In order to exploit new uses we have attempted to improve their solubility in water by introducing oxyethylene radicals into the molecule.

The addition reaction of ethylene oxide with the sucrose diesters was carried out in an autoclave in the presence of alkaline catalysts. With the reaction temperature maintained between 100–130° the pressure decreased as the reaction proceeded, and one to two hours were required to consume the ethylene oxide used.

The addition products are yellow or orange oily materials soluble in water. Aqueous solutions showed good surface-active properties.

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Hydrogenation of Fatty Oils with Palladium Catalysts. V. Products of the Tall Oil Industry

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Conditions were found for reducing tall oil distillate to an iodine number of 22 with a sufficiently small amount of palladium catalyst to make the process commercially feasible. The operating conditions were 200°C. and 2,600 psi.

Tall oil fatty acids were reduced with palladium and the concentration of linoleic acid, *cis*-oleic acid, saturated acid, and *trans* isomers were determined as a function of iodine number. The five-platinum group metals (Pt, Pd, Ir, Rh, Ru) were compared as to activity, selectivity of partial hydrogenation, and tendency to form *trans*-isomers.

HYDROGENATION of tall oil products results in materials with new properties and of increased value and utility. The hydrogenation of good prerefined whole tall oil to 95 to 100 I.V. with nickel or nickel-copper catalysts (1) is fairly easy even at low pressure, although a relatively large amount of catalyst is needed (2). Hydrogenation to a low iodine number is considerably more difficult. Even refined tall oil products still contain catalyst poisons, mostly sulfur compounds of unsaponifiables. Distilled products contain less poisons, but distillation isomerizes the rosin acids to a more difficult form to hydrogenate (3). Various methods for the removal of poisons have been published and patented (4–7). Treatment with spent catalyst before hydrogenation is frequently suggested (8). In the case of rosin acids this procedure removes poisons, but complicates hydrogenation by promoting isomerization to compounds more difficult to reduce.

Commercial hydrogenations of tall oil are done exclusively with nickel. Platinum metals have received so far no attention commercially and only scant mention in the literature. One excellent study of hydrogenation of tall oil rosin acid with catalysts of the platinum metal group has been made (3). One patent has been issued on hydrogenation of rosin with rhodium, ruthenium, and palladium catalysts (9), two other patents mention platinum and palladium catalysts (10) and platinum oxide (11).

Two specific aspects of the tall oil hydrogenation problem are examined in this paper. One is the hydrogenation of a tall oil distillate to a low iodine number, yielding a commercially interesting product, stable to oxidation; the other is the hydrogenation of tall oil fatty acids with the aim of producing the maximum amount of the valuable *cis*-oleic acid in a suitable mixture of other products. This means that reduction should be directed toward removing linoleic acid selectively, and minimizing formation of trans-isomers and saturated acids.

Experimental

Four different hydrogenation units were used in these experiments. At atmospheric pressure and room temperature a one-liter glass flask shaken at 280 strokes per minute was used. At pressure up to about 50 psig. and room or elevated temperature and with a high degree of agitation, a one-gallon stainless steel autoclave with a stirrer, cooling coil, and electrical heater controlled by a thermocouple was employed. High-pressure hydrogenation with a low degree of agitation was done in a Parr shaking bomb of 100-ml. capacity. A higher degree of agitation at high pressure was achieved by use of a 500-ml. Magne Dash autoclave.

The tall oil distillate used in these experiments had the analysis: fatty acids, 53%; rosin acids, 45%; unsaponifiable, 2%; acid number, 187; iodine number, 138. The fatty acids were 42% linoleic acid, 55% oleic acid, 3% saturated acids. Tall oil fatty acids had the analysis: fatty acids, 97%; rosin acids, 1.0%; unsaponifiable, 2%; acid number, 195; iodine number, 130. The composition of the fatty acids was: linoleic acid, 38%; oleic acid, 51%; conjugated diethenoid acids, 6%; palmitic acid, 3%; stearic acid, 2%.

Analyses of the products obtained in this work were made according to official methods of the American

TABLE I
Hydrogenation of Tall Oil Distillate with Pd Catalyst

Experiment	% Pd in feed	Temperature °C.	Pressure psig.	Time in hours	Hydrogenated product I. N.	Hydrogenated product Acid No.	Remarks
1	0.50	25	Atm.	2	22.0	185	Product light colored
2	0.05	185	50	18	22.0	171	
3	0.006	200	2,000	6	70.0	185	
4	0.01	190	2,200	18	24.0	163	Product dark colored
5	0.0075	200	2,650	23	31.0	170	
6	0.0082	200	2,450	36	22.0	165	
7	0.0085	200	2,520	25	23.5	170	
8	0.0057	200	2,600	30	22.5	171	Light color

Catalyst: 5% Pd on carbon powder. Agitation, 800 r.p.m., Ex. 2, autoclave; Ex. 3–8, Parr rocking bomb; Ex. 1, methanol, 10 parts; oil, 1 part.

Oil Chemists' Society (12). The *trans* content was determined from the infrared absorption of a carbon disulfide solution with a Perkin-Elmer Model 21 infrared spectrophotometer, according to the procedure of Swern (13), and using the recommendation of the Spectroscopy Committee (14). The order of activity for various catalysts was determined by calculation of the catalyst functioning rate (15), defined as decrease in iodine number per minute per 1% of catalyst. The presence of rosin and unsaponifiables in the tall oil introduced certain complications in the measurements and calculations. To eliminate these, the reasonable assumption was made that there were no conjugated diethenoid acids in products of iodine number less than 100.

The catalysts used were mostly commercial catalysts obtained from Engelhard Industries, Newark, New Jersey. Preparation of the palladium and partially deactivated palladium catalysts was given in an earlier paper (16).

Discussion and Results

Hydrogenation of Tall Oil Distillate. Tall oil distillate was hydrogenated with the intent of finding economical conditions to give a product of iodine number of 20 to 25 and with a minimum of decarboxylation. The conditions used and the analysis of the products obtained are given in Table I. A satisfactory product can be obtained at room temperature and atmospheric pressure, Experiment 1, but the amount of catalyst is excessive for industrial use. The conditions of Experiment 8 gave a product of low iodine number [1] and a tolerable decarboxylation with a practical amount of catalyst. Decarboxylation is increased if poisons are removed from the feed by pretreatment with spent catalyst: the feeds of Experiments 4 and 6 were treated with spent palladium catalyst for one hour at room temperature in a nitrogen atmosphere and then filtered. The acid numbers of the product from these feeds were the lowest obtained.

It is important that a good quality stainless steel (316) be used in the hydrogenation equipment (18) even when a glass liner is employed, to obtain a product of good color and to avoid poisoning of the palladium catalyst by iron salts. In Experiments 4–7 the glass liner was closed by common steel springs and the product was dark. In Experiment 8 the liner was closed by nickel chromium springs and the product was light. In addition to producing an off-color product, the use of common steel springs required about 20% more catalyst. Color was easily removed from the product by washing with dilute hydrochloric acid.

Hydrogenation of Tall Oil Fatty Acids. Hydrogenation of tall oil fatty acids was directed toward finding conditions that would produce the maximum amount of *cis*-oleic acid in a suitable mixture. The price differential of tall oil fatty acids mixture and oleic acid makes a selective hydrogenation a decidedly attractive operation.

All the platinum metals, except osmium, were examined for activity and for selectivity of hydrogenation, and for tendency to form *trans* isomers. The activity increased in the order of ruthenium, iridium, platinum, rhodium, and palladium. The tendency to form *trans* isomers increases in the same order except for the interchange of platinum and ruthenium; the order for increasing *trans* isomers is platinum, iridium, ruthenium, rhodium, and palladium. Selectivity of hydrogenation followed the increasing order, iridium, ruthenium, platinum, rhodium, and palladium. Despite palladium's tendency to *trans* formation, its high activity and selectivity and relatively low cost makes it the most attractive of the platinum metals for fatty acid hydrogenation.

As palladium becomes more highly dispersed on the carrier, it becomes more active and more selective; 1% Pd on carbon is more active and selective than 5%. At the expense of activity, selectivity may be increased and *trans* formation decreased by partial deactivation of the catalyst. The changes brought about by deactivation and dispersion are probably linked with the effect these changes have on the availability of hydrogen at the catalyst surface. These relationships were discussed at length in an earlier paper (15).

At low pressures the amount of *trans* isomers formed with palladium is high and materially decreases the yield of the *cis*-oleic acids. To circumvent excessive *trans* formation, hydrogenations were done at elevated

TABLE II
Hydrogenation of Tall Oil Fatty Acids with Pt Group Metal Catalysts

Experiment	Catalyst % metal in oil	Time, minutes	I. N.	Th. N.	Linoleic acid %	Saturated acid %	Oleic acid total %	*Trans* %	*Cis*-oleic acid %	△ I. N. minute	Catalyst functioning rate
1	5% Rh/C 0.05%	19	92.4	78.1	16.5	14.0	69.5	26.0	43.5	1.98	39.6
2	5% Ru/C 1.0%	37	93.0	75.7	20.0	17.2	62.8	13.2	49.6	1.00	1.0
3	5% Ir/C 0.5%	35	88.5	69.9	21.6	23.6	54.8	9.7	45.1	1.19	2.4
4	5% Pt/C 0.05%	123	94.2	77.0	19.9	15.3	64.8	6.0	58.8	0.29	5.8
5	5% Pd/C 0.025%	20	92.7	82.4	11.6	8.8	79.6	30.6	49.0	1.82	72.8
6	1% Pd/C 0.025%	19	91.3	82.2	10.2	8.8	81.0	27.8	53.1	2.01	80.4
7	1% Pd/C[a] 0.10%	54	91.7	82.7	10.0	8.3	81.7	24.8	56.9	0.72	7.2

[a] Partially deactivated with Ag and Bi (16). Solvent 1:10 oil/methanol. Pressure, atmospheric. Temperature, 28°C.

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[1] Iodine numbers of distilled tall oil products containing considerable amounts of rosin acids do not give a true measure of unsaturation; they are approximate but afford a convenient comparison (17).

TABLE III
Hydrogenation of Tall Oil Fatty Acids with Pd Catalysts

Experiment	Catalyst % Pd in oil	Temp. °C.	Press. psig.	Time, min.	Hydrogenated product						
					I. N.	Th. N.	Linoleic acid %	Saturated acid %	Oleic acid %	*Trans* %	*Cis*-oleic %
1	C 0.005	24.45	20.30	390	93.0	83.2	11.0	8.0	81.0	34.0	47.0
2	A 0.0125	25.27	Atm.	360	81.3	80.1	0.8	10.4	88.8	42.0	46.8
3	B 0.009	25.30	10.15	400	79.7	76.2	3.5	15.1	81.4	44.0	39.4
4	A 0.010	25.27	10.20	280	76.5	73.0	3.4	18.8	77.8	48.0	27.8
5	D 0.012	28.00	1900	440	98.5	85.0	15.4	6.2	78.4	13.6	64.8
6	A 0.004	28.30	1900	330	98.4	84.5	15.9	6.8	77.3	17.0	60.3
7	A 0.005	28.30	500	300	87.7	79.0	9.8	12.3	77.9	28.0	49.9
8	A 0.004	28.30	1900	270	87.5	77.0	11.9	14.8	73.3	22.0	51.3
9	A 0.004	30.40	2000	180	86.9	75.6	12.9	16.4	70.7	24.6	46.1
10	D 0.015	30.40	1900	460	86.5	77.6	10.0	14.0	76.0	23.0	53.0
11	D 0.012	28.30	1850	990	84.0	76.0	8.9	15.8	75.3	22.5	52.8
12	A 0.004	28.30	1900	450	77.4	69.8	8.5	22.6	68.9	25.0	43.9
13	D 0.015	28.30	1900	445	74.4	68.4	6.6	23.0	70.4	24.0	46.6
14	A 0.005	28.30	1950	1700	70.6	65.5	5.5	27.2	67.3	23.9	43.4
15	A 0.006	28.30	2000	1100	68.5	63.9	4.9	28.9	66.2	22.7	43.5
16	A 0.006	28.30	1750	2200	64.7	60.9	4.0	32.2	63.8	21.5	42.3
17	D 0.018	28.30	1850	440	63.6	60.7	2.9	32.4	64.7	19.5	45.2
18	A 0.006	28.30	1750	2400	58.8	55.1	4.0	38.7	57.3	19.8	37.5
19	D 0.015	28.30	1900	1300	59.4	56.7	2.8	36.8	60.4	18.5	41.9
20	A 0.006	28.30	2000	2400	46.8	43.4	3.7	51.8	44.5	13.6	30.9
21	D 0.018	28.30	1900	1600	40.0	37.5	2.7	58.3	39.0	11.8	27.2

Catalysts: A, 5% Pd/C; B, 2% Pd/C; C, 1% Pd/C; D, 1% Pd/C + Ag + Bi. Ex. 1, no solvent; Ex. 3 and 4, 1:10 oil:CH_3OH; Ex. 2, 5–21 1:6 oil/CH_3OH; Ex. 1–4, autoclave, 800 r.p.m.; Ex. 5–8, 11–21 Parr rocking bomb; Ex. 9–10, Magne Dash. 240 cycles/minute.

pressures. The results of these experiments are shown in Table III. The first four experiments, made at atmospheric pressure or slightly elevated pressure, showed good selectivity, but the amount of *trans* isomers was high, 34 to 48%. Of these the product of Experiment 2 was the best. Fourteen experiments were made under high pressure in a Parr rocking bomb and two in a Magne Dash autoclave. As expected the amount of *trans* isomers decreased at high pressures, but selectivity also decreased.

In Figure 1 the changes of saturated, linoleic acid, oleic acids, and *trans* isomers during processing at high pressure are shown with two of the palladium catalysts tabulated in Table III. The ratio of these materials constantly changes as hydrogenation proceeds, and from the chart the composition of the product at any iodine number may be determined. It can be seen that the use of a partially deactivated catalyst, D, gives a higher *cis*-oleic acid content and lower linoleic acid and *trans*-isomer content than the more active catalyst.

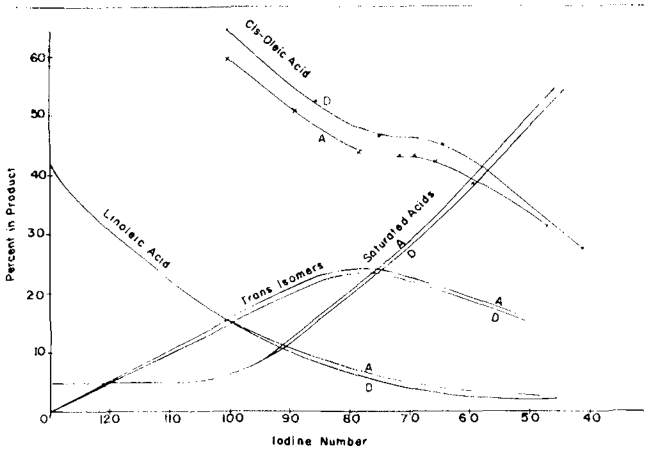

FIG. 1. High-pressure hydrogenation of tall oil fatty acids with Pd catalysts. Product distributions shown are based on data of Table III for 1,750 to 2,000 psig. (except Magne Dash Experiments 9 and 10).

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Polymers Derived from 9,10-Dihydroxystearic Acid

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A number of film forming polyester resins have been produced from 9,10-dihydroxystearic acid. The resins cured readily at room temperature when crosslinked with 20% toluene diisocyanate to form flexible films. The properties of the films indicated that useful, internally plasticized polyester resins can be readily obtained from condensations of 9,10-dihydroxystearic acid and polybasic acids. Maleic anhydride derived films gave the most desirable properties.

A PRELIMINARY investigation of film-forming polymers from 9,10-dihydroxystearic acid was undertaken as a part of a general program for developing new uses for fats and oils. Products from the condensation of dibasic acids with the low melting form of 9,10-dihydroxystearic acid were mixed with diisocyanates and cast into films. This paper describes the properties of these and related films.