Experimental

Reaction of Glycidyl Stearate with Stearic Acid. Into a 500-ml. flask were charged 60.1 g. (0.177 moles) of glycidyl stearate (4), 25.2 g. (0.885 moles) of stearic acid, and 250 ml. of anhydrous xylene. The reactants were heated at reflux for 28 hrs. On standing over-night, a white, powdery material (38.8 g., m.p. 76–77°C.) precipitated out. Fractional crystallization of the mother liquor, followed by further purification of the two major components by crystallization from acetone and ether yielded 34.0 g. (61.6% of theory) of the 1,3-distearin [m.p. 78–79.5°C., reported 80.2°C. (3)] and 14.4 g. (26.2% of theory) of the 1,2-isomer [m.p. 66–68°C., reported 68.0°C. (3)]. Data obtained with these compounds are reported in Table I.

TABLE I

Compound	Saponification value	Acetyl value	% Carbon	% Hydrogen
1,3-Distearin	175.1	86.0	74.95	12.23
1,2-Distearin	175.0	84.0	75.07	12.19
Theory	179.5[a]	84.1[a]	74.92[a]	12.26[a]

[a] Calculated from $C_{39}H_{76}O_5$, molecular weight, 624.61 g.

Reaction of Glycidyl Palmitate with Palmitic Acid. A similar experiment was performed, using 62.3 g. (0.2 moles) of glycidyl palmitate (4), 25.6 g. (0.1 moles) of palmitic acid, and 250 ml. of anhydrous xylene. Following the reflux period and after standing over-night at room temperature, 20.0 g. of 1,3-dipalmitin [m.p. 71–72.5°C., reported 73.2°C. (3)], separated. The mother liquor, after a series of fractional crystallizations, yielded an additional 9.8 g. of the 1,3-dipalmitin, a total yield of 29.8 g. (52.4% of theory), and 11.6 g. (23.9% of theory) of the 1,2-isomer [m.p. 60–61°C., reported 62.8°C. (3)]. The constants of these compounds are reported in Table II.

TABLE II

Compound	Saponification value	Acetyl value
1,3 Dipalmitin	196.5	94.5
1,2 Dipalmitin	198.0	88.7
Theory	197.2[a]	91.8[a]

[a] Calculated from $C_{35}H_{68}O_5$, molecular weight 568.53 g.

The p-bromobenzoate derivative of the 1,2-dipalmitin was prepared by direct esterification, according to the method of Daubert and King (5), (m.p. 69–71°C., reported, 69°C.).

Infrared Spectra. A difference in structure between isomeric diglycerides was observed by means of infrared absorption curves, obtained with a Perkin-Elmer Model 21 infrared spectrophotometer. The settings used were: resolution, 927; suppression, 2; gain, 5; response, 1; and speed 2μ/min. All spectra were obtained in carbon tetrachloride at concentrations of 50 mg./ml. with an absorption cell (NaCl) 0.50 mm. in path length. The same solvent was added to a matched cell placed in the reference beam, eliminating the absorption of the carbon tetrachloride.

The absorption curves of all the compounds were almost identical with the exception of the C–OH deformation region. The spectra of the 1,2-isomers showed a strong peak at 9.50μ, indicating the presence of a primary hydroxyl group. These peaks were absent in the absorption curves of the 1,3-isomers. Instead weak peaks were found at 9.64μ, indicating the presence of a secondary group.

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Alkyd Resins from Fumaric and Maleic Modified Pine Oleoresin

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Fumaric and maleic modified pine oleoresin can be used to prepare oil modified nonphthalic alkyd-type surface coating vehicles. These vehicles may find use in trim enamels, concrete maintenance paints, and as a fortifier for linseed oil exterior paints. Processing of these resins requires that the temperature be raised to 285°C. for 1 to 1.5 hours and then lowered to 265°C. for a time during the procedure. Fumaric modifications may hold some advantages over maleic modifications. Clear films formed from these resins are characterized by good hardness, flexibility, adhesion, toughness, gloss, and color retention. The shorter oil length resins exhibit these properties to the greatest extent.

FUMARIC ACID and maleic anhydride both react with pine oleoresin to form complex polyfunctional resinous materials useful in the production of nonphthalic alkyd-type surface coating vehicles (3). These resins could be conveniently and economically produced by pine gum processors and may be commercially available in the future. Coating resins have been prepared from various products of maleic anhydride and fumaric acid with terpenes and with resin acids and rosin and are reported in numerous patents. Littmann (4) gives the chemistry and reactions of terpene-maleic resins and describes their unique properties as used in alkyd resins. Alkyd resins prepared from modified whole oleoresin have not been reported.

The resins reported here could be considered to be intermediate between oil modified phthalic alkyds and oleoresinous varnishes and should be competitive with either, being superior to both in some respects. These resins should be suitable for use in trim paints, fortifying linseed oil exterior paints for wood, and in com

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TABLE I

Drying Time and Hardness of Oil-Modified Alkyd Vehicles from Pine Oleoresin

No.	Polyol	Oil	Gal. length	Color[a]	Drying time (hours)		Sward hardness (hours)						30 Days
					Set to touch	Tack-free	24	48	72	96	120	163	
Maleic modified oleoresin													
1	Glycerol	Linseed	20	5–6	2	16	10	14	....	24	24	22[b]	....
2	Glycerol	Linseed	25	5–6	1	42	6	10	....	18	18	18	18
3	Glycerol	Lin-tung[c]	25	5–6	3	21	....	12	18	18	....	18	22
4	Glyce-penta	Linseed	20	5–6	4	16	10	12	14	16	....	28	28
5	Penta	Linseed	20	5	1	16	....	....	....	18	22	22	22
6	Penta	Linseed	25	5–6	....	19	6	12	....	18	22	22	26
7	Penta	Lin-tung[c]	25	5–6	4	16	12	14	16	18	....	30	....
8	Penta	Soybean	15	6–7	1–1.5	26[d]	2[d]	....	24	22	22	20[b]	30[e]
Fumaric modified oleoresin													
9	Glycerol	Linseed	20	5–6	4	20	8	12	14	16	....	28	....
10	Glycerol	Linseed	25	5–6	4	23	8	10	10	12	....	22	....
11	Glycerol	Lin-tung[c]	25	5–6	2	48	....	10	10	....	....	22	....
12	Glycerol	Linseed	15	7–8	1	19.5	14	....	28	28	26	24[b]	36[e]
13	Penta	Linseed	20	5	3.5	16	8	14	14	....	....	30	....
14	Penta	Linseed	25	5	3.5	16	10	14	14	....	....	26	....
15	Penta	Lin-tung[c]	25	5	2	16	10	14	18	20	....	24	....
16	Penta	Linseed	12.5	6–7	2	7	16	26	28	....	....	48	....

[a] Hellige color comparator. [b] Due to temperature and humidity conditions. [c] All linseed tung mixtures contained 90% linseed oil and 10% tung oil. [d] Due to thick film. [e] 10 days.

bination with chlorinated rubber for concrete floor enamels and maintenance paints.

Resins from both maleic and fumaric modified pine oleoresin, modified with linseed oil, linseed-tung mixtures, and soybean oil were prepared and tested for drying time, hardness, flexibility, water and alkali resistance, and color retention. Oil lengths of 12.5, 15, 20, and 25 gal.[2] were used. Glycerol and pentaerythritol were used as polyols.

Experimental

The fusion method of cook was used with the acidolysis technique. [Although Ellis (2) reports that very little ester interchange takes place between rosin or abietic acid and oils, considerably more acidolysis is expected with the modified pine oleoresins.] The modified pine oleoresin used contained 30 parts fumaric acid or 25.3 parts maleic anhydride (molar equivalent to the fumaric) per 100 parts oleoresin. Sufficient turpentine was added to the original oleoresin so that it contained 36% turpentine, which is the approximate turpentine content of commercially cleaned oleoresin (3). After experimentation, the following procedure was adopted.

The modified oleoresin and oil were charged to a 3-necked flask equipped with thermometer, stirrer, gas inlet, and Dean-Stark trap and condenser. The mixture was heated to 275°C. and held ½ hour. Ninety percent of the stoichiometric amount of glycerol (or 100% of the pentaerythritol) was added and the temperature held at 265°C. for about 1.5 hours, then raised to 285°C. and 10% of the stoichiometric amount of glycerol was added. The temperature was held at 285°C. 1 to 1.5 hours and any excess pentaerythritol was added at this temperature. The temperature was dropped to 265°C., and any excess glycerol was added and the mixture held at this temperature for desired viscosity and acid number. During the process an atmosphere of inert gas was maintained in the flask and the flask was swept with the gas periodically.

It was found that the higher temperature was necessary to obtain satisfactory acid values. (Ester gum is usually made at these temperatures.) It was further found that although the acid value dropped very little during the time the temperature was high, a great decrease took place after the temperature was lowered. It is postulated that an ester interchange takes place wherein the hindered rosin carboxyl groups are esterified at the higher temperatures at the expense of the monoterpene esters previously formed at the lower temperatures. Then, upon reduction of the temperature these monoterpene adducts reesterify if excess polyol is present. Supporting evidence for this is seen in the recovery of monoterpene-maleic adducts from the condenser and trap after some high temperature runs.

Solutions of the resins at 50% solids in mineral spirits and containing drier concentrations of 0.25% lead and 0.05% cobalt naphthenate were prepared. These solutions ranged in viscosity from C to N on the Gardner-Holdt scale, but most were in the range C to D, and films cast with the Baker film applicator set at a clearance of 3 mils gave a dry-film thickness ranging between 0.58 and 0.75 mils. Films were allowed to dry in the laboratory where the relative humidity underwent wide variation. The temperature averaged 79°F. Set to touch time was determined by the finger-touch method, tack free time by the foil tack tester described in ASTM designation D154–58 (1). Hardness was determined by the Sward Hardness Rocker. Results of the drying time tests are given in Table I.

Water and alkali resistance tests were performed by placing 3 or 4 drops of the reagent on a panel and covering the puddle with a 5 ml. beaker.

Flexibility, adhesion, hardness, and toughness were evaluated on steel and tinplate panels baked for one hour at 135°C. after set to touch dryness. Adhesion, toughness, and water resistance were evaluated on aluminum panels baked on the above schedule. For the flexibility tests, the steel panels (0.035 in.) were bent 90° over a ¼-in. mandrel. The tinplate panels (30–31 gage) were bent 180°, then creased and finally bent again at right angles to the crease. The adhesion and toughness were estimated by consideration of scratches made by the Gardner scratch thickness gauge. Comparative estimations are given in Table III.

Stability was evaluated according to the ASTM method for skinning tests for varnishes in closed con-

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[2] Number of gallons of oil used with 100 lbs. of resin (*i.e.*, alcohol + acid components).

TABLE II

Comparison[a] of Maleic Modified Oleoresin with Fumaric Modified Oleoresin in the Preparation of Oil Modified Alkyd Vehicles

Maleic modified							Fumaric modified						
No.	Gal. oil length	Cook time hrs. at °C.	Acid No. (solids)	Visc.[b]	% Excess polyol	Stability[d]	No.	Gal. oil length	Cook time hrs. at °C.	Acid No. (solids)	Visc.[b]	% Excess polyol	Stability[d]
1A[e]	20	6.0 /265–300	13.5	E–F	20.0G[c]	Hard gel 4 mos.	9A[e]	20	4.75/265–300	9.8	E–F	5.8G	Lt. med. gel 4 mos.
1	20	7.5 /250–285	9.5	C	14.9G	Good 4 mos.	9	20	6.5 /265–285	8.1	C	16.0G	Good 4 mos.
2	25	4.5 /265–300	10.1	C–D	20.0G	Hard gel 4 mos.	10A[e]	25	5.75/275–300	9.4	F–G	10.0G	Good 4 mos.
5	20	4.8 /275–300	9.0	D	12.0P[c]	Hard gel 4 mos.	13	20	2.75/275–290	9.5	C	5.5P	Good 4 mos.
6	25	3.25/270–300	13.0	C	13.7P	Hard gel 4 mos.	14	25	4.25/270–290	7.4	F–G	8.4P	Gel 4 mos.
3	25	5.17/250–300	10.6	C–D	17.5G	Light gel 4 mos.	11	25	6.75/270–300	9.0	E	10.0G	Good 4 mos.
7	25	4.25/260–295	12.8	D–E	13.7P	Hard gel 4 mos.	15	25	3.7 /250–300	7.8	C	10.0P	Good 4 mos.

[a] Maleic runs and fumaric runs on same line are comparable. [b] Gardner Bubble Viscometer at 50% solids in mineral spirits. [c] G = glycerol, P = pentaerythritol. [d] ASTM method for skinning tests for varnishes in closed containers. [e] A = the same formulation but a different run.

tainers (1). An evaluation of the relative color retention of the films was made on the baked films.

Results and Conclusions

Some observations can be noted for the series of resins tested. Most are apparent from a study of the tables. The resins responded normally to variations in oil length, type of oil, and type of polyol (Table I). Hardness was affected considerably by the amount of oil used in the modification. Greater oil lengths gave softer films. Substitution of 10% of the linseed oil with tung oil had only slight effect, improving the drying rate somewhat and increasing the hardness on some comparative tests. Soybean oil modifications show a considerably slower drying rate than the linseed oil modifications. Pentaerythritol gave resins with improved drying rate and hardness compared to those made with glycerol. Furthermore the total cooking time required for the pentaerythritol resins was considerably shorter, and the excess polyol used was less than for the glycerol resins (Table II).

There is a noticeable difference between products made from maleic modified oleoresin and those made from fumaric modified oleoresin (Table II). Resins made from fumaric modified gum have lower acid numbers and they show less tendency to gell on aging than those from maleic modified gum. The overall cooking time is less for some of the fumaric runs than for the corresponding maleic runs and in almost all instances less excess polyol was used for the fumaric runs. (It should be noted that in the fumaric runs that were cooked longer than the corresponding maleic runs, a satisfactory resin could have been made in the shorter time.) It has been stated (6) that the fumaric adduct of levopimaric acid gives alkyds of superior exterior durability to those of the maleic adduct. No exterior exposure tests on the vehicles reported here were made, but in view of the apparent processing advantages indicated above the fumaric resins might be the more desirable of the two.

Resistance to cold water was about equal for all resins tested. Water damage was manifested by minute blisters in the film and loss of adhesion to the glass. This became evident at about five hours of contact. If the water was then removed, the film regained its original appearance in 10 to 20 minutes. After 16 hours of contact, recovery was much slower and less complete. Appearance of the water-damaged spot, however, was little different from that of shorter exposures. Water spot tests on films baked on aluminum panels showed less damage on both 5- and 16-hour tests and more rapid recovery than tests of films on glass.

All films tested were equally poor in resistance to 3% NaOH. In the spot tests all films were completely removed by the alkali at room temperature in one to two minutes. Films baked on aluminum, however, showed improved alkali resistance.

Flexibility, adhesion, and toughness of the films were judged good. Baked films, bent 90° on 0.035-in. steel panels and 180° with creasing on 30–31 gage tinplate panels, showed no cracking or loss of adhesion at the bend. Table III shows comparative ratings for adhesion, flexibility, and toughness on some of the resins. This table shows that the shorter oil length (12.5 to 15 gal.) resins have the best properties. These baked films also show that the shorter oil length resins darken or yellow less on aging. The soybean-oil modified alkyd darkened least of all of those tested and the 12.5- and 15-gal. length linseed alkyds darkened only slightly more.

TABLE III

Flexibility, Adhesion, Toughness and Hardness Compared[a] for Some Representative Resins Baked on Steel, Tin, and Aluminum for 1 Hour at 135°C.

Resin No.	Steel		Tinplate			Aluminum	
	Flex.	Sward hard.	Flex.	Adh.	Tough.	Adh.	Tough.
4	4	34	....	....	....	3+	4
8	4	24	4	3	4	4−	4
9	4	28	4	3	4	....	....
12	4	20	4	3+	2	....	....
15	4	....	4	2	3	....	....
16	4	30	4	4	4	4	4

[a] Rated 1 to 4 where 1 is minimum properties and 4 is best.

The 15-gal. resins were found to be compatible in solution and film with medium bodied linseed oil. One of the resins has been tested and found compatible with chlorinated rubber (5). All of the resins reported here are soluble in mineral spirits.

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