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

Acknowledgment

The authors express their appreciation to R. R. Mod for assistance in the plasticizer screening tests.

REFERENCES

1. Daugherty, P. M., Sineath, H. H., and Wastler, T. A., Georgia Inst. Technol, Eng. Expt. Sta. Bull. *No. 17*, 36 pp. (1953).
2. McKinney, R. S., and Jamieson, G. S., Oil & Soap, *13*, 289–292 (1936).
3. Green, T. G., Hilditch, T. P., and Stainsby, W. J., J. Chem. Soc., *1936*, 1750–1755.
4. Hilditch, T. P., "The Chemical Constitution of Natural Fats," 3rd ed., Chapman and Hall Ltd., London (1956).
5. Hensch, E. J., and Wilbur, A. G., Am. Chem. Soc., Div. Paint, Plastics, Printing Ink Chem. Papers, *17*, No. 2, 216–220 (1957).
6. Magne, F. C., and Mod, R. R., Ind. Eng. Chem., *45*, 1546–1547 (1953).

[Received March 3, 1958]

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:

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

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, 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).

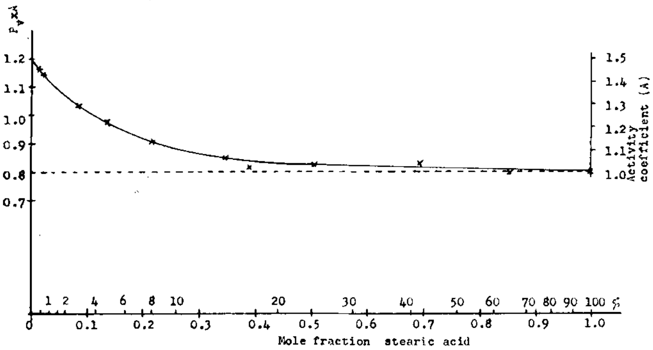

FIG. 1. Activity coefficients of stearic acid in peanut oil solutions.

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–

2%) and with the low oil level and absolute pressure (5–20 mm. Hg.) obtaining in a laboratory deodorizer, this hydrolytic effect is negligible.[1] In plant deodorizers with their higher oil levels the hydrolysis factor must be taken into account and determined experimentally or graphically.

Influence of Design and of Working Conditions on the Vaporization Efficiency of Laboratory Deodorizers

A series of efficiency determinations was made in a laboratory deodorizer (as shown in Figure 2, but without heating elements); 30 g. of steam were blown through 250 g. of oil containing 1.5% stearic acid at different rates of flow and at a pressure of 10 mm. The vaporization efficiencies obtained are recorded in Table I.

TABLE I

Influence of Steam Flow Rate on Vaporization Efficiency in a Laboratory Deodorizer (as in Figure 2, but Without Heating Elements)

Steam flow rate (g./min.)	0.15	0.30	0.50	1.0	1.5	1.7	1.9
Vaporization efficiency	0.12	0.16	0.27	0.30	0.50	0.51	0.46

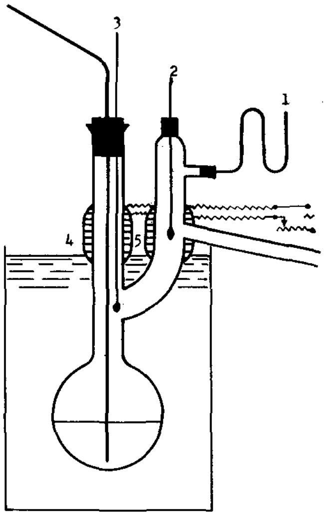

FIG. 2. Laboratory deodorizer—1. manometer; 2–3. thermometers; 4–5. heating elements.

The figures show that in this frequently used type of apparatus the vaporization efficiency is very low and is dependent on the steam flow rate, *viz.*, the efficiency increases with increasing steam flow rate.

Correlation was also found between absolute pressure and efficiency at constant steam volume rate: the vaporization efficiency decreases with decreasing absolute pressure (Table II).

TABLE II

Influence of Absolute Pressure on Vaporization Efficiency in a Laboratory Deodorizer (as in Figure 2, but Without Heating Elements)

Pressure	Steam	Time	Vaporization efficiency
(mm. Hg.)	*(g.)*	*(min.)*	
30	100.00	72	0.39
20	66.50	69	0.33
15	50.00	60	0.33
10	33.33	66	0.22
6	20.00	68	0.24
4	13.35	62	0.13
3	10.00	42	0.15
2	6.65	66	0.026
1	3.33	45	0.039

Bailey (1) found no decrease in the vaporization efficiency of plant deodorizers at absolute pressures down to 6 mm. and therefore concluded that the saturation of the steam bubbles is a very rapid process.

In the shallow oil layer of laboratory deodorizers rapid saturation might not occur, and the above values seemed to indicate this. However, as is shown in the present investigation, even in this case there is sufficient contact between steam bubbles and oil to obtain complete saturation. The decrease in the vaporization efficiency, as indicated in Tables I and II, is caused by other phenomena.

The head of the deodorizer is relatively cold; it is not insulated, and heat transfer from the heating bath to the head is very poor. Temperature measurements with an experimental deodorizer (as depicted schematically in Figure 3) showed, surprisingly, that the temperature, even in that part of the flask below the surface level of the heating-bath, may be considerably lower than that of the bath itself, probably because of radiation losses. The exact temperature differences are dependent on the steam flow rate (*i.e.*, heat supply by the vapor to the head) as shown in Table III.

TABLE III

Temperatures (°C.) Inside the Experimental Deodorizer (Figure 3)

Measuring point	Steam flow rate (g./min.)			
	0	0.2	1	2
1	160.0	164.0	165.5	167.5
2	168.0	170.5	171.7	......
3	177.0	178.0	179.0	179.0
4	180.0	180.0	180.0	179.0

The temperature differences recorded in Table III are not high enough to cause condensation of stearic acid, even with an acid content of 4%, as may be seen from Table IV. It is clear however that the cooling of the oil surface by 1°C. has the same effect on vaporization efficiency as does the lowering of the temperature of the whole oil by 1°C. Therefore reduction in the vaporization efficiency may occur even when no condensation of volatile substances takes place.

TABLE IV

Condensation Temperatures of Stearic Acid in Peanut Oil Solution

Stearic acid	Mole fraction	Part. pressure $p_v = P_v A X$	Condensation point[a]
(%)	*(X)*	*(mm.)*	*(°C.)*
0.5	0.0155	0.0180	125
1.0	0.0317	0.0358	134
2.0	0.060	0.064	142
4.0	0.115	0.114	149

[a] Temperatures at which $P_v = p$.

In the deodorizer depicted in Figure 3 vaporization efficiencies of 0.55 to 0.88 have been measured, dependent on the steam flow rate.

Use of the stirrer, which at 1,000 r.p.m. caused pronounced turbulence and the steam bubbles to rise in a spiral instead of vertically, did not raise the vaporization efficiency above this value despite the greater contact between steam and oil.

Increase in vaporization efficiency with increased steam flow rate (Table I) may therefore be attributed to the effects of cooling and condensation. The decrease, at lower absolute pressure (Table II) may be similarly explained since less heat is supplied to

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[1] Details of this investigation will be submitted for publication in due course.

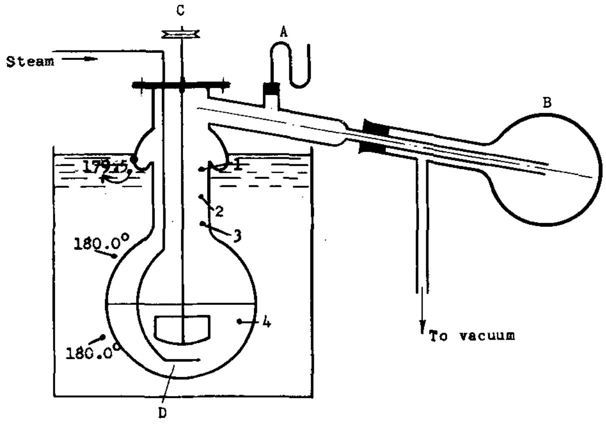

FIG. 3. Laboratory deodorizer with stirrer—A. manometer; B. condenser; C. stirrer; D. steam distributor.

the head by the vapor because of the decrease of the heat content per volume unit with decreasing pressure. It is also evident from the data given in Table III that the steam, which was at 25–55°C. on entering the flask, is instantaneously heated to the temperature of the oil. In view of the very high specific volume of the steam at this low pressure and its consequently low heat content, this rapidity is not surprising, nor is it surprising that the temperature of the oil does not change appreciably.

To eliminate cooling effects, the head of the deodorizer must also be heated. The deodorizer depicted in Figure 2 was therefore equipped with heating jackets, the temperature of which was maintained at 200°C. This resulted in an increase in vaporization efficiency to unity, using relatively low steam flow rates independent of the absolute pressure (Tables VI and VII).

TABLE VI

Influence of Absolute Pressure on Vaporization Efficiency in a Laboratory Deodorizer (Figure 2)

Pressure in mm. Hg.	3.5	4.0	5.0	10	30
Vaporization efficiency	1.04	0.98	0.90	0.97	0.98

TABLE VII

Influence of Steam Flow Rate on Vaporization Efficiency in a Laboratory Deodorizer (Figure 2)

Steam distributor	Steam flow rate (g./min.)				
	0.1	0.2	0.6	1.0	2.0
	Vaporization efficiency				
Fritted glass plate (diameter 6 mm.)	1.03	0.97	1.09	0.84	0.77
1 opening (diameter 1.5 mm.)	0.95	1.02	0.92	0.78	0.76

The values given in Table VII show that the replacement of the steam distributor plate by a single opening 1.5 mm. in diameter has practically no influence on the vaporization efficiency.

The decrease in vaporization efficiency at very high rates of flow has important consequences. When the flow of stripping steam is irregular, thus subjecting the oil to violent bumping (as with wet steam or when boiling is retarded), the vaporization efficiency should be lower than with a regular steam flow. Therefore a regular flow of dry steam is essential although, as the experiments described above demonstrate (Table III), superheating is not necessary.

Isothermic Laboratory Deodorizer

The elimination of cooling effects by electrically heating the head of the deodorizer cannot be considered an ideal solution to the problem. Only part of the head is heated, and the electrical heating must be carefully controlled. If the temperature is too high, heat transfer to the oil takes place (especially when the neck of the flask is short) and a vaporization efficiency greater than unity may be obtained.

The most satisfactory procedure is to immerse also the head of the deodorizer in the heating-bath. A deodorizer capable of being so immersed was therefore constructed (Figures 4 and 5) and gave very satisfactory results. The high performance is shown by the efficiency curve plotted from the results obtained with 150 g. of oil (Figure 6).

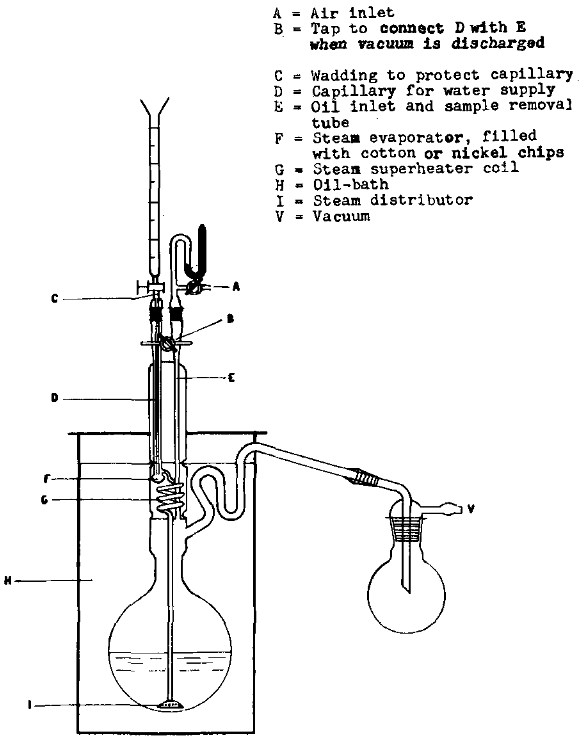

FIG. 4. Isothermic laboratory deodorizer.

This type of deodorizer is much simpler and easier to handle than any other apparatus used hitherto since no separate steam generator is needed. Deaerated water, flowing from a burette through a capillary, is evaporated in a small tube heated by the oil-bath. The wet steam so developed passes through a heated coil, where it is superheated and probably reaches the same temperature as the oil. To ensure regular evaporation a cottonwool filling in the evaporator tube is satisfactory at lower rates of flow, but at higher rates it is useless since it is a good insulator and therefore incapable of transferring heat needed for evaporation. Nickel chips were found to be very effective at high rates of flow.

The shape of the outlet tube to the condenser was designed to minimize carry-over losses and proved to be very effective even at high rates of flow.

The steam distributor has 14 holes, each 0.5 mm. in diameter. With holes of this size no excessive spattering was observed even at high rates of flow, and the steam distribution remained good.

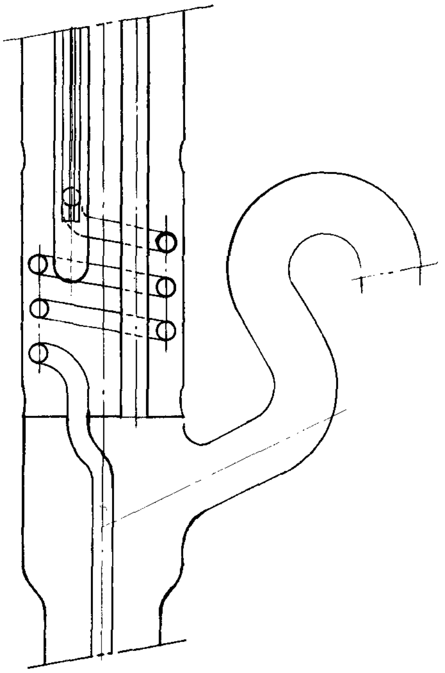

FIG. 5. Steam generator of the isothermic laboratory deodorizer (scale 1:1).

This deodorizer can readily be modified to suit different purposes. In the form shown in Figure 5 it was used for routine deodorizations at pressures of 15 to 20 mm. The size of the flask can be varied (one for 75 g. and one for 250 g. of oil are in use) without altering the dimensions of the upper part of the apparatus.

By electrically heating the outlet, all volatile substances condense exclusively in the condenser and are therefore available for analysis. The volatile substances can be obtained in more concentrated form by steaming at lower pressures (0.5–1 mm.), and a microburette is then used to control the steam supply.

This type of deodorizer is also suitable for the determination of vapor pressures; various liquids then replace water as carrier. For accurate measurements the temperature of the contents of the flask, not that of the oil bath, must be determined. For this purpose a thermocouple is used, which may be inserted through E after suitable modification of the manometer plug.

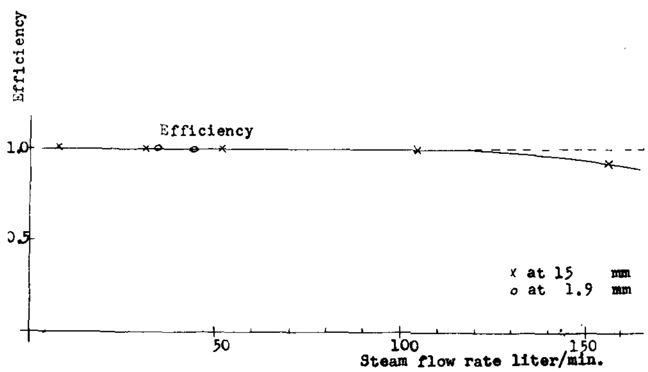

FIG. 6. Vaporization efficiency in the isothermic deodorizer on deodorizing 150 g. of peanut oil at 180°C. with 1.6 m^3 steam at various pressures and flow rates.

Summary

Fatty acid/triglyceride systems deviate from ideality, consequently the use of activities is needed when determining the vaporization efficiency in deodorizers.

In normal laboratory deodorizers the vaporization efficiency is low and is dependent on the steam flow rate, also on the absolute pressure.

To obtain a vaporization efficiency of unity, independent of the steam flow rate and of the absolute pressure, heating of the head of the deodorizer is necessary in order to eliminate cooling and condensation effects.

An isothermic deodorizer has been constructed, the steaming flask of which is immersed entirely in the heating bath. No separate vapor generator and superheater are needed; these are incorporated in the deodorizer and ensure a regular steam flow.

At very high flow rates the vaporization efficiency decreases slightly.

REFERENCES

1. Bailey, A. E., "Industrial Oil and Fat Products," Interscience Publishers Inc., New York, 1951.
1a. Sarkadi, D. Szabo, and de Boer, J. H., Rec. Trav. Chim., *76*, 628 (1957).
2. Pool, W. O., and Ralston, A. W., Ind. Eng. Chem., ***34***, 1104 (1942); Jantzen, E., and Witgert, H., Fette u. Seifen, ***54***, 198 (1952).
3. Bailey, A. E., Ind. Eng. Chem., Anal. Ed., *15*, 280 (1943); Baldwin, A. R., J. Am. Oil Chemists' Soc., *25*, 33 (1948).

[Received February 26, 1957]

The Hydrogenation of Fatty Oils with Palladium Catalyst. I. Hydrogenation of Castor Oil

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FULLY hydrogenated castor oil is a valuable product with wide and diverse industrial use (1). About 6,000,000 lbs. are produced annually in the United States. It enjoys a wide popularity through a number of desirable properties (1) including hardness, low solubility in organic solvents, nontoxicity, oxidation stability, and high dielectric constants (12 at 30° and 22 at 60° for 100 cycles). These properties are insured only if the hydrogenation of castor oil is carried out selectively, that is, most of the olefinic linkages are reduced without appreciable hydrogenolysis of the hydroxyl function.

Castor oil contains glycerides of ricinoleic acid (85–87%), oleic acid (6–8%), linoleic acid (3.0–3.5%), saturated acids (2.5–3.0%), and a small amount of dihydroxystearic acid (0.5–2%) (2, 3). The castor oil used in the present work had a typical analysis: an iodine value of 86, a hydroxyl value of 160, and an acid value of 1.7. A satisfactory hydrogenated castor oil has an iodine value of 2.5–8.5, a m.p. of 85–86°, a hydroxyl value of 145–160, and an acid value less than 2. Thus in the hydrogenation of castor oil the iodine value must be reduced by about 90 to 97% while the hydroxyl value may be