

TABLE I
Best Crystallizations of Indian Beef Tallow Fatty Acids from Aqueous Ethanol at Various Temperatures

Temp., °C.	Ethanol concn., % wt.	S/A ratio	Precipitated acids P			Soluble acids S		
			%	I.V.	% unsatd. acids present, Ol.	%	I.V.	% satd. acids present, St.
20.....	70	3.5 ^a	63.6	14.5	9.1	36.4	75.7	9.2
10.....	75	4 ^a	65.8	11.9	7.8	34.2	85.9	5.2
6.....	80	5	65.8	10.4	6.8	34.2	85.2	5.5
-5.....	{ 80	5	70.3	10.9	7.6	29.7	95.1	1.8
	{ 85	5	67.9	10.5	7.0	32.1	88.6	4.0
-12.5.....	{ 85	10	69.7	11.0	7.6	30.3	93.5	2.3
	{ 90	5	68.7	10.3	7.0	31.3	88.5	4.0

^a External solvent needed for filtration.

as an entity. There is a wider graphical spread of the descending lines at higher temperatures. Hence the lowering of solubility of the precipitated acids is more marked at higher temperatures and for stronger ethanols as the S/A ratio increases. Solubilities of saturated acids are affected more strongly by aqueous dilution than those of unsaturated acids. As ethanol is diluted, higher S/A ratios are necessary to obtain discrete filterable crystals.

Optimum separations are judged by a maximum yield of precipitated acids of minimum I.V. and a concurrent maximum of soluble acids of maximum I.V. In practice, the sum of unsaturated acids in the precipitate and saturated acids in the solubles, *i.e.*, Ol. + St., should be a minimum. From Table I the separation at -5°C . with 80% ethanol and S/A ratio 5 is very similar to that at -12.5°C . with 85% ethanol and S/A ratio 10. The possibility of filtration difficulties in the first set of conditions would make the second the optimum conditions of choice.

Assessment. Ethanol crystallization can yield from Indian tallows products similar in purity (but varying in relative proportions) from those obtained from American tallows by the Emersol process, using 90% methanol, -12°C ., and an S/A ratio of 4, *viz.*, precipitated acids of I.V. 7-15 and soluble acids of I.V. *ca.* 104. The higher solubility of fatty acids in ethanol necessitates the use of a more dilute solvent. The higher total saturated acid content of Indian tallows requires a higher S/A ratio and yields soluble acids lower in I.V. by *ca.* 10 units. The temperature of crystallization is the same in both systems. Toxic hazards involved in the use of methanol are eliminated with ethanol.

Practical Considerations. The actual choice of commercial conditions will, of course, be governed by economic considerations, for which pilot-plant work is necessary. Since the crystallization is single-stage,

it is adaptable to continuous operation. Aqueous ethanol corrodes steel equipment, and metallic contamination discolors fatty acids by salt formation, hence stainless steel equipment would be necessary. Ester formation during ethanol removal can be overcome by proper equipment design. Indian tallow, lacking a parent meat-packing industry, is not yet an industrial commodity. Until it is, imported tallows will have to be used. Alternately the controlled hydrogenation of suitable vegetable oils to yield mainly palmitic-stearic-oleic mixtures can be considered. Such work is in progress.

Summary

Crystallization of Indian beef tallow fatty acids (total saturated acid content 64.3% by wt.) from six dilutions of ethanol (95 to 70%) at five temperatures (20° to -12.5°C .) and at six solvent/acid ratios (2.5 to 20) was systematically studied. Optimum conditions of choice would use 85% ethanol at -12.5°C . at a solvent/acid ratio to 10 to give 69.7% precipitated acids, I.V. 11.0, and 30.3% soluble acids, I.V. 93.5. Other conditions of a similar order are possible. The comparatively saturated character of Indian beef tallows and the use of ethanol cause a departure from the Emersol process operating conditions using methanol, which is designed for American tallows. Considerations bearing on large-scale application are discussed.

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Epoxidized Jojoba Oil as a Stabilizer for Vinyl Chloride Containing Plastics

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JOJOBA (*Simmondsia chinensis*) may become of economic significance as a crop for the southwestern area of the United States. The seed of the plant contains about 50% of an oil having potential industrial importance. Jojoba oil can serve not only as a

direct replacement for sperm whale oil but also as a raw material for chemical modification. Sulfurization of the oil produces a superior high pressure lubricant additive, and the hard wax obtained on hydrogenation of the oil can serve well in polishing wax formulations (1).

Jojoba oil is unusual among vegetable oils in that

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it reportedly contains no glycerides and is essentially a liquid wax composed principally of eicosenol, 13-docosenol, docosenoic acid, and 11-eicosenoic acid (2, 3). The double bonds of eicosenol and docosenoic acid are thought to be located in the 11 and 13 positions, respectively (4). Since jojoba oil contains monounsaturations in both its acid and alcohol moieties, epoxidation of the oil would result in the formation of a unique product. Epoxides of unsaturated glycerides and of simple fatty acid esters are currently being employed as plasticizers and stabilizers for vinyl chloride containing plastics. Recently attention has been directed to the stabilizer properties of epoxidized synthetic polyol esters (5). Epoxidized jojoba oil has been intercompared with these three classes of materials and found to be an effective stabilizer.

Experimental

MATERIALS

Epoxidized Butyl Oleate. This material (I.V., 30.4), which was of commercial origin, had an oxirane oxygen content of 4.0%.

Epoxidized Soybean Oil. The product (I.V., 4.8) was obtained from a commercial source and had an oxidant oxygen content of 5.9%.

Epoxidized Ethylene Glycol Dioleate. A toluene solution containing oleic acid (2.2 moles), ethylene glycol (1.0 mole), and *para*-toluene sulfonic acid (0.025 mole) was refluxed until the theoretical amount of water had been evolved. The recovered acid-free diester (I.V., 82.1) was epoxidized with a 10% excess of perbenzoic acid solution at 5°C. The recovered reaction product (I.V., 0.2) contained 4.7% oxirane oxygen.

Epoxidized Jojoba Oil. A sample of jojoba oil (I.V., 83.4; S. E., 90.0) containing 1.0 equivalent of ethylenic bond was dissolved in chloroform (1 g.: 5 ml.) and maintained at 20°C. during the dropwise addition of peracetic acid (1.1 mole) in acetic acid solution (2 g.:3 g.). The epoxidized oil (I.V., 5.0; m.r., 44-50°C.), isolated in the usual manner, contained 4.1% of oxirane oxygen (calculated maximum 5.0%).

Stabilizer Screening. Two basic formulations were employed in the screening of these epoxides for their stabilizing characteristics with vinyl chloride-vinyl acetate copolymer. In one, 30 parts of plasticizer and 5 parts of the epoxide were utilized while, in the second, an amount of epoxide equivalent to 5 parts of a 5% oxirane-containing material was employed. The plasticizer was adjusted so that the total of epoxide stabilizer and plasticizer would be 35 parts. These will hereafter be referred to as formulations I and II. Both tricresyl phosphate (TCP) and di-2-ethylhexyl phthalate (DOP) were used as the primary plasticizers in formulation I. In formulation II, only TCP was employed as a primary plasticizer because its greater sensitivity to thermal and ultraviolet exposure would offer the more critical test of the relative stabilizing effectiveness of the epoxides.

The over-all formulation used was:

Resin (Vinylite VYDR) ²	63.5%
Plasticizer or plasticizer-stabilizer combination	35.0%
Stearic acid	0.5%
Basic lead carbonate.....	1.0%

All formulations were milled and molded at 310°F.

The ultraviolet stabilization characteristics were determined on 20 mil sheets in accordance with A.S.T.M. test D822-46T.

Relative heat stabilities were determined by observing color changes in the 20 mil sheets, as measured on a "Hunter Multipurpose Reflectometer,"² using the amber 45°, 0° directional reflectance, at intervals during a 2-hr. exposure to a temperature of 176°C. (350°F.) in a forced draft oven.

The detailed procedure followed in other test operations as well as the preparation of the test specimens has been described previously (6).

Results and Discussion

A preliminary investigation had shown that neither the epoxides of jojoba oil nor epoxidized glycol dioleate were usable as primary plasticizers because of their poor compatibility characteristics with vinyl copolymer. They are however adequately compatible at concentrations of 5% in combination with such primary plasticizers as DOP or TCP. When employed at this level (formulation I), the epoxide of jojoba oil has no adverse effects on the physical characteristics of the DOP or TCP plasticized stock. In fact, as can be seen from Table I, incorporation of 5% epoxidized jojoba oil with TCP results in an improve-

² It is not the policy of the Department to recommend the products of one company over those of any others engaged in the same business.

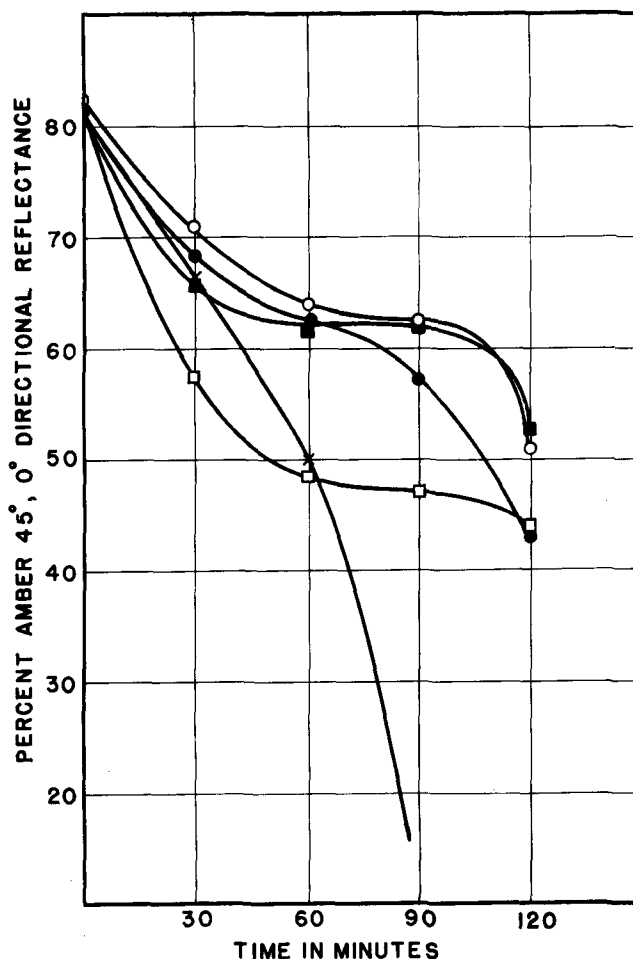


Fig. 1. Reflectance values of DOP formulations I containing 5 parts of (O) epoxidized jojoba oil, (●) epoxidized glycol dioleate, (□) butyl epoxystearate, (■) epoxidized soybean oil, (X) control vs. exposure to 350°F.

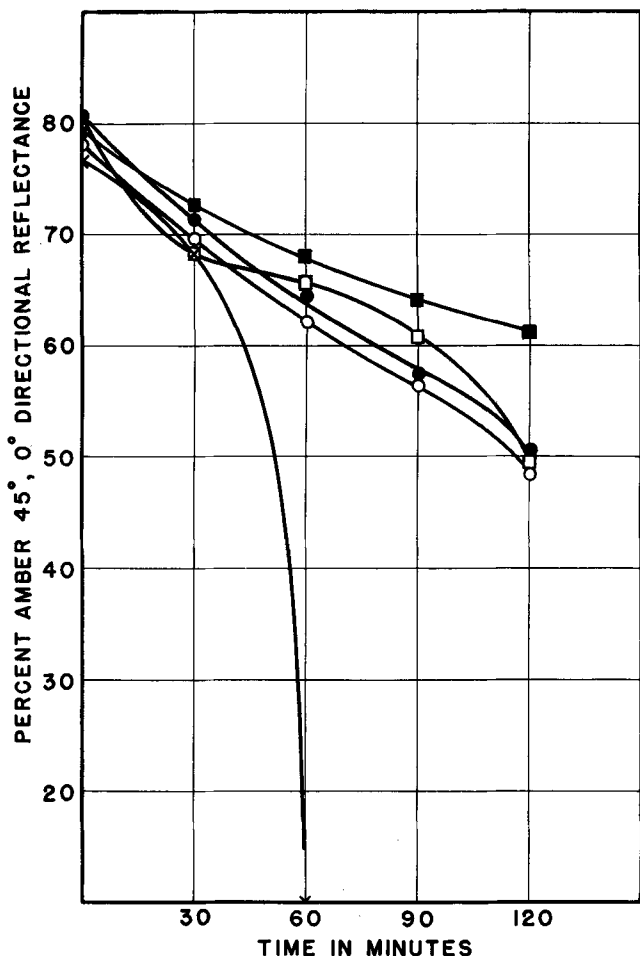


FIG. 2. Reflectance values of TCP formulations I containing 5 parts of (○) epoxidized jojoba oil, (●) epoxidized glycol dioleate, (□) butyl epoxystearate, (■) epoxidized soybean oil, (x) control vs. exposure to 350°F.

ment of modulus and low-temperature performance of the stock.

The results of the thermal stability tests of the various epoxides in formulation I are shown in Figures 1 and 2 for DOP and TCP, respectively. Figure 3 represents the results obtained from formulation II, employing TCP.

These results show that, with the exception of the TCP combination in formulation I, epoxidized jojoba oil gives stabilization comparable to that of epoxidized soybean oil and is superior to the other epoxides in two instances (Figures 1 and 3) and comparable to them in the other instance. In contrast to the unstabilized control formulations which are badly degraded after 1 hr. for TCP combinations and 1½ hours for DOP, as indicated by a total loss

TABLE I
Physical Characteristics of Stabilized, Plasticized Vinyl Copolymer Stock

Plasticizer 35%	Tensile strength, p.s.i.	100% modulus, p.s.i.	Elongation, %	Brittle point, °C.	Volatility, % loss ^a
Epoxidized jojoba oil-DOP (1 to 6)	2980	1620	320	-35	0.90
Epoxidized jojoba oil-TCP (1 to 6)	3400	2080	260	-9	0.40
DOP control	3040	1590	340	-33	0.90
TCP control	3500	2280	270	0	0.30

^a ASTM D1203 on 14-18 mil sheets.

of reflectance, the formulations stabilized with the epoxide of jojoba oil still retain from 62 to 74% of their original reflectance.

In formulations of type I employing DOP, butyl epoxystearate was not as effective an ultraviolet stabilizer as the other epoxides, showing localized discoloration after 200 hrs. of exposure. This formulation, stabilized with the epoxides of jojoba oil, soybean oil, or glycol dioleate, was unaffected during this same exposure period. These three specimens did show moderate failure at 300 hrs. The degree was somewhat less in the specimens stabilized with epoxidized jojoba or soybean oil than in the case of the epoxidized glycol dioleate. The unstabilized DOP plasticized specimen exhibited slight failure, evidenced by the development of yellow spotting, at 100 hrs.

Ultraviolet stabilization of TCP plasticized specimens was measured in formulation II only. All of these specimens showed moderate failure after 100 hrs. of exposure. The epoxidized jojoba oil stabilized specimen however, while not any better colorwise, was the only one which did not develop surface tackiness. The unstabilized TCP plasticized specimens showed moderate failure after 50 hrs. and failed completely after 100 hrs.

Based upon these observations, it appears that

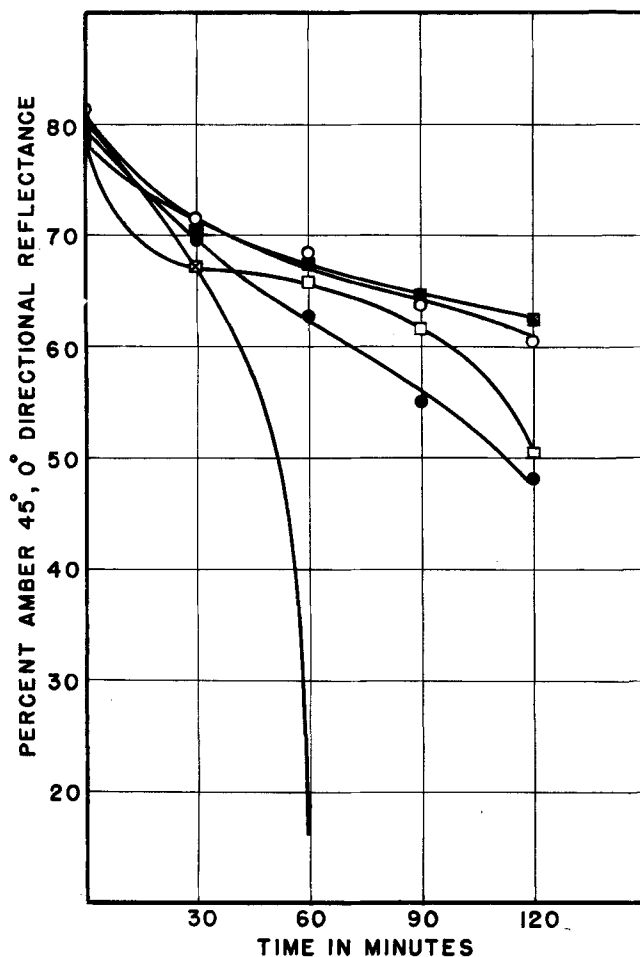


FIG. 3. Reflectance values of TCP formulations II containing an amount of epoxide equivalent to 5 parts of a 5% epoxy material, (○) epoxidized jojoba oil, (●) epoxidized glycol dioleate, (□) butyl epoxystearate (■) epoxidized soybean oil, (x) control vs. exposure to 350°F.

epoxidized jojoba oil is at least comparable and, in some instances, superior to other epoxides as a thermal or ultraviolet stabilizer and that it can be satisfactorily employed in DOP or TCP plasticized vinyl copolymer stock without adversely affecting other physical characteristics.

Summary

Epoxidized jojoba oil has been evaluated as a light and heat stabilizer for vinyl chloride containing plastics and its properties, intercompared with those of other epoxides representative of three major classes of oxirane stabilizers. The results obtained show that epoxidized jojoba oil is a satisfactory thermal and ultraviolet stabilizer for both TCP and DOP plasticized stocks and has no adverse effects on the plasticizer properties of these materials. In general, epoxi-

dized jojoba oil was found to be equivalent to or, in some instances, superior to the other epoxides tested.

Acknowledgment

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Laboratory Deodorizer with a Vaporization Efficiency of Unity

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VAPORIZATION efficiencies in plant deodorizers have been determined by Bailey (1), using fatty acids as model volatile substances. Bailey fully realized that the efficiency values so obtained were relative in nature and could be regarded as absolute only in the event that a given vegetable oil/fatty acid system behaved ideally in accordance with Raoult's Law. Such behavior in practical systems is however unusual.

Recent investigations (1a) carried out by the present author have established that, as a result of molecular association, the peanut oil/stearic acid system does, in fact, show a significant positive deviation from theory. The experimentally obtained vapor pressure data have enabled the absolute vaporization efficiency value to be determined and have formed the basis of investigations to establish the conditions necessary for achieving a vaporization efficiency of unity. Laboratory experiments relevant to this latter problem and a laboratory deodorizer having a vaporization efficiency of unity are described in this article.

Determination of Vaporization Efficiency

Vaporization efficiency can be determined by dissolving a model volatile substance of known vapor pressure in a refined oil and by steaming the solution with a specific amount of steam at specific pressure and temperature.

Provided that the solution behaves in accordance with Raoult's Law, vaporization efficiency values can be calculated by means of Bailey's equation, *viz.*:

$$E = \frac{PO}{SP_v} \ln \frac{V_1}{V_2}$$

in which S = moles steam; O = moles oil; P = absolute pressure; P_v = vapor pressure of the pure volatile substance and V_1 and V_2 = initial and final concentrations of the volatile substance in the oil, respectively. When "non-ideal" solutions are involved, activities have to be used in lieu of concentrations. Should the difference between initial and final concentrations be small, the activity coefficient (A) applicable to the

average concentration may be used. The formula is then:

$$E = \frac{PO}{SP_v A} \ln \frac{V_1}{V_2}$$

A fatty acid/vegetable oil system shows significant positive deviation from theory. The activity coefficients of solutions of stearic acid in peanut oil at 180°C. are shown in Figure 1. It will be seen that,

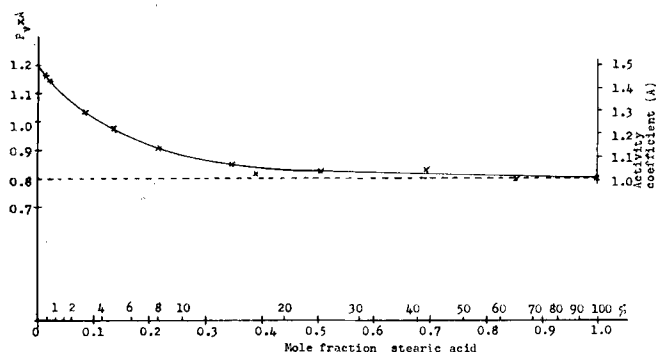


FIG. 1. Activity coefficients of stearic acid in peanut oil solutions.

at high acid concentrations, the deviations are small, but at low concentrations they are considerable. For the pure acid at 180°C. a vapor pressure of 0.80 mm. Hg. was found, which is in agreement with other recent measurements (2).

Although theoretically any concentration of acid is convenient for the determination of vaporization efficiency, the above equation is applicable only to low (not higher than 1-2% stearic acid) concentrations because in deriving the formula, it was assumed that the number of moles of volatile substance is negligible in comparison with the number of moles of oil. Moreover, at higher concentrations, fatty acids catalyze the hydrolysis of triglycerides and thereby interfere with the measurement. Investigation has shown that, with low fatty acid concentrations (1-