

Analyses of Samples

A chromatogram of tall oil fatty acid esters using a hot-wire filament instrument is shown in Fig. 1. The complete separation of the stearate from the oleate peak should be noted, as well as the appearance of an unknown peak between oleate and linoleate. As columns of ethylene glycol succinate age, this excellent degree of separation is lost. However, continuous operation of such columns at 190C has been found satisfactory for about 1 mo.

Certainly, a more stable column material with the resolution of EGS, would be very helpful for the analysis of fatty acid methyl esters. The peaks which are not identified in the chromatogram are compounds for which positive identifications have not been made. Preliminary results from identification work indicate that all peaks with retention times longer than for methyl stearate are probably isomeric C_{18} compounds. Many samples of tall oil fatty acids contain a third unknown compound eluted after the two unknowns past methyl linolenate.

Analyses of the same tall oil fatty acid samples using both the hot-wire filament detector and the beta-ray ionization detector are shown in Table IV. The sample was esterified and then 31.3 parts of methyl margarate per 100 parts of sample were added. The instrument conditions used were the same as those used for the standards.

The total fatty acid content by the internal-standard method was 98.9 weight % for the hot-wire filament detector and 98.1 weight % for the beta-ray ionization detector. The relative deviations for the major components, methyl oleate and methyl linoleate, were 2.9% and 3.6%, respectively, based on the Aerograph results. The major difference in the analyses appeared in the methyl stearate results.

A number of tall oil samples from various sources was analyzed, and the total fatty acid contents ranged as low as 85 weight %. The use of the total-area method for samples with a low content of fatty acids leads to large errors. This is particularly true if the unsaturated acids have undergone any degree of oxidation.

Discussion of Results

The rapid oxidation of unsaturated fatty acids and their esters makes their quantitative analysis difficult, regardless of the analytical method. The internal-standard method of analysis has the follow-

TABLE IV
Gas Chromatographic Analyses of Tall Oil Fatty Acids
Comparison of Hot-Wire Filament and β -Ray Ionization Detector

Methyl ester	Hot-wire detector			Ionization detector		
	Correc-tion factor	Reten-tion time, min	Weight, %	Correc-tion factor	Reten-tion time, min	Weight, %
Margarate*	1.000	24.8	(31.3)	1.000	21.4	(31.3)
Stearate	1.001	32.2	2.6	1.000	28.9	1.6
Oleate	1.011	37.7	53.7	1.000	32.7	52.1
Unknown	1.016	42.0	0.7	1.000	35.7	0.7
Linoleate	1.020	46.7	37.1	1.000	39.8	38.5
Unknown	1.025	52.5	1.6	1.000	43.9	1.5
Linolenate*	1.032	60.5	1.8	1.000	51.8	2.1
Unknown	1.037	65.7	0.2	1.000	56.1	0.6
Unknown	1.042	70.5	1.2	1.000	60.3	0.9
Unknown	1.055	85.0	Trace	1.000	76.2	0.1
Total			98.9			98.1

* Internal standard.

* NOTE: Subsequent work on the peak material identified as methyl linolenate has been done. Sufficient material was obtained from a preparative gas chromatographic unit to permit infrared, ultraviolet, and nuclear magnetic resonance studies. This material is now identified as a conjugated, *cis-trans*-methyl linolenate. The position of the unsaturation has not been determined.

ing advantages: (a) it is not necessary for all compounds in the sample to appear in the chromatogram to obtain reliable results, and (b) if unsaturated samples have oxidized, the analysis will indicate this by giving low results.

Based on analyses of the standard mixtures of fatty acids, the accuracy for oleic and linoleic acids, the major components of tall oil, was better than 2% relative on duplicate determinations. The accuracy for compounds present in low concentration was 4% relative, based on the stearic acid content of the standards.

The accuracy of the sample analysis is no doubt less than the accuracy obtained for standards, since the samples contain several unknown compounds in low concentration.

The relative accuracy for the hot-wire filament detector and beta-ray detector was the same. The beta-ray detector had the advantage of not requiring correction factors.

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Alkyd Resins Modified with Cyclic Fatty Acids. A Preliminary Evaluation¹

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Alkyd resins were modified to 50% oil length with crude, flash-distilled, and 78% pure cyclic fatty acids. These resins were compared with ones modified with naturally occurring fatty acids and with vegetable oils. Those modified with the cyclic acids process more rapidly than those prepared with linseed, safflower, or soybean fatty acids, and they also have good nonyellowing properties. Resins modified with 78% pure cyclic acids show definite improvement in drying time, hardness, and chemical resistance in air-dried films, and an almost equal improvement in baked

films, over resins obtained with the other modifiers. Distilled cyclic acids also improve alkyd resins although not to the extent that pure acids do. Both give resins superior to commercial oil-modified resins under the test conditions. Resins with crude cyclic acids are as good in air-dried films as are the others, but are poorer in baked films.

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RECENT RESEARCH at the Northern Laboratory has led to new cyclic fatty acids prepared from linolenic acid and from linseed oil (2,7). These acids have many interesting properties. We have been seeking new industrial applications for them.

Modification of alkyd resins with fatty acids is a well-known process (3). Such modification alters the properties of the resin with respect to drying time, hardness, and the like. The degree of alteration depends upon the kind of modifying acid used and the quantity of acid, expressed as oil length.

We have prepared alkyd resins modified with crude, flash-distilled, and 78% pure cyclic acids. Preliminary comparisons have been made with alkyds modified with linseed, soybean, and safflower fatty acids, and with commercial resins modified with safflower and soybean oils. The cyclic acids resins process faster than the natural acid resins and also show good non-yellowing characteristics. Films from the resin modified with 78% pure cyclic acids are generally superior to films from the other resins with respect to drying times, hardness, and chemical resistance; the resins modified with distilled cyclic acids are almost as good. Crude cyclic acids give resins which are good in air-dried films but give poorer baked films.

Experimental

Cyclic fatty acids were prepared by the Engineering and Development Laboratory by alkali cyclization (2). "Crude" cyclic acids were obtained by acidification and removal of solvent from the crude cyclization mixture. "Distilled" cyclic acids were obtained by flash distillation of crude acids to remove dimeric and polymeric materials. The 78% pure cyclic acids (hereafter referred to as "pure") were prepared from distilled acids by removal of the noncyclic materials as urea inclusion complexes (9). Analysis of the pure acids used in this study is given in Table I. Linseed, safflower, and soybean fatty acids were prepared from the corresponding oils by standard procedures.

TABLE I
Analysis of 78% Pure Cyclic Fatty Acids^a

Iodine value, Wijs.....	127.8
Iodine value, rapid Wijs.....	133.7
Neutral equivalent.....	290.7
Cyclic acid content (determined by hydrogenation and crystallization).....	78%

^a Obtained by separation of noncyclic material as urea inclusion complexes from distilled cyclic acids.

TABLE II
Alkyd Resin Formulation

Phthalic anhydride.....	33.9%	91 g.
Glycerol.....	21.1%	57 g.
Fatty acid.....	45.0%	121 g.
Total charge.....	269 g.
Ester-H ₂ O.....	-19 g.
Theoretical yield.....	250 g.
Mineral spirits.....	15 ml ^a

^a More solvent was added if needed for efficient processing.

TABLE III
Processing and Properties of Modified Alkyd Resins

Modifying acids	Processing time, 220-230C, min	Gardner-Holdt viscosity	Acid value ^a
Pure (78%) cyclic.....	128	X ⁺ ^b	18
Distilled cyclic.....	65	Z-1	19
Crude cyclic.....	38	Z-5	21
Linseed.....	323	Z-1	8
Safflower.....	265	X ⁺	11
Soybean.....	302	X ⁺	8

^a Based on solids.

^b Contains 50% solids in xylene; all others in mineral spirits.

The formulation (4) given in Table II was used to prepare alkyd resins of 50% oil length by the solvent technique (1). Table III gives their processing characteristics.

Resin solutions containing 50% solids in mineral spirits (except for the resin modified with pure cyclic acids which was made up in xylene) were made up for use in evaluations.

Yellowing was determined on the resins by the accelerated yellowing test method of Privett, Blank, and Lundberg (6), somewhat modified. To facilitate even distribution on filter paper, resin solutions were diluted to 25% solids. The equivalent of 50 mg of solid was applied to rectangles of filter paper, which were dried overnight under vacuum in the dark at room temperature. The filter-paper films were then placed in loosely covered Petri dishes in a forced-draft oven at 50C. Reflectance measurements at 520 and 650 m μ were made at intervals on a Beckman model DU spectrophotometer.

Drying times, Sward hardness, and chemical resistance tests were performed on films cast from 50% resin solutions. A drier consisting of 0.3% lead and 0.03% cobalt was used. Both air-dried and baked (0.5 hr at 150C) films were tested. Drying times were determined at room temperature by the sand-trails method described by Schwab, Teeter, and Cowan (8). Chemical resistance tests were run with water and with 1% and 5% NaOH. Films were drawn down (doctor blade) to 5 mils wet thickness on 4 x 8 in standard steel "Q" panels (The Q-Panel Company). After drying, approximately 0.2 ml of test solution was placed on the film, and a watch glass (No. 1 $\frac{1}{2}$) was inverted over the drop. The edge of the watch glass was sealed with wax to prevent evaporation. During the first 8 hr observations were made hourly and at 24-hr intervals thereafter. Films were considered to have failed when they showed definite signs of dissolution.

Results and Discussion

In Table III, which gives processing characteristics and properties of alkyd resins modified with crude, distilled, and pure cyclic acids, data are also given for resins modified with linseed, safflower, and soybean fatty acids. The processing was planned to obtain a predetermined viscosity, but the time required for sampling, quenching the reaction, and the other steps, made viscosities less uniform than we had visualized. Additional experience with the technique should permit resins to be made that have almost any viscosity desired. Processing times for alkyd resins modified with cyclic acids were all much shorter than those for resins modified with natural fatty acids. Because of short processing times, resins modified with cyclic acids had fairly high acid values. By changing the resin formulation, these values may be lowered when necessary. The very short time for the resin modified with crude cyclic acids is possibly due to the presence of dimer in the crude mixture. Viscosities were determined in mineral spirits, except for the resin modified with pure cyclic acids. Since this resin was insoluble in mineral spirits, xylene was used as the solvent. This change in solvent made comparable viscosity measurements difficult, which complicated processing control.

The accelerated yellowing test, developed for use with relatively homogeneous materials such as oils or fatty acid esters, gives, with such materials, a fast-rising, sharp-breaking curve when the differences in

optical density are plotted against time. When this test is used with a typical alkyd resin, the curve becomes a straight line (Fig. 1). These differences can be observed visually; for example, methyl linolenate yellows much faster than any alkyd tested. Since the point of departure from the axis, defined by Privett, Blank, and Lundberg (6) as the time of onset of yellowing, has no significance for the plot shown in Figure 1, another means of comparison had to be used. The slope of the lines obtained for different resins, by plotting differences in optical density against time, were found to be proportional to yellowing rates. When yellowing is sufficiently advanced to permit visual comparison, there is generally good agreement between visual and optical evaluation. Figure 2 compares rates of yellowing, as determined from these slopes, for resins modified with cyclic acids with those for resins modified with natural fatty acids and for two commercial resins modified with safflower and soybean oils. Small differences in yellowing should not be exaggerated, but a difference of one unit in these figures does represent a visible difference in yellowing. Variations in starting materials or processing could affect yellowing characteristics of the resins and could shift the relative values somewhat. However, Figure 2 shows that, at least for the present series of resins, those modified with cyclic fatty acids have good resistance to yellowing. Those modified with crude and with distilled fatty acids are either equal or superior to all the other resins tested. The resin modified with pure cyclic acids is superior to all but two of the others.

Conventional after-yellowing tests are in progress. After 6 mo, insufficient yellowing of the films prevents the making of reliable comparisons.

Drying times are given in Table IV. "Dry-to-touch" and "tack-free" times were determined at room temperature. Because the shortest dry-to-touch time without a drier was 7 hr for the resin modified with pure cyclic acids, data in Table IV are for resins containing a drier.

The resin modified with pure cyclic acids has the fastest dry-to-touch time, requiring less than 1 hr, and one experiment took only 23 min. Its tack-free time was 3.5 hr, which is somewhat slower than that for the resin modified with safflower fatty acids. Resins modified with distilled and crude cyclic acids had the slowest dry-to-touch times and required more than 22 hr to become tack-free. None of the resins developed after-tack. All the resins gave tack-free films on baking for 0.5 hr at 150C.

Sward hardness is also shown in Table IV for both air-dried and baked films. Of the air-dried films, the one from resin modified with pure cyclic acids is the hardest, followed by those modified with crude and distilled cyclic acids. Baking increases hard-

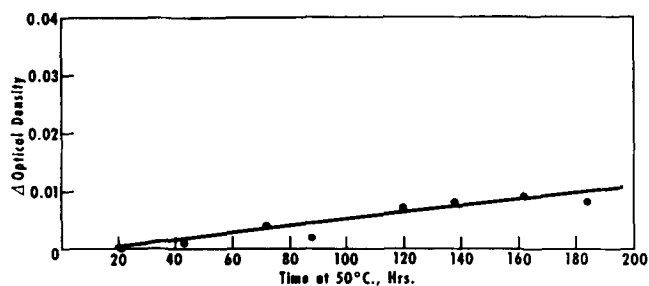


FIG. 1. Accelerated yellowing test on a typical alkyd resin.

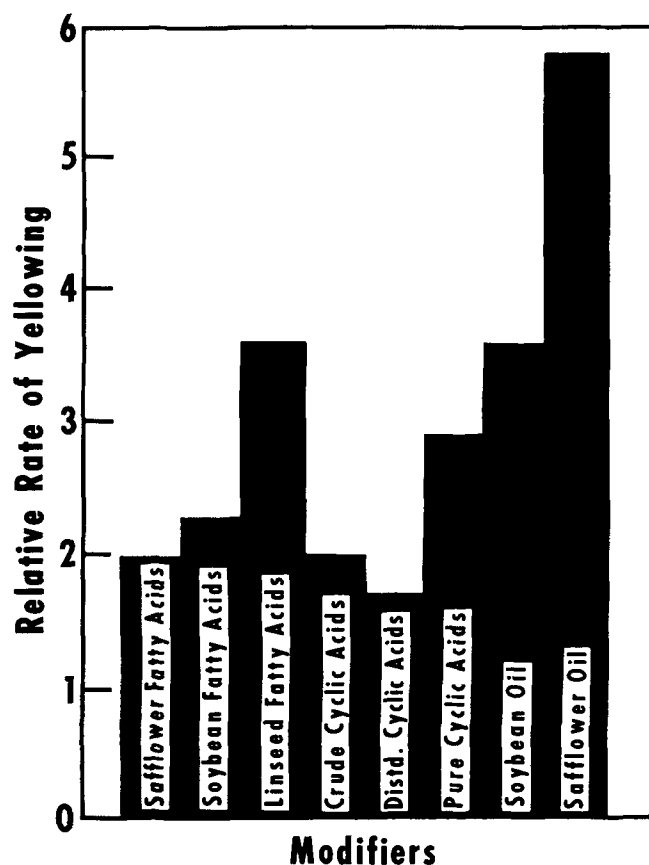


FIG. 2. Relative rates of yellowing of modified alkyd resins.

ness of noncyclic acid films considerably but changes the cyclic acid-modified films little, if at all. Consequently, film from resin modified with pure cyclic acids is softer after baking than film from resins modified with either linseed or safflower fatty acids. Baked films from resins modified with distilled and crude cyclic acids are the softest.

Resistance of baked films to water and to alkali is given in Table IV. All the films, except those from

TABLE IV
Properties of Films from Modified Alkyd Resins

Modifiers (0.3% Pb, 0.03% Co drier)	Drying times		Sward hardness		Time for failure of baked films, days			Cumulative rankings	
	Dry-to-touch, hr	Tack-free, hr	Air-dried film	Baked film	H ₂ O	1% NaOH	5% NaOH	Air-dried film	Baked film
Pure (78%) cyclic acids ^a	<1	3.5	20	24	>14	14	7	1	2
Distilled cyclic acids.....	3	>22	10	12	14+	14	7	5	3
Crude cyclic acids.....	3.5	>22	14	14	14+	7	2	4	5
Linseed fatty acids.....	1.75	3.5	10	26	>14	7	4	3	3
Safflower fatty acids.....	2	3	10	28	>14	14	14	2	1
Soybean fatty acids.....	2.25	4	8	18	>14	4	4	7	3
Safflower oil ^b	2	>22	2	20	8	8	1	8	4
Soybean oil ^b	2	>22	4	16	7	7	3	6	5

^a Films were drawn from solutions containing 25% solids in xylene; all others in mineral spirits.
^b Commercial resins, 65%, oil length.

the two commercial resins are about equally resistant to water. Only films from resins modified with pure and distilled cyclic acids and with safflower fatty acids remained resistant to 1% NaOH for 14 days. The film from the safflower fatty acid-modified resin retains its resistance (14 days) even with 5% NaOH. Although films from the two resins modified with pure and distilled cyclic acids are less resistant than this one, they are considerably more resistant than any of the others to 5% NaOH.

In summarizing results of evaluations on drying times, hardness, and chemical resistance, each resin was ranked for each test and individual rankings for each resin were added. The order of these sums is shown in Table IV. This summary shows that modification of the alkyd resins with pure cyclic acids definitely improves properties over those obtained with the other modifiers in air-dried films, and gives an almost equal improvement in baked films. Use of distilled cyclic acids also improves resins although not to the same extent as do pure acids. Both the pure and distilled cyclic acids give resins superior to commercial oil-modified resins under conditions of our tests. Crude cyclic acids are good in air-dried films but are poor in baked films.

Tests reported in this paper are preliminary evaluations and are not intended to be exhaustive. They represent a limited number of tests on a single formulation. Modification either of the formulation or of the resin, perhaps by a process such as styrenation (5), might further enhance the good properties imparted by pure and distilled cyclic acids and might also improve the utility of crude acids in alkyd resin modification.

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Analyses of Pecan, Peanut, and Other Oils by Gas-Liquid Chromatography and Ultra-Violet Spectrophotometry

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Comparative analyses of oils obtained from 12 varieties of pecans, 11 of peanuts, two of avocados and one each of citrus seed, Wesson oil, corn, and of lard by GLC and UV procedures showed good agreement except for Wesson oil, corn oil, and lard. Iodine values computed from GLC results checked Wijs values closely. Oleic acid ranged from 51 to 77% in pecans and from 43 to 64% in the peanut with linoleic acid in complementary percentages.

Level of palmitic acid in the peanut varied directly with level of linoleic acid, in the avocado it apparently varied directly with level of hexadecenoic acid while in the pecan the level of palmitic remained constant even though the level of unsaturated acids varied widely. Both peanuts and pecans were locally grown under similar environmental conditions.

INFORMATION on the composition of certain natural oils was needed for an experiment designed to test cholesterologenic effect of oils in diets on rat blood serum. Analyses were made on the oils by methods of gas-liquid chromatography (GLC) and by ultra-violet (UV) spectrophotometry. Analyses by the two procedures were compared on oils expressed in the laboratory from 11 varieties of peanuts, 12 of pecans, 2 of avocado, and on market purchased samples of citrus seed oil, Wesson oil, corn oil, and lard.

Apparatus and Methods

Gas-liquid chromatograms were obtained with an A-100 Aerograph using a 4-filament thermal sensitive cell with an oven temperature of 200C and a gas flow rate of 60 ml/min of helium. One to 3 lambda, the volume depending upon the oleic acid content of the sample, of a 20% solution of the fatty acid methyl-esters (1d) in benzene was placed in the heated injection

chamber. Passage through a 5-ft. column packed with 10% Lae 446, a glycol adipate polymer, on 30-60 mesh firebrick gave sharply shaped curves for the methyl esters of the fatty acids with 14 to 20 carbons in their chains. The area under each curve was computed by multiplying the height of the peak by width at middle height and ascribed to each fatty acid as indicated by the time it left the column.

Iodine values were determined by the Wijs method (2), and the polyunsaturated acids by the UV spectrophotometric procedure (3).

Samples

The oil samples were chosen from 12 popular varieties of pecans grown in north-central Florida, and from 11 varieties of peanuts which have been or probably will be recommended to growers (4). The pecans were purchased from an Alachua County merchant who handled locally-grown nuts. The peanuts, which included Spanish, runner, and Virginia types, were all grown on the Florida Experiment Station farm in 1958 under the same supervision and under the same environmental conditions. The pecan and peanut oils were cold pressed in a Carver laboratory press. The 2 avocado samples, supplied by a grower in the Miami area, were dried and the oil extracted with hexane. The citrus seed oil was a commercial Florida product. The Wesson oil, corn oil, and leaf lard were purchased in local stores. The lard organoleptically showed a trace of rancidity. All fats were kept frozen under prepurified nitrogen until analyzed.

Results and Discussion

The GLC analyses are given in Table I. The analyses of oils from the 11 peanut and 12 pecan vari-

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