Anionics. For the anionics tested, a decreasing order of effectiveness was sodium oleate, alkylbenzene sulfonates, and sodium lauryl sulphate (practically ineffective). Alkylbenzene sulfonates showed maximum soil removal at two pH levels: 3 to 4 or 11 to 12. None was particularly effective though the pentadecyl compound was superior to those of lower alkyl chain-length.

If the mechanism of fatty soil removal is one of displacement and if polarity of compound is important, the multiplicity of ether linkages of the nonionics may afford an explanation for their effectiveness.

Surfactant-Builder Mixtures. All surfactants tested were improved by STP admixture. Synergistic effects were found for 1:4 molar ratios of tridecanol-10 EO and STP, and slight synergism for dodecylphenol-5-, 10-, and 30-EO adducts. Of the alkylbenzene sulfonates tested, only the pentadecyl compound (1:2 ratio) showed synergism. However, without exception, admixture with STP improved soil removal over the surfactant used alone.

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[Received August 19, 1960]

Preparation and Properties of Esters of Monohydric Alcohols and Fatty Acids of Tall Oils[1]

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Esters of pure tall oil fatty acids and commercially available monohydric alcohols were prepared, distilled, and analyzed for pertinent values. The tall oil fatty acid fraction used in the esterification contained approximately 0.6% rosin acids with essentially equal distribution of fatty acids into oleic and linoleic acids. The use of various techniques, such as fast cooling by the addition of cold water to ester solution, vacuum topping before water washing, and/or use of carbon dioxide as a blanketing gas resulted in the production of light-colored ester products. These esters, low in acidic impurities and light in color, are another source of chemical intermediates for the preparation of plasticizers, cutting oils, hydraulic fluids, and lubricants.

THE PHENOMENAL INCREASE in the consumption of tall oil over the past 10 years is due mainly to the concerted efforts of the industry to improve, purify, and separate the rosin and fatty acid constituents and to convert these products into many useful derivatives. Tall oil fatty acids containing less than 1% rosin acids are now a reality and should be regarded as a mixture of essentially equal amounts of linoleic and oleic acids available for the preparation of many chemical derivatives. They, of course, readily undergo reaction at the carboxyl group to yield esters, amides, amines, soaps, etc.

This paper presents information on a series of monohydric alcohol esters prepared in the laboratory and pilot plant. We have endeavored to prepare esters of all commercially-available monohydric alcohols from methyl through eicosyl.

In this work it was realized that rosin acid impurities of the fatty acids do not esterify under normal conditions with low-boiling alcohols. This implies that tall oil ester products will always have an acid value equivalent to twice the percentage of rosin acids of the initial fatty acids.

The above has been advocated by a number of investigators as a useful method for the separation of the fatty and rosin acid constituents of crude tall oil. Christenson and Harpt (1) separate the components of crude tall oil by esterification of the fatty acids with methyl alcohol in the presence of sulfuric acid. Rosin acids are separated as soaps in a column employing extraction naphtha as the solvent for the methyl esters. Mayer, Jacini, and Jacini (2) also use methyl esters as a means of separating the abietic acids from the fatty acids of all oil. Distillation is the means of effecting the final separation. The patent by Freeman and Gloyer (3) proposes the fractionation of tall oil by selectively esterifying the fatty acids present and contacting the mixture with furfural or other polar solvent. Esterifying agents may be methyl, ethyl, propyl, isopropyl, butyl, or various glycols. Sulfuric acid was the catalyst employed in methyl ester preparation. Litharge was used in butyl and glycol esterifications.

Most of the work on esterification of tall oil reported in the literature is concerned with the preparation of polyol esters for drying oils. Very little information has been reported on exact procedures for the preparation of monohydric esters of fatty acids. Markley (4) states, "Although the method of esterification used in the preparation of the methyl and ethyl esters of the higher molecular weight fatty acids may be stated in the general terms indicated above, the details given in the literature are surprisingly variable." Eckey (5) reports that unsaturated fatty acids esterify more slowly than saturated fatty acids. He also states that rosin acids of tall oil esterify much more slowly than the fatty acids. A temperature of at least 75°C. higher is generally required to make the rosin acids esterify at a rate comparable with that of fatty acid. Konen *et al.* (6) found that direct esterification of fatty acid with alcohol will not go unless a strong acid catalyst is present. Water formed by the reaction must be removed to cause the reaction to go to completion. Althouse *et al.* (7) prepared methyl esters of C_6–C_{18} fatty acids by direct esterification with excess methanol and sulfuric acid as the catalyst. Propyl and isopropyl esters were

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[1] Presented at the 51st annual meeting, American Oil Chemists' Society, Dallas, Tex., April 4–6, 1960.

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prepared from the reaction of the respective alcohols with the fatty acid chloride in pyridine.

TABLE I

Chemical and Physical Characteristics of Tall Oil Fatty Acids

Acid value	196
Iodine value	127
Saponification value	197
Unsaponifiables, %	1.7
Titer, °C.	4
Color	2–3
Rosin acids, %	0.6
Composition of Fatty Acid Components	
Saturated acids, %	3
Oleic acid, %	51
Linoleic acid, %	46
Linolenic acid, %	Trace

Table I contains a listing of the various physical and chemical characteristics of the tall oil fatty acids used in the preparation of esters described in this work. It will be noted that the rosin impurities of the tall oil fatty acids have been reduced to a negligible amount. The almost equal distribution between oleic and linoleic acids implies a two-component reaction medium of 1½ units of unsaturation. It is therefore plausible to assume that tall oil fatty acids of this grade could be used satisfactorily in the preparation of ester derivatives where a prescribed amount of unsaturation is desired.

Experimental

Reactions were run in three-necked flasks equipped with stirrer, condenser, thermometer, and gas-dispersion tube. A Dean-Stark trap was used in all runs where the water of reaction could be removed by azeotropic distillation. In the preparation of methyl esters, excess methyl alcohol was used as a means of keeping the reaction medium sufficiently anhydrous to permit completion of the esterification.

TABLE II

Methyl Esters. Esterification of Tall Oil Fatty Acids

Run	Hours reflux	Methanol,[a] ml.	Sulfuric acid, ml.	Acid value
1	3	500	15	4.3
2	5	250	15	4.7
3	4	250	20	4.5
4	4.5	200	20	4.8
5	5	150	20	5.1

[a] Per mole (280 g.) fatty acids.

Data in Table II illustrates the effects of catalyst concentration and methyl alcohol excess upon the completeness of the reaction. Ordinarily we have followed a rule of using two milliliters of methyl alcohol for each gram of fatty acid. Concentrated sulfuric acid, as the catalyst, was used in percentages of 1.5 to 3% (based on weight of alcohol). The sulfuric acid was always added to the alcohol prior to mixing with the fatty acids. From these data it will be noted that a much smaller quantity of methyl alcohol functions equally well in the esterification, provided sufficient sulfuric acid is present to remove the water formed by reaction.

A similar set of experiments was also made to test the efficiency of a number of different catalysts as well as the required excess of methyl alcohol. In all runs the catalyst was first dissolved in the alcohol, then this solution was added to the flask containing the fatty acids. Samples were removed at regular intervals for the determination of acid value.

TABLE III

Methyl Esters. Esterification of Tall Oil Fatty Acids

Reaction mixture[a]	Acid Values After Various Reflux Times					
	Hours					Final color
	1	3	5	6	7	
Methanol 100 T.S.A. 1	34.6	17.1	15.3	14.7	12.1	6
Methanol 100 T.S.A. 2	25.3	14.0	10.0	9.0	8.0	5
Methanol 100 T.S.A. 5	16.0	8.0	7.0	6.0	6.0	6
Methanol 100 T.S.A. 2 Superfiltrol 2	29.0	13.0	12.0	11.0	9.0	6
Methanol 50 T.S.A. 2	49.0	31.0	27.0	24.0	20.1	5
Methanol 100 H_2SO_4 5	16.0	8.0	7.0	7.0	7.0	7
Methanol 100 H_2SO_4 10	12.0	8.0	7.0	6.0	6.0	7
Methanol 100 Naphthalene Disulfonic acid 2	33.0	19.0	18.0	15.0	15.0	6

[a] Fatty acids 200 g.

Data obtained in this work are listed in Table III and illustrate that esterification reaches equilibrium after heating at reflux for about 5 hrs. Toluene sulfonic acid (T.S.A.) appeared to have an advantage over concentrated sulfuric acid in producing lighter-colored products. One to 2% of the toluene sulfonic acid was all that was necessary to promote a fast and efficient reaction.

TABLE IV

Butyl Esters—Tall Oil Fatty Acids. Effect of Quantities and Catalyst on Rate of Esterification

Run	Parts			Acid Value			
				Hours			
	Alcohol	Fatty acid	Catalyst[a]	½	1	2	4
1	100	200	T.S.A. 1.0	69.0	43.0	15.0	9.0
2	40	140	T.S.A. 1.0	41.0	25.0	13.0	12.0
3	40	140	T.S.A. 0.25	48.0	29.0	8.0	1.6
4	40	140	T.S.A. 0.75	......	......	......	3.7
5	100	200	H_2SO_4 1.5	13.0	......	......	5.4
6	100	200	N.D.S.A. 0.5	120.0	......	107.0	95.0
7	100	200	HCl 12.0	No reaction			

[a] T.S.A.—Toluene sulfonic acid. N.D.S.A.—Naphthalene disulfonic acid.

Data concerned with the preparation of the butyl esters of tall oil fatty acids are listed in Table IV. Although butyl alcohol is listed as having a solubility of 7.9 g. per 100 g. of water at 20°C., it was an effective azeotrope and was very efficient in the removal of water from the reaction. The Dean-Stark water trap was generally filled with butyl alcohol at the start of the reaction. Here again it will be noted that the toluene sulfonic acid was the best catalyst of those tried. Naphthalene 1,5-disulfonic acid was very inefficient, and no reaction was obtained from the use of hydrochloric acid.

Interest was also expressed in the possibility of reducing the unsaponifiable and acidic content of the butyl esters by fractional distillation under vacuum. A simple distillation apparatus consisting of a ground glass, jointed flask equipped with a variable reflux ratio distilling head was used for this purpose. Distillations were made at a pressure of 3–5 mm. over a narrow range.

A series of cuts was made, and the materials were

TABLE V

Butyl Esters–Tall Oil Fatty Acids
Fractional Distillation

Fraction	B.R.[a] °C.	Acid value	Sap'n value	Unsap'n %	Color
Original	......	9.3	159	1.7	9
1	198–200	11.8	165	2.1	3
2A	196–200	8.6	162	1.4	2
2B	194–196	6.4	165	1.0	1
3	194–196	4.8	159	1.0	1
Residue	......	3.5	155	1.7	Black

[a] 3–4 mm.

analyzed. From data in Table V it is evident that both the unsaponifiables and acidic constituents boil sufficiently close to the butyl esters to make their separation difficult. The only apparent advantage distillation would have is in the removal of color bodies which concentrate in the residue.

The preparation of 2 ethylhexyl esters of tall oil fatty acids follows the procedure for the butyl derivative. These esterifications were run, using 1.1 mol of alcohol per mole (280 g.) of fatty acid. Toluene sulfonic acid catalyst (0.3%) dissolved in the alcohol prior to addition of the fatty acids produced esters with low acid values in 4–5 hrs. Reaction temperatures of 120–180°C. were necessary to promote satisfactory esterification. In general, the major portion of water was collected during the first 30–45 min. at a reflux temperature. As the excess of 2 ethylhexyl alcohol was used up in the reaction, the temperature increased to 180°C., at which time the reaction was complete as judged by the measurement of water collected in the Dean-Stark trap and the titrated acidity of the sample.

The finishing operation consisted in cooling the material in a flask, addition of water, followed by several water washes, and final vacuum treatment to remove excess alcohol and moisture from the product. During this finishing cycle it was noted that there was considerable darkening of the product.

Distillation of the esters in some instances resulted in the formation of gummy residues which clung tenaciously to the walls of the distilling flask. Difficulties in removal of these gum deposits from plant equipment would create problems in large-scale operations.

Data listed in Tables VI and VII are concerned with methods for the elimination of gummy residues and the preservation of colors of esters during cooling from reaction temperature. It will be noted that a number of treatments were beneficial in yielding a light-colored product. The use of nitrogen gas did not function as well as carbon dioxide as the inert media. Use of carbon dioxide as a blanketing atmosphere rather than bubbling through the reaction mixture gave a lighter-colored product. Anthraquinone (0.1%) in the mixture of alcohol and fatty acids prior to reaction produced a lighter-colored ester than when this antioxidant was added to the ester before purification treatment of water washing, distillation of excess alcohol, and drying. Di-tert-butyl-p-cresol (D.B.P.C.) was not as effective as anthraquinone. When the ester product was cooled rapidly, it was noted that there was less darkening than when the reaction mixture was allowed to cool slowly to room temperature. The addition of cold water to the hot ester solution was beneficial in retarding color degradation.

TABLE VI

2-Ethylhexyl Esters–Tall Oil Fatty Acids. Production of Light-Colored Products

Treatment	Color		Bleach 1% Super-filltrol	Acid value
	Before vacuum	After vacuum		
Nitrogen sparge	7	10	8–9	4.0
Fast cooling	7	9	7–8	3.0
Add'n H_2O at highest temp.	6	8	6	4.0
Anthraquinone before reaction	6	8	6	4.0
Anthraquinone after reaction	7	8	7	3.0
D.B.P.C. before reaction	7	8	6	3.0
D.B.P.C. after reaction	8	9	7	4.0
Superfiltrol, 1% in reaction	10	11	10	3.0
Blanket instead of sparge CO_2	6	8	6	4.0
No washing before vacuum	....	7	6	2.0
Xylene azeotrope	....	10	7[a]	6.0
Regular procedure	....	11	6[b]	4.0

[a] Bleach 2%. [b] Bleach 3%.

TABLE VII

2-Ethylhexyl Ester–Tall Oil Fatty Acids.
Treatment to Prevent Darkening

Treatment[a]	Ester		Distillates color		
	Acid value	Color	Initial	Middle 85%	Residue
Superfiltrol, 2%	4.0	10	5	2	Black
Powdered carbon, 2%	2.6	3–4	3	W.W.	18+
Powdered carbon, 0.5%	5.2	4–5	3	W.W.	Black
Granular carbon, 2%	3.4	4–5	4	W.W.	Black
Granular carbon, 0.5% and superfiltrol, 0.5%	4.0	6	3	W.G.	Tan
Powdered carbon, 0.5% and superfiltrol, 0.5%	4.1	6	4	W.W.	Black
None	5.1	5	4	W.G.	Black

[a] Reaction temperature 120–180°C. for 4½ hrs.

Again however the use of high temperature and vacuum during removal of unreacted alcohol caused a darkening of the ester product. Bleaching at 110°C. with 1% Superfiltrol generally restored color to that of the ester before vacuum purification. When Superfiltrol was introduced as an ingredient of the esterification mixture, there was rapid darkening of the solution during the first hour of reflux. One effective way of producing a light-colored ester was to pull the vacuum directly on the reaction mixture to remove excess alcohol and volatile materials, then cool under vacuum, and finally water-wash and dry under slight heat and vacuum. Bleaching of this product with 1% Superfiltrol also was beneficial in reducing color.

Interest in the production of ester products which would distill readily to yield light-colored fractions and also yield a residue which could be easily drained and cleaned from the still pot prompted the following investigation. In this series either Superfiltrol or carbon, or a combination of both, was added in the initial charge before esterification. Table VII lists the results from this work and illustrates the effects of carbon in producing light-colored products. Superfiltrol appeared to cause a darkening of the ester. Distillations were made under vacuum, using a simple distillation apparatus consisting of Glascol heating mantle and a ground glass, jointed flask equipped with variable reflux ratio distilling head. Distillations were regulated to remove a 5% heads cut and an 85% middle fraction and to leave about 10% residue. As will be noted from Table VII, most of the color bodies remained in the residue. However middle fractions water-white (WW) with colors less than Gardner 1 were obtained in all runs where powdered carbon in amounts of 0.5% or greater was used in the esterification reaction. Superfiltrol was instrumental in ad-

TABLE VIII

Chemical and Physical Characteristics of Monohydric Esters—Tall Oil Fatty Acids

Ester	Boiling range °C. @ 2–4 mm.	Acid value	Sap'n value	Iodine value	Refractive index (20°C.)	Gardner color	
						Initial	Distillate
Methyl	156–160	3.0	187	118	1.4581	4	1
Butyl	182–188	3.2	163	105	1.4593	5	1
Amyl	187–190	1.7	160	99	1.4587	7	1
n-Pentyl	183–187	3.6	161	100	1.4590	10	1
n-Hexyl	185–189	2.6	155	94	1.4596	6	1
Iso-hexyl	216–223	2.5	155	94	1.4600	4	1
2-Ethylhexyl	224–230	2.6	142	90	1.4600	5	1
Iso-octyl	216–218	1.0	145	88	1.4600	6	1
n-Decyl	214–220	1.0	135	80	1.4620	7	1
Isodecyl	195–200	5.4	128	84	1.4634	5	2
Tridecyl	220–225	2.3	120	75	1.4639	7	2
Hexadecyl	243–248	1.0	112	69	1.4634	6	1
Eicosyl	......	6.0	95	57	1.4663	6	..

sorbing gums formed during the reaction and heating and prevented the formation of insoluble resins in the still bottoms.

While the greater part of this work was done on the production of 2 ethylhexyl esters suitable for use in the preparation of epoxy plasticizer derivatives, it was also decided to prepare a series of tall oil esters of other commercially-available alcohols.

Various alcohol samples were solicited from Carbide and Carbon Chemicals Company, Enjay Company Inc., and Shell Chemical Corporation. A listing of these esters prepared from the alcohols by a variety of the above methods is presented in Table VIII. Esters of butyl and higher alcohols were made, using 1.1 mole of alcohol for each mole (280 g.) of fatty acid. Catalyst concentration was 0.3%.

The initial ester after a purification treatment of water washing, vacuum topping, and drying was distilled. Distillation was by batch method, using a vacuum of 2–4 mm. A small precut was removed, then the main portion of the ester, boiling over the distillation range as listed in Table VIII, was collected and used in subsequent analyses. The residue in all instances contained the major portion of color bodies. Initial colors are listed for the esters prior to distillation. All distillates were clear, water-white liquids.

While the above listings of esters and their properties is by no means complete, it does serve to illustrate the ease of esterification and variety of useful chemical entities which can be prepared from purified tall oil fatty acids, which are now available commercially.

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[Received April 7, 1960]

Analyses of Lipids and Oxidation Products by Partition Chromatography. Dimeric and Polymeric Products[1]

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A liquid-partition chromatographic method was developed to determine dimers in fats. Silicic acid treated with 20% methanol in benzene served as the immobile phase. A mixture of 2% methanol in benzene was the mobile solvent. Chromatographic separation of free fatty acids from oxidized-deodorized oils gave three well-isolated fractions composed of unoxidized acids, dimeric or polymeric fatty acids, and polar fraction (ethyl ether eluate). Recovery of acidic materials from the column was essentially quantitative (96–100%), reproducibility was good, and the standard error of regression was ±0.26.

A linear relationship exists between the dimer content of deodorized soybean oil and the peroxide value of the oil before deodorization. An increase of 1% in dimer concentration corresponds to an increase in peroxide value of approximately 40. Dimer content of different vegetable oils varied from 1 to 3%.

The chromatographic method can be used to estimate the degree of oxidation that an oil has received before deodorization and to follow various phases of fat oxidation, polymerization, and processing.

THE EXTENT OF OXIDATION in deodorized vegetable oils is difficult to determine because deodorization rapidly destroys hydroperoxides. A quantitative measure of this "hidden oxidation" would help to predict the quality and future stability of an oil. Oxidation at different stages of processing and before deodorization is detrimental to stability of vegetable oils (1,6). This detrimental effect of oxidation in soybean oil is attributed to dimerization products derived from hydroperoxides by their decomposition prior to or during deodorization (2). The term "dimer" describes polymeric products derived from autoxidation and known to be principally dimeric in nature. The dimers were isolated from autoxidized-deodorized soybean oil and autoxidized-heated fatty esters and were characterized chemically and spectroscopically (3). They contain approximately 1 mole hydroxyl, 0.5 mole carbonyl, and 2 double bonds per mole of dimer. Attempts to show the presence of ether linkages and of a 6-membered ring in their structure failed.

The present paper deals with a liquid-partition chromatographic method used to determine dimers in oxidized-deodorized or heated fats. Since these dimers are derived from fatty acid hydroperoxides, this chromatographic method is useful in estimating the degree of oxidation that an oil has received before deodorization. This method also determines and characterizes dimers derived by thermal polymerization of conjugated or nonconjugated fatty acids and methyl esters. The method has been applied to determine hydroper-

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[1] Presented at spring meeting, American Oil Chemists' Society, Dallas, Tex., April 4–6, 1960.

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