oil had the ideal composition for this purpose. At that time the entire national output was purchased. This was about 4½ drums or about 250 gallons. In spite of this limited supply, in the period 1937–40, and a doubtful continued production for this oil, alkyd resins were prepared and evaluated.

At the present time the story is quite different. Safflower oil, because of its continued good performance in the surface coatings, has attracted more consumers. Protective coatings incorporating safflower oil exhibit good initial and excellent through dry, good gloss and gloss retention, excellent initial color with minimum after-yellowing, low tendency to wrinkle, good outside durability and uniform polymers giving good film flexibility. Its excellent color and heat-bleachability characteristics enable safflower oil to be used wherever light-colored end products are required.

Discussion

Safflower oil, because of these properties, enjoys its largest use in alkyd resins. There appears to be no other oil used today in alkyd resin technology which equals the rapid and good through dry, nonyellowing and color retention of those prepared from safflower oil. These alkyd resins as simple oil and copolymer types with styrene, other vinyls, and acrylic compounds have a rather large range of composition and a wide range of applications.

With respect to the use of drying oils in coating compositions, developments with safflower oil have kept abreast of the changing times. This implies that safflower oil is also used in water-thinned systems as a house paint vehicle.

In order to understand better the performance and use of safflower oil, how these uses and product performance are related to its composition and why it has been widely accepted, a comparison of the component acids of all the oils commonly used in the coatings industry must be considered. Table I shows the composition of the important coating oils. The property of any coating oil composition is a function of the predominating fatty acid with respect to both type and the amount.

Linseed oil, which is still the "workhorse" of the industry, is high in linolenic acid. This acid is found in negligible amounts in other oils listed in Table I. In soybean, dehydrated castor and safflower oils linoleic acid predominates. Consequently, it would be expected that the properties of these oils are a function of the amount of linoleic acid present in each.

Since soybean oil contains the lowest amount of linoleic acid, it has weak properties when compared to both dehydrated castor and safflower oils.

Dehydrated castor oil came into the market in the late 1930's and has been widely accepted for use in alkyd resins. In this oil, the linoleic acid and its conjugated isomer, 9, 11 octadecadienoic acid, predominate. Because of the conjugated system in the dehydrated castor oil, some of its properties are quite different from those of unprocessed safflower oil although the combined amount of dienoic acid is only about 10% greater than that in safflower oil. But here cost enters the picture. Safflower oil is cheaper at the present time than the dehydrated castor oil.

Linseed oil exhibits a good through dry, but it has the weakness of after-yellowing on aging, especially in the dark or in diffused light. This limits the use of linseed oil largely to products for outside exposure. In inside exposure, linseed products are unsatisfactory. Soybean oil has quite good nonyellowing properties but overall film characteristics are not as good as desired. Dehydrated castor oil dries to a good film which is nonyellowing. However, unless

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TABLE I

Component Fatty Acids in Ois Used in Coating Composition

	Per cent acid in			
	Linseed (6)	Safflower (8)	Soybean (6)	Dehydrated castor (7)
Linolenic	52.0	0.0	9.0	......
Linoleic	16.0	78.0	51.0	65.0
Conjugated[a]	.....	.....	......	22.0
Oleic	22.0	13.0	25.0	7.5
Saturates[b]	10.0	9.0	15.0	0.5
Hydroxy acids	......	......	......	5.0

[a] 9,11 Octadecadienoic acid.

[b] Comprises, myristic, palmitic, stearic, archidic acids, and small amounts of other mono- enoic acids.

TABLE III

Dilution Characteristics of Linseed and Safflower Oils

	Viscosities in stokes	
Oil	Base oil	75% NV[a]
Safflower	4.57	.60
	14.50	1.34
	24.10	1.93
	38.70	2.81
	220.00	10.70
Linseed	4.50	.58
	15.30	1.28
	39.60	2.40
	148.00	6.80

[a] Mineral spirits KB = 39.

carefully processed it shows syneresis or after-tack on aging about one week and it may wrinkle or "gas-check" in a foul atmosphere.

Safflower oil does not exhibit after-yellowing, it dries to a good film, does not exhibit an after-tack on aging, and does not "gas-check."

It would therefore be concluded that safflower oil has the best composition for coating products. It possesses the good properties of the oils in Table I without their disadvantages.

Heat Polymerized Safflower Oil

Heat-bodied safflower oils are similar to their linseed oil counterparts with respect to drying time, color, pigment wetting and leveling characteristics. Rhoades and DaValle (2) show data on bodying safflower oil at 302C, 307C and 310C. The curves obtained from these data are not unlike those which are obtained for linseed oil and soybean oil.

Table II shows the comparative dry times of several unbodied and bodied oils with the same trimetal drier concentration. In all cases the bodied oils dry faster than the unbodied oils.

Table III and Figure 1 show viscosity dilution characteristics in various solvents. In Table III the viscosity of various oils before and after reduction to 75% nonvolatile is listed. These data are based on the observations of Prane (3). A comparison of linseed and safflower oils shows that above a viscosity of about 40 poises, the linseed oil suffers the greater viscosity reduction when diluted to 75% nonvolatile. In regular and aromatic mineral spirits the dilution characteristics are much the same. However, at low nonvolatile both oils appear quite similar, but above 20–25% dilution the safflower oil shows the higher viscosity. In the case of odorless spirits the trend is reversed at about 40% nonvolatile.

These properties are useful in the formulation of safflower-oil-based sealers and interior finishes where a high viscosity at low solids is desired.

The reasons for these trends are not clearly understood. A possible explanation for this might rest in the fact that bodied safflower oil has a more uniform composition than bodied linseed oil. Hence, there may be better solvation. This might be expected because of the difference in structure of the linolenic and linoleic acids. The larger molecules no doubt become solvated by the breakdown products and upon dilution with aromatic or regular mineral spirits the large structures are desolvated and viscosity drops. Odorless spirits is a very poor solvent and is not sufficiently strong to desolvate. Rather, there is evidence for a reverse effect since this solvent may solvate with the large oil molecules.

TABLE II

Comparative Dry Times[a]

Dehydrated castor oil G–H	6:00 Hours
Nonbreak safflower	6:20 Hours
Isomerized safflower	2:40 Hours
V.M. linseed oil	4:30 Hours
Nonbreak soybean	8:00 Hours
Dehydrated castor oil Z_3	1:50 Hours
Safflower Z_2	3:20 Hours
Isomerized safflower Z_3	2:45 Hours
Linseed oil Z_2	3:45 Hours

[a] Based on .24% Pb, .03% Co, .015% Mn.

The molecular weights of bodied oils have always been a question. The early work of Mattiello (4) indicates that bodied oils probably had molecular weights in the neighborhood of not over 2,500 even at a viscosity of 278 stokes (weight average). Since the Mattiello publication many improvements have been made in the study of molecular weights. A recent technique (unpublished) in which linseed and safflower oils were compared shows that the polymer of an oil with a viscosity of about 75 stokes has a molecular weight probably not over 5,000 or 5,500 (weight average).

These measurements were based on gel permeation chromatography. By a series of differential refractive index measurements it has been shown that the main fraction in both bodied linseed and safflower oils are of a molecular weight of about 5,500. In addition, a rather large quantity of unbodied oil, molecular weight of around 900, and breakdown products of molecular weights of less than 600 are present. Both safflower and linseed oil are identical in this respect.

While such data may be identical as far as molecular weights are concerned, they do not take into account the polarity of degradation products and low molecular weight polymer molecules. This does not necessarily explain the difference between the faster dilution characteristics of bodied linseed and safflower oil in Table III.

With respect to paint performance it has always been felt that a binder with a uniform molecular size has the tendency to give better flow characteristics and also a more uniform film structure. This seems to be reflected in house paints. From a tech-

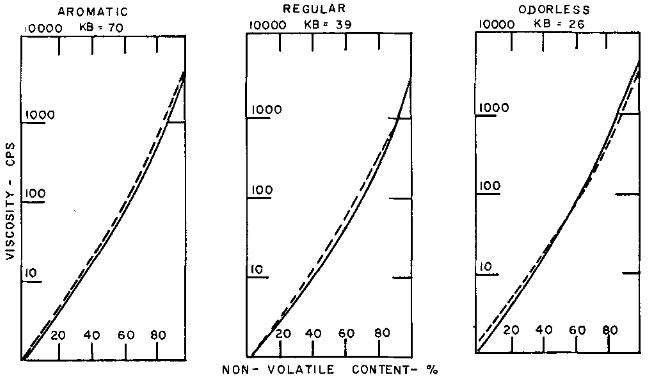

FIG. 1. Solvent reduction of Z_2 viscosity bodied safflower and linseed oils in several mineral spirits.

nical point of view, the heat-bodied safflower oil blended with a lower viscosity oil can be formulated into an ideal exterior house paint which shows durability characteristics equal to those manifested by corresponding linseed-based formulations.

As might be expected, from the data shown on Table I, the drying characteristics of both safflower and linseed oil need not necessarily be the same. It would appear that the higher functionality of the linolenic acid in linseed oil would have a tendency to make a product skin dry more than it would through dry. Although thas can be controlled with driers, it is felt that the drying of safflower oil proceeds more via polymerization following the preliminary oxidation reaction. It would also appear that there would be less tendency for the oil surface to skin dry in the case of safflower oil than in the case of linseed oil. Thus, wrinkling, since this is a surface phenonomon, would be essentially eliminated in safflower-oil-based paints.

Some years ago a great amount of work was undertaken to evaluate catalysts to reduce the oil bodying times, especially as applied to linseed oil. Safflower oil responds to the same catalysts and its cooking time may also be reduced.

A recent improvement has been the preparation of an isomerized safflower oil. An oil of this type may contain between 18% and 21% of a conjugated isomer of linoleic acid. This oil is similar in some respects to dehydrated castor oil. As expected, the properties conveyed to the final products by the conjugated structure are quite beneficial. This means that lower kettling time, lower cooking temperatures, and shorter equipment hold-up time are possible. The isomerized oil will body about 20% faster than the regular alkali refined safflower oil.

Evaluation of Safflower Oils in Paints

No attempt is made to give any paint formulations showing how the heat-bodied safflower and unbodied safflower oils may be used. However, several properties with respect to safflower-oil-based paints are worthy of mention, the most important of which is the nonyellowing property. Exterior house paints based on this oil remain essentially white as compared to color changes in linseed oil paints, which show a marked increase in yellowing where exposed in darker areas, e.g., under eaves.

There have been many studies of the gloss change of linseed and safflower house paint films on aging. These studies show that safflower oil can have less tendency to wet pigments than linseed oil. In this case the safflower paints may lose gloss faster than linseed oil. However, when the paints are made with equal pigment wetting, the gloss retention of safflower paints can be greater than linseed paints. One such example is shown in Figure 2 using Federal Specification TTP 103 type pigmentation.

Safflower oil has less tendency to wrinkle than linseed oil. An explanation for this might again be reflected by reinspection of Table I, showing the compositions of these two oils. The oxidation apparently takes place faster on the linolenic moiety of the linseed oil than on the corresponding higher concentration of linoleic moiety in the safflower oil. Thus, a skin or oxidized layer tends to form on a linseed oil film where safflower tends to oxidize throughout the film. Wrinkling is associated with early skin formation of a drying film.

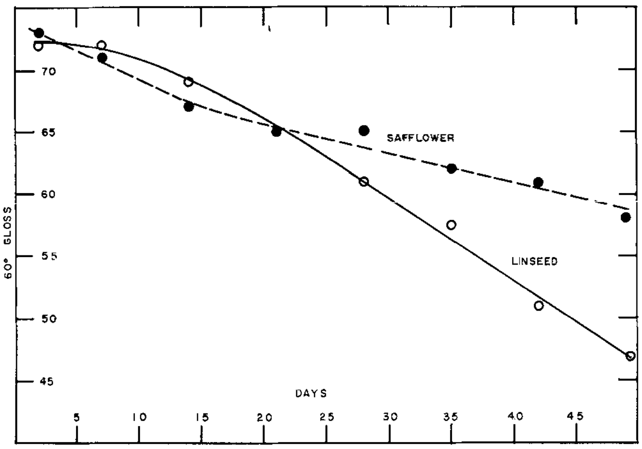

FIG. 2. This chart shows 60° gloss readings TTP 103 type white house paints based on safflower and linseed oils.

There is a related effect in which house paints sometimes lose gloss when freshly applied during late afternoon hours at a time when dew or fog is prevalent. This phenomenon, known as "dew flatting," is less pronounced in safflower paints than in linseed paints. Studies show that linseed films form a skin quickly which takes the permanent pattern of the tiny water droplets on the paint surface. Safflower films which do not skin dry rapidly are more pliable during the time the water drops are on the surface and may flow out to a smooth surface after the water has evaporated in the morning.

Safflower Oil Alkyds

Safflower oil is especially valuable in long- to medium-length alkyds where oil structure predominates. These are used in interior and exterior enamels and also in flat interior paints. In this case, their fast air dry and nonyellowing in the interior types is well known and of a definite advantage.

Of the few references in the literature on comparative data of alkyd properties, the work of DeSesa

TABLE IV

Properties, Performance Characteristics and Composition of Alkyd Resins (4)

		Modifying oil				
		Tall oil fatty acids	Soy-bean oil	Men-haden oil	Saf-flower oil	Lin-seed oil
Composition						
Oil or fatty acid	g	760	797	797	797	797
Litharge	g	...	0.4	0.4	0.4	0.4
Glyceride 99%	g	83.8	......	......	......	......
Penthaerythritol	g	225	225	225	225	225
Phthalic anhydride	g	346	346	346	346	346
The above compositions yielded a 60% oil, 26.2% phthalic anhydride, pentaerythritol alkyd composition in the final resin.						
Resin Solution						
N.V.		69.4	69.0	70.3	69.8	69.7
Solvent		M.S.	M.S.	Super high flash naphtha	M.S.	M.S.
Visc.		Z–Z_1	Z	Z_1	Z–Z_1	Z–Z_1
Color		4–5	6–7	8	6–	6–7
Cure[a]		96	94	18	55	30
A.N.		2.7	8.5	7.7	7.2	7.4
Wt/gal. (lb)		8.01	8.05	8.41	8.03	8.03
Performance						
Drying (hr)	Set	1⅙	5¾	1⅔	3¾	2¾
	Dust-free	12	12	7½	11	10
	Tack-free	30	30	16	30	27
123-hr hardness		4	6	16	6	7
Boiling water resistance[b]		G	G	G	G	Ex
2% NaOH resistance[b]		F	F	G	G	G

[a] Cure is derived by amount of time in seconds for a tiny drop of resin to gel on a hot plate at 200F constant temperature.

[b] F = Fair, G = Good, Ex = Excellent.

(5) shows safflower oil alkyds compared with alkyds of other oils exactly the same oil length and phthalic content. These data are shown in Table IV.

It can be seen that when safflower is compared to other vegetable oils in these alkyds that drying properties and chemical resistance properties of the films are intermediate between soy and linseed oil alkyds.

The present trends in safflower oil based alkyds is to use the conjugated isomer. The presence of the conjugated structure makes it very easy to produce copolymers with vinyl and acrylic monomers which have heretofore been difficult to prepare. These particular monomers generally are not very reactive with isolated double bonds such as one finds in natural oils, especially of the *cis* structure. With conjugated systems the reactivity ratio of the diene in the fatty acid moiety and the above-mentioned monomers is such that the reaction can proceed without too much difficulty.

These vehicles today are made from medium to long oil alkyd resins which are then reacted with the vinyl monomers such as styrene, vinyl toluene, and methacrylates.

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