The mercuric salts such as oxalate, benzoate, etc., were not tried. Neither were the higher homologs of oxalic acid, which are capable of forming cyclic mercuric salts with 6- and 7- rather than 5-membered rings.

Monomer Purfiication and Polymerization. EVE was removed from the transetherification mixture by evaporation at 100°C., first at atmospheric pressure and then under vacuum, and the stripped crude was distilled under vacuum. Products of equivalent purity were obtained with distillation pressures of 0.4 to 4 mm. A packed column gave distillates of the highest purity, usually 95 to 97%. A Vigreux column or a Claisen distilling head differed little in rectification ability and produced distillates of significantly lower purity. The Claisen head unit was much easier to operate. Fatty vinyl ether recovery approximated 85% with a packed column but was slightly higher with the Vigreux and Claisen head units.

The 23-mm. i.d. packed column contained 560 mm. of 1/8-in. ceramic Berl saddles while the Vigreux column was a typical 23-mm. i.d. unit with 17 sets of indentations spaced 25 mm. apart. The Claisen head had a 17-mm. i.d. x 200 mm. side arm tube. The three columns were operated at distillation rates of approximately 200, 115, and 230 g./hr., respectively, at about 2-mm. pressure and with a limited amount of reflux.

Various methods for purifying the linseed vinyl ether were compared because monomer purity directly influences the molecular weight and other characteristics of the polymer. The monomer was first purified by a single vacuum-distillation in a packed column containing 75 mm. of 1/8-in. Berl saddles, and the distillate was further purified by one of three methods. These were a second distillation in a Vigreux column, solvent extraction at 40°C. with an equal volume of anhydrous methanol, or an alumina adsorption treatment employing 1 g. of alumina per gram of monomer in a hexane solution. Polymers were prepared by the solvent polymerization technique, using a 6% solution of stannic chloride (6 ml. per 100 g. of fatty ether) as a catalyst (4). Monomer purities and molecular weights of the resultant polymers are given in Table I.

TABLE I
Influence of Monomer Purification Treatment upon Monomer Purity and Polymer Characteristics

Method of purification	Monomer purity	Polymer		
		Mol. wt.	Gardner viscosity	Gardner color
	%			
Single distillation	95.5	3700	X–Y	5–6
Redistillation of above	97.0	4650	W	1–2
Distillation and methanol extraction	97.7	3920[a]	X–Y	6
Distillation and alumina extraction	99.4	9350	Z_1–	2–3

[a] Molecular weight may have been reduced by a possible trace of methanol, which inhibits polymerization.

All monomers were of polymerization quality, and molecular weights of the polymers generally increased with the improvement in monomer purity. Although the molecular weight of the alumina-treated polymer was higher than normal, it illustrates the desirability of final monomer purification by alumina adsorption when the highest molecular weight is needed.

Subsequent exploratory studies indicated that polymerization conditions can be adjusted to produce polymers of higher molecular weight. By use of the best conditions, polymers that are satisfactory for a number of purposes should be producible from vacuum-distilled monomers.

Mercury Recovery. Free mercury was released from the linseed vinyl ether during the vacuum-distillation step and appeared in both the distillation flask and the product receiver. About 60% of the quantity used for the transetherification step at the 0.0250 molar level was recovered by a simple decantation.

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A Note on the Formation of 1,2-Diglycerides

S. B. RADLOVE,[1] R. V. MADRIGAL,[2] and R. SLUTKIN, The Glidden Company, Chicago, Illinois

The reaction of glyceryl esters with fatty acids has been demonstrated to form an equilibrium mixture containing the 1,2-isomer as well as the 1,3-isomer previously reported (2). This procedure offers a method of synthesizing simple or mixed 1,2-diglycerides.

HERETOFORE the synthesis of 1,2-diglycerides has been feasible only through the use of special blocking techniques because of their tendency to isomerize to the 1,3-isomer by acyl migration (1). The work of Kester (2) describes the preparation of 1,3-diglycerides (simple and mixed) by the reaction of fatty acid with glycidyl ester. In our preparation of some pure 1,3-diglyceride compounds by Kester's procedure we also found appreciable quantities of the 1,2-isomer in the reaction mixture, indicating that an equilibrium mixture exists. Thus we have been able to prepare useful quantities of 1,2-distearin (26% yield) and 1,2-dipalmitin (23% yield) by this simple procedure.

These findings are in accord with the recent work of Crossley *et al.* (3), wherein equilibrium mixtures were produced by heat treatment of either of the two pure isomers.

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[1] Present address: Continental Can Company, Chicago, Ill.

[2] Present address: Northern Utilization Research and Development Division, U.S.D.A., Peoria, Ill.

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

NOAH J. HALBROOK, JOHN A. WELLS, and RAY V. LAWRENCE,
Naval Stores Research Station,[1] U. S. Department of Agriculture, Olustee, Florida

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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[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.