

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

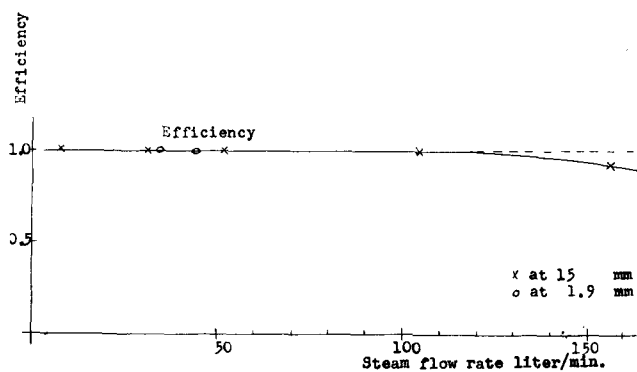


Fig. 6. Vaporization efficiency in the isothermic deodorizer on deodorizing 150 g. of peanut oil at 180°C. with 1.6 m<sup>3</sup> steam at various pressures and flow rates.

inserted through E after suitable modification of the manometer plug.

### 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.

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## 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, non-toxicity, 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

TABLE I  
 Hydrogenation of Castor Oil

Experiment	T°C.	Pressure p.s.i.g.	Agitation r.p.m.	Catalyst	% Pd in oil	Time, min.	Hydrogenated castor oil			
							I. N.	Capil. m.p.	OH #	Acid value
1 <sup>a</sup> .....	30-60	atm.	.....	A	0.1	160	3.7	83.0	126.0	....
2.....	100	50	420	A	0.1	100 <sup>b</sup>	25.0	56.0	110.0	....
						200	3.5	70.0	95.2	....
3.....	112-115	30	800	C	0.01	120 <sup>b</sup>	7.3	85.5	138.6	....
						180	5.5	85.7	138.8	....
4.....	122-125	40	800	B	0.002	180	5.4	82.2	128.5	....
5.....	122-125	40	620	B	0.001	330	34.6	71.0	123.0	....
6.....	86-90	30	620	B	0.004	285	5.6	83.5	135.5	....
7.....	86-90	40	620	C	0.005	440	12.0	83.0	136.5	....
8.....	92-95	40	620	B	0.005	275	2.8	82.5	129.7	....
9.....	96-100	45	620	C	0.0055	400	3.8	85.8	144.8	1.8
10.....	96-100	45	620	C	0.0065	375	4.0	86.0	145.0	1.8

<sup>a</sup> One part of castor oil was dissolved in 60 parts of ethanol, and the hydrogenation was done in a shaking apparatus. The temperature was increased as the reaction rate dropped.

<sup>b</sup> Samples removed before finish of hydrogenation. Catalysts: A 5% Pd on charcoal; B 1% Pd on charcoal; C 1% Pd on charcoal, modified by addition of 0.35% Ag and 0.2% Bi. (A discussion on selectivity of palladium catalyst will be given in a subsequent paper.)

reduced only by about 9%. Catalysts for this hydrogenation are therefore necessarily limited to those having an adequate selectivity.

This paper deals with the use of palladium catalysts for the hydrogenation of castor oil. These are widely used for the reduction of olefins, and since they inherently, or with modification, display a notable selectivity in hydrogenation, it seemed worthwhile to investigate their use in a problem where selectivity is of prime importance.

Nickel is the catalyst that has been most widely used in industry for the hydrogenation of castor oil. Generally nickel hydrogenations are made at high pressures, 15 to 150 atmospheres, and temperatures at 160-170°C. Higher temperatures are usually avoided to minimize dehydroxylation, but the use of temperatures as high as 260° at a pressure of 110 atmospheres has been reported to give little loss of hydroxyl with a copper catalyst (4). The use of platinum metal catalysts as well as iron, cobalt, and manganese (5-8) has also been reported. No details for the use of platinum metals have been given previously.

### Experimental

All hydrogenations were done in a laboratory stainless steel hydrogenator with a 3-lb. charge of oil and intensive agitation. Selectivity was not affected by changing agitation, but the reaction rate increased appreciably with increasing agitation. Processing was controlled by a rapid softening-point determination of the product (modified A.O.C.S. method Ce-3-25, 10 min. on the ice). Castor oil, nonselectively hydrogenated, consists mostly of glycerides of stearic acid having a melting point in the range of 70°C. Iodine values were determined at constant temperature of 24° by Hanus' method. In agreement with recent publications (3, 9) it was found that the use of Wijs solution necessitated lower reaction temperatures, 15-20°, for an exact determination of unsaturation in castor oil. Determination of capillary melting points, hydroxyl numbers, and acidities was made according to the official methods of the American Oil Chemists' Society (10).

**Catalyst A and B.** The palladium on high surface carbon catalysts was prepared by the addition of a solution of palladous chloride in distilled water to Norite and reduction with hydrogen according to the directions of Shriner (11).

**Catalyst C: Ag, Bi, Pd.** Basic bismuth acetate, to the amount of 3.75 g., was boiled in 300 ml. of glacial

acetic acid, and evaporated to 200 ml. of clear solution. To this were added 8.13 g. of silver acetate in 900 ml. of a 1% acetic acid solution and then made up to 1,500 ml. with distilled water. This solution was then added slowly, over a period of 30 min., to 1,500 g. of 1% palladium on Norite (prepared as above), suspended in 15 liters of water. To this mixture 25 g. of sodium formate dissolved in 100 ml. of water were added dropwise. The resulting solution was heated to boiling for 20 min. After settling, the solution was decanted; the catalyst was filtered, washed with distilled water, and dried at 100°C.

### Results and Discussion

The experimental results are summarized in Table I. The very mild conditions used in these hydrogenations are in marked contrast to the conditions usually employed for the production of castor wax. Even so in some cases the hydrogenation was carried too far. With an unmodified 5% palladium on charcoal catalyst, A, a satisfactory product could not be obtained. This catalyst was nonselective, and hydroxyl groups were too rapidly reduced concomitantly with the olefin, Experiment 2. However the use of a solvent, Experiment 1, improved selectivity greatly.

A 1% palladium on charcoal catalyst, B, gave a more suitable, although not completely, satisfactory product. This catalyst produced a product with a maximum m.p. of 83.5°C. and a maximum hydroxyl value of 135.5 (Experiment 6).

An entirely satisfactory product was obtained from a special palladium catalyst so modified as to give better selectivity. The products described in Experiments 9 and 10 are entirely satisfactory. There was no increase in the acidity value, showing the absence of such side reactions as hydrolysis, estolide formation, and etherification. The selectivity of this catalyst is demonstrated by Experiment 3, where in 60 min. of processing the iodine value decreased 25% while the hydroxyl number was unchanged.

These castor wax products were obtained under extremely mild working conditions, which would in practice permit important operating economies. In addition to these operating benefits, preliminary calculations indicate that the catalyst cost involved in hydrogenating castor oil with palladium catalysts would be competitive with that of nickel.

### Summary

A good quality of castor wax was prepared in the laboratory at 100°C. and 45 p.s.i.g., using a modified

palladium catalyst. The product obtained had an iodine value of 4, a hydroxy value of 145, and acid value of 1.8, and a capillary melting point of 86°.

#### Acknowledgment

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## Preparation of Pure Palmitic Acid and a By-Product Plasticizer from Cottonseed Oil<sup>1</sup>

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IN THE COURSE of investigating methods for fatty acid purification it was observed that very pure fatty acids could be obtained by recrystallization of their amine salts from organic solvents. The cyclohexylamine salts of the higher fatty acids were found to be particularly amenable to this procedure because of their excellent filtration characteristics and high temperature coefficients of solubility. While this method had never been applied to such a complex mixture as the cottonseed acids, where the acid to be recovered was not in the predominant concentration, it nevertheless appeared promising because of the unique composition of the cottonseed acids. Although palmitic acid accounts for only about 22-24% of the total acids, the major constituents of which are linoleic and oleic acids, it is the dominant saturated acid in a ratio of at least 10 to 1.

Application of the amine salt method to the cottonseed acids proved to be very effective when cyclohexylamine was the amine used. From the point of view of the by-products formed however, it was found advantageous to use a mixture of cyclohexylamine and morpholine. The residual unsaturated fatty acids can thus be recovered as the morpholine salts, which can be converted to useful morpholide plasticizers (2).

#### Experimental and Results

**Materials and General Procedure.** The cottonseed acids were obtained by saponification and subsequent acidulation of a refined and bleached cottonseed oil with an iodine value of 108.8 and a thiocyanogen value of 69.9. The hydrogenated cottonseed acids were similarly derived from the same oil after selective hydrogenation to an iodine value of 63.1 and a thiocyanogen value of 62.9. The cyclohexylamine and morpholine were White Label Eastman Kodak products. Drum C. P. acetone was employed as the solvent.

In general, one part by weight of cottonseed acids was dissolved in about four parts by weight of

acetone containing a slight excess (0.5%) of the amine as calculated from the neutralization equivalent of the acids. The heat of solution was usually sufficient to cause complete solution, but in some instances it was necessary to warm to 40-45°C. The crude amine salt of palmitic acid was separated on a Buchner funnel at the crystallization temperature and washed *in situ* with a small volume of cold solvent. The moist filter cake was then redissolved in acetone and subjected to a number of recrystallizations in a centrifugal filtration tube (4). There were no intervening crystal washings in these operations. All concentrations were reported in terms of the dry amine salt, taking into account the residual solvent in the filter or centrifuge cake, as determined on an aliquot. The acid was regenerated from the amine salt by exhaustive extraction with warm hydrochloric acid solution by a modified Soxhlet-type liquid-liquid extraction. Unless otherwise mentioned, all freezing points were determined by the sealed tube thermostatic method (3).

**Cyclohexylamine Method.** A 100-g. portion of the cottonseed acids and 35.8 g. of cyclohexylamine were dissolved in 500 ml. of acetone. Crystallization and filtration of the crude cyclohexylamine salt of palmitic acid from this solution were carried out at room temperature (about 27°C.). An aliquot of the filter cake was taken from this and subsequent recrystallizations for iodine value and freezing point determinations on the regenerated acid in order to follow the improvement in purity. The regenerated acid at this point had an I.V. of 42 and a f.p. of 51.8°C. The remainder of the moist filter cake, consisting of 47 g. of the dry amine salt and 66 g. of residual solvent, was dissolved in 34 g. of additional acetone and recrystallized at room temperature in a centrifugal filtration tube. The regenerated acid now had an I.V. of 10.2 and a f.p. of 59.6°C. The centrifuged cake, amounting to 25.6 g. (dry basis), was redissolved in 95 g. of acetone, allowed to crystallize at room temperature, and centrifuged. Analysis of the filter cake then indicated an I.V. and f.p. for the regenerated acid of 1.2 and 62.3°C., respectively. The last recrystallization was carried out from 48 g. of acetone (7.6 g. of cake, dry basis) and the mother

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