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.

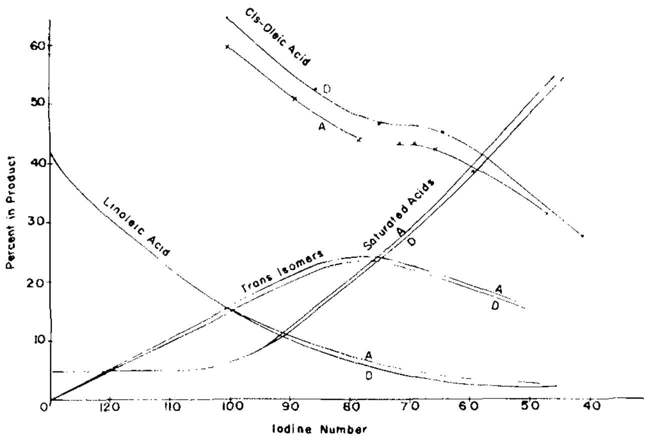

FIG. 1. High-pressure hydrogenation of tall oil fatty acids with Pd catalysts. Product distributions shown are based on data of Table III for 1,750 to 2,000 psig. (except Magne Dash Experiments 9 and 10).

REFERENCES

1. Zajcew, M. (Zajcew, M., Zavody Kosmos), German Patent 797,901 (1954).
2. Zajcew, M., Scient. Bull. of Ukrain, Techn. University, Regensburg No. III–IV, 47, 1949.
3. Montgomery, J. B., Hoffmann, A. N., Glasebrook, A. L., and Thigpen, J. I., Ind. and Eng. Chem., *50*, 313 (1958).
4. Dressler, R. G., and Vivian, R. E., U. S. Patent 2,336,472 (1943). Dressler, R. G., and Vivian, R. E., U. S. Patent 2,369,446 (1945). Dressler, R. G., Vivian, R. E., and Hasselstrom, T., U. S. Patent 2,371,230 (1945).
5. Oliver, A. F., and Palmer, R. C. (Newport Industries Inc.), U. S. Patent 2,317,797 (1943).
6. Taussky, I., U. S. Patent 2,413,009 (1946).
7. Stevens, A. (Armour and Company), British Patent 630,686 (1949).
8. Zajcew, M., Fette, Seifen, Anstrichmittel, *60*, 1051 (1958).
9. Glasebrook, A. L., Hoffmann, A. N., and Montgomery, J. B. (Hercules Powder Company), U. S. Patent 2,776,276 (1957).
10. Baldwin, W. S., and Floyd, Don E. (General Mills Inc.), U. S. Patent 2,656,371 (1953).
11. Schultz, E. D., and Schaefer, W. E. (Hercules Powder Company), U. S. Patent 2,346,793 (1944).
12. American Oil Chemists' Society, "Official and Tentative Methods," 2nd ed., Chicago, 1946.
13. Swern, D., Knight, H. B., Schreve, O. D., and Heether, M. R., J. Am. Oil Chemists' Soc., *27*, 17 (1950).
14. O'Connor, R. T., *et al.*, J. Am. Oil Chemists' Soc., *34*, 600 (1957).
15. Zajcew, M., J. Am. Oil Chemists' Soc., *37*, 11–14 (1960).
16. *Ibid.*, *35*, 475 (1958).
17. Nihlen, H., Svensk Pappers Ind., *48*, 345 (1945).
18. Barnes, E. O., and Potts, R. H., J. Am. Oil Chemists' Soc., *36*, 158 (1959).

[Received February 1, 1960]

Polymers Derived from 9,10-Dihydroxystearic Acid

F. V. MORRISS, G. F. BECHTLE, and H. M. GADBERRY,
Midwest Research Institute, Kansas City, Missouri

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.

TABLE I

Polymers of 9,10-Dihydroxystearic Acid-Dibasic Acid Resins

Resin No.	31	33	32	34	35	39	40
Resins							
Dihydroxystearic acid (mol)	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Litharge (g.)	0.1	0.1	0.1	0.1	0.1	0.1	0.1
% Prepolymerized	50	50	0	0	0	35	35
Maleic anhydride (mol)	0.1	0.1	0.1	0.1	......	......	......
Phthalic anhydride (mol)	......	......	......	......	0.1	......	......
Dimethyl isophthalate (mol)	......	......	......	......	......	0.067	......
Chlorendic anhydride (mol)	......	......	......	......	......	......	0.049
Process	C	D	A	B	B	C	D
Reaction time (hr.)	5	5	......	7	......	11	16
Cure time (sec. at 200°C.)	1	5	9	5	>120	5	1

Processes: A = Copolymerization, no solvent. B = Copolymerization using equal quantity of xylene as solvent. C = Prepolymerization of dihydroxystearic acid before condensation with dicarboxylic acid, no solvent. D = Same as C, using equal quantity of xylene as solvent.

Bruson (1) reported that resins produced from polyhydroxy long-chain fatty acids differed greatly in physical character from those produced from glycerol, ethylene glycol, etc. The product from the high melting 9,10-dihydroxystearic acid and phthalic anhydride, for example, was a tough rubberlike mass that showed promise as a suitable base for compounded coating compositions. Mori (2) described the preparation of resins suitable for use in paint from 9,10-dihydroxystearic acid and maleic acid or its anhydride. The preparation of polymeric plasticizers from esters of the low melting form of 9,10-dihydroxystearic acid and phthalic anhydride has been described by Knight (3). We found that resinous materials resulted from the interesterification of 9,10-dihydroxystearic acid. At the gel point the condensation was about 75% complete as measured by water eliminated. The possibility of crosslinking the unreacted hydroxyl groups with diisocyanate appeared to offer an opportunity for the selective design of internally plasticized products.

Experimental Procedures and Data

Polymerization of 9,10-Dihydroxystearic Acid. Sixty-three grams of 9,10-dihydroxystearic acid, m.p. 92° (0.2 mol), were melted in a three-necked flask fitted with a stirrer, thermometer, Dean-Stark condensation trap, and carbon dioxide addition tube, and 0.1 g. of litharge was added. The mixture was heated and stirred. Water was expelled and the temperature slowly increased to 420°F. At this point, when 2.6 ml. of water had been collected (72%), the mixture gelled very rapidly. The gelled mass did not dissolve in xylene.

The experiment was repeated at 420°F. and after 2.7 ml. of water had been collected, 100 ml. of cyclohexanone were added to dissolve the resin. The cure time (4) at 200°C. for this product was 15 sec.

In a third experiment, at 400°F. after 2.2 ml. of water had been collected, the resin was cooled. It dissolved in acetone. The cure time at 200°C. was 165 sec.

Polymerization of 9,10-Dihydroxystearic Acid with Maleic Anhydride (No Litharge). A mixture of 63 g. of 9,10-dihydroxystearic acid (0.2 mol), 9.8 g. of maleic anhydride (0.1 mol) and 70 g. of xylene in a three-necked flask, fitted with a stirrer and a Dean-Stark condensate trap, was stirred and heated to maintain reflux. After 4 hr., 2.5 ml. of water had been collected. The reaction mixture was cooled overnight. On the following day the mixture was reheated and stirred, some xylene condensate was removed and the temperature of the mass was raised to 330°F. When a total of 3.4 ml. of water (0.19 mol) had been collected, gelation occurred. The gelled mass swelled, but did not dissolve in 100 cc. of xylene.

Copolymerization of 9,10-Dihydroxystearic Acid and Maleic Anhydride. Process A: A mixture of 63 g. of 9,10-dihydroxystearic acid (0.2 mol), 9.8 g. of maleic anhydride (0.1 mol) and 0.1 g. of litharge was heated and stirred under carbon dioxide to expel water. The temperature slowly increased to 325°F. and 2 ml. of water was obtained. At this point the mixture was cooled to room temperature. The resinous product showed a cure time at 200°C. of 9 sec. Process B: In a similar experiment 50 g. of xylene were added to the above ingredients. The reaction was continued until a total of 2 ml. of water had been collected and the temperature of the mixture was 325°F. The cure time (200°C.) of the cooled product was 5 sec.

Reaction of Polymerized 9,10-Dihydroxystearic Acid with Maleic Anhydride. Process C: A mixture of 63 g. of 9,10-dihydroxystearic acid (0.2 mol) and 0.1 g. of litharge was heated under carbon dioxide in the reaction apparatus as before. When the temperature reached 320°F. and 1.7 ml. of water had been collected, 9.8 g. of maleic anhydride (0.1 mol) were added. The mass became very viscous after 5 hr. reaction time.

On the following day, the cooled mass had gelled. It could not be remelted. It did not disperse or dissolve in 75 cc. of cyclohexanone. The cure time at 200°C. was 1 sec. Process D: A similar experiment was conducted in the same manner with the same

TABLE II

Properties of Polyester/Isocyanate Films

Resin No.	31	33	34	35	39	40
Solvent	Cyclohexanone	Xylene	Xylene	Xylene	Cyclohexanone	Xylene
% Solids	50.5	79.7	77.7	69.2	65.5	57.3
Toluene-2,4-diisocyanate used (%)	20	20	20	20	20	20
Color	Light amber	Light amber	Light amber	Very light	None	None
Clarity	Clear	Clear	Clear	Clear	Clear	Sl. translucent
Elasticity	Very slight	Slight	Slight	Slight	Very-slight	Slight
Toughness	None	Fair	Fair	Little	Little	Little

TABLE III

Curing of Polyesters with Toluene-2,4-Diisocyanate

Resin type	Resin cure (200°C.)	Crosslinking agent used	Drying characteristics[a] and Sward hardness			
			24 hr.	72 hr.	96 hr.	144 hr.
	sec.	%				
Maleic	10	5	S.T.	S.T.	S.T.	S.T.
		10	V.S.T.	12	....	8–10
		20	Dry	34	....	26
		25	30	....	32	....
		30	34	....	42	....
Maleic	31	5	V.T.	V.T.	T.	T.
		10	T.	6	....	4
		20	Dry	36	....	28
		25	30	....	30	....
		30	34	....	34	....
Phthalic	6	5	T.	T.	S.T.	S.T.
		10	V.S.T.	12	....	8-10
		20	Dry	24	....	18
Phthalic	15	5	T.	T.	T.	S.T.
		10	S.T.	8	....	2
		20	Dry	24	....	20
		25	18	....	20	....
		30	24	....	28	....
Dimethyl isophthalic	98	5	S.T.	S.T.	S.T.	S.T.
		10	V.S.T.	2	....	2
		20	Dry	8	....	14–18
		25	S.T.	....	8	....
		30	S.T.	....	10–12	....
Dimethyl isophthalic	121	5	S.T.	S.T.	S.T.	S.T.
		10	V.S.T.	2	....	2
		20	Dry	4	....	8
		25	S.T.	....	8	....
		30	S.T.	....	8	....

[a] T = tacky, S.T. = slightly tacky, and V.S.T. = very slightly tacky.

ingredients as above and 50 g. of xylene. After 1.5 ml. of water had been removed during the polymerization of the 9,10-dihydroxystearic acid, the anhydride was added. The reaction was continued until a total of 2 ml. of water (0.11 mol) had been collected. The resin was cooled. The cure time at 200°C. was 5 sec.

Preparation of Polyester/Isocyanate Films. Solutions of the resins were prepared and analyzed for solids content (N.V.M.). The requisite amount of toluene-2,4-diisocyanate was dissolved in 5-g. quantities of the solution. Films of the mixture were flowed on tin plates immediately and allowed to cure at room temperature for 2 days. The films were stripped from the panels by a simple amalgamation technique and examined. The amalgamation technique involved the immersion of one end of the panel in a small amount of mercury (to about $\frac{1}{4}$-in. depth), until the tin plate was amalgamated and the film could be easily removed from the panel. The data are presented in Table II.

The polyester resins for tests that are summarized in Table III were prepared by Process A. The polymerizations were conducted until a probe sample demonstrated a desired cure time. The resins were cooled and employed for the preparation of the test solutions. Twenty-five grams of the resin were dissolved in a mixture of 25 g. of xylene and 2 g. of butylcellosolve. Additional xylene was added as required to completely dissolve the resin in some cases.

The solutions were analyzed for solids content. Weighed quantities of toluene-2,4-diisocyanate were mixed with weighed samples of the solutions and they were used to cast 3 mil films on glass plates. The films were cured at room temperature in air.

Preparation of Pigmented Polyester/Isocyanate Films. A typical maleic resin was pigmented with titanium dioxide and mixed with 20% by weight of toluene-2,4-diisocyanate. Test panels prepared by casting 3 mil films showed excellent gloss. These films withstood the $\frac{1}{8}$-in. mandrel test and at least 30-in.-lb. impact. The Sward hardness was 20. After $2\frac{1}{2}$ years the films show the same properties.

Discussion

In the presence of litharge, water was readily removed by heating 9,10-dihydroxystearic acid and the product gelled on continued heating. The quantity of water obtained indicated that somewhat less than one molar equivalent was expelled. Essentially the same quantity of water was evolved when maleic anhydride and dihydroxystearic acid were condensed simultaneously. When maleic anhydride was added to prepolymerized 9,10-dihydroxystearic acid very little water was subsequently eliminated.

When the reactions were stopped just before the gel stage, soluble hydroxylated resinous products were obtained.

Processing times for the maleic resins were shorter than for the phthalic, chlorendic, and dimethylisophthalic resins (Table I).

The polyesters obtained by the various preparative methods described showed no significant differences either in their physical properties or the properties of the films prepared from the resin-diisocyanate mixtures (Table II).

The films cured with 20% by weight of diisocyanate showed the best properties and were cured dry in 24 hr. Less crosslinking agent was generally unsatisfactory, 10% giving very long cure times and 5% giving films which did not cure tack free. Larger amounts of diisocyanate led to brittle films (Table III).

It is interesting that the optimum quantity of the isocyanate for satisfactory film curing was essentially the same for each of the resins investigated. Moreover the quantity of isocyanate (20%) suggested that the resin contained an unusually large quantity of free hydroxyl groups. The stoichiometry of the reactions involved and the small quantity of water evolved during the condensation suggested that the product must also contain an appreciable quantity of free carboxyl groups. Electrometric titration of one of the polyesters prepared from 9,10-dihydroxystearic acid and maleic anhydride in 80% ethanol showed this to be true. It titrated as a monobasic acid (pK ≅ 7.2, N.E. = 386).

REFERENCES

1. Bruson, H. A. (Rohm and Haas), U. S. Patent 1,815,886 (1931).
2. Mori, S., Plastics Kogyo (Osaka) *9*, No. 1, 11–14 (1940); Chem. Abstr. *36*, 187 (1942).
3. Knight, H. B. (Secretary of Agriculture), U. S. Patent 2,613,157 (1952).
4. Gardner, H. A., and Sward, G. G., "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," 11th ed., Henry A. Gardner Laboratory Inc., Bethesda, Md., 1950, p. 395.

[Received April 7, 1960]

The Extraction and Constitution of Peat Wax. A Review of Peat Wax Chemistry

A. J. HOWARD and D. HAMER, Department of Industrial and Forensic Science, Ministry of Commerce, Belfast, Northern Ireland, and Chemistry Department, the College of Technology, Belfast

EXTRACTION of peat with organic solvents produces a crude dark-colored wax in about 5 to 15% yield. Interest in such extracted waxes has arisen for two reasons: (1) the fact that peat can be regarded as a precursor of coal suggests that a comparison of extracts obtained from peat with those obtained from coal might yield interesting information on the mode of formation of coal, and (2) the close similarity between peat and lignite suggests that extracts of peat might have properties and industrial uses similar to montan wax and its derivatives. It was particularly with this second aspect in view that a detailed examination of the extraction of peat wax has been carried out in the laboratories of the Department of Industrial and Forensic Science, and coupled with this, an examination of the chemical nature of the wax. This paper presents a review of earlier studies on the extraction and chemistry of peat wax and the related montan wax.

Peat—Its Formation and Occurrence

Peat is a term used to describe the material produced by the incomplete decomposition of vegetable matter either under water, or in the presence of water, under anaerobic conditions. The texture and uniformity of peat depends upon the conditions under which it was formed, and upon the nature of the vegetation which contributed towards its formation. Although the accumulation of living, dead, and partially decomposed vegetable matter usually known as "bog" contains a very large number of species of plants, only a comparatively small proportion of this number has supplied the bulk of the contents of bogs. Prominent among peat-forming plants are: mosses such as *Sphagnum* and *Hypnum*; marsh plants such as *Nymphaea* and *Calla*; heath plants including several species of *Erica* and *Vaccinium*; grasses, rushes, sedges, ferns, algae; marine plants such as *Phragmites, Scirpus,* and *Equisetum;* the leaves of trees and sometimes their trunks and roots.

Peat in its natural state ranges in color from yellowish brown to jet black. A freshly cut surface of raw peat usually tends to darken on exposure to the air. The most characteristic feature of peat in its natural state is its high moisture content which may rise to 97%, a range of 92 to 95% being commonly encountered.

As would be expected from the nature of the processes involved in the formation of peat there is considerable variation in its chemical composition. Some typical figures quoted by Miller (1) for Irish peat are shown in Table I.

TABLE I

Ultimate Analysis of Irish Peat

	Percentage of dry weight
Ash	1.5 – 5.0
Carbon	50.0 – 62.0
Hydrogen	3.0 – 7.0
Sulphur	0.15 – 0.6
Nitrogen	0.5 – 1.7
Oxygen	30.0 – 38.0

The organic constituents of peat are essentially the substances present in the plants forming the peat together with their decomposition products, and the material obtained when peat is extracted with organic solvents has been called variously peat bitumen, peat wax, or crude peat wax.

Crude Peat Wax

Crude peat wax is regarded as consisting of three main components, namely, asphalt, resins, and wax, although there are very many different methods of fractionation into these groups. For example a recent definition of the terms used in this connection is that of Boyd-Barrett and co-workers (2). They regard the resins as highly polar compounds readily absorbed by activated earths because of polar groupings and extractable from the crude wax by virtue of their solubility in cold methyl or ethyl alcohol. The term wax is reserved for the fraction soluble in light petroleum, and miscible in all proportions with paraffin. The asphalt fraction derives its name from its insolubility in light petroleum; the definition of asphalt in the petroleum industry, for example, is any substance present in petroleum, other than inorganic constituents, not soluble in such solvents.

In addition to Boyd-Barrett several workers have published schemes for the separation of the crude wax into resin, wax, and asphalt fractions which have been