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The Selective Esterification of Tall Oil[1]

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TALL OIL has been produced for many years in this country and abroad from the black liquor resulting from the production of Kraft paper by the sulphate process. Crude tall oil characteristically contains 40-45% resin acids related to rosin or abietic acid and 34-45% fatty acids, with 3-4% of sterols present, the remainder being other unsaponifiables such as hydrocarbons. The most authoritative and generally accepted analysis of the fatty acids of American tall oil is that of Anderson and Wheeler (1), who found that on the average tall oil fatty acids comprise about 7% saturated fatty acids, 45% oleic acid, and 48% linoleic, including 11% of conjugated linoleic acids. The saturated acids are mostly palmitic with perhaps 1% of palmitoleic.

The uses of tall oil stem naturally out of its composition. It is used very largely as a constituent in soaps and other detergents and as an extender for drying oils, particularly for finishes which are not intended for outdoor exposure. During the recent shortage of drying oils tall oil was used quite considerably as an extender for materials in short supply, and its degree of usefulness as a drying oil extender and its limitations have become very generally known.

In recent years more attention has been given to processes for the refining of tall oil than in the several decades previously. The crude material is dark, odorous, and inexpensive. Refining methods have generally had as their objective the removal of the odor and color and the stabilization of the resin acid fraction. The methods used have always kept in mind the low cost of tall oil and have been developed to add as little as possible to that cost. More elaborate methods of refining developed recently provide for the separation of resin acids from fatty acids and for the chemical modification of the fatty acids and resin acids themselves. These latter methods of refining can conveniently be classified under three headings: a) distillation, b) solvent extraction and c) esterification. The objective of the first two of these methods has been the separation, more or less, of the resin acids from the fatty acids. The esterification has generally been with polyhydric alcohols to produce a material more closely resembling a mixture of a drying oil and ester gum. Combinations of these methods have also been suggested. The significance of the present study can be more easily determined by considering these various methods in some detail.

The resin acid fraction generally contributes to the film undesirable properties of brittleness, excessive thermoplasticity, and dark color. There have been many methods devised to reduce the content of or remove the resin acids, and there have been extensive descriptions of these methods in the patent literature. At the present time there are two apparently practical methods for the substantially complete separation of resin acids from fatty acids. The first method is that of vacuum fractional distillation. The fatty acids are more volatile than the resin acids and under careful conditions can be separated quite cleanly with only 2 or 3% resin acids remaining in the fatty acid fraction. The fatty acids themselves can be separated to some degree by fractional distillation into two fractions, one of which contains most of the saturated material which is primarily 16 carbon fatty acids, and the other containing most of the unsaturated material which is mostly 18 carbon fatty acids. The separation by distillation of the 18 carbon unsaturated fatty acids one from the other is of course not practical.

The second method consists of selective solvent extraction. One process for the selective separation of resin acids from fatty acids calls for the solution of the oil in liquefied low boiling hydrocarbons such as propane (10). Some resin and oxidized and charred material, constituting tar and pitch, may settle out. The tall oil is then heated under pressure to perhaps 65°C. to 95°C. and the resin acids precipitate. It is claimed the resin acids will separate when the solution is cooled also. The propane is then distilled from the fatty acid fraction and recovered. Other methods call for the distribution of fatty acids and resin acids between non-polar and polar solvents, such as naphtha and furfural (11), and it is claimed some separation by this means is possible. It has been reported that a greater difference in polarity can be obtained by first partly esterifying the fatty acids with polyhydroxy alcohols so as to have free hydroxyl groups remaining (5). These partial esters are less polar than the resin acids and can be selectively separated. Some rather complex procedures have been devised for separation of fatty acids, oxidized resin acids, unoxidized resin acids, sterols, and pitch (14). By another method the oleic acid fraction from tall oil is claimed to be precipitated on cooling in acetone solution to −60°C. (22).

Another method for the separation of resin acids from fatty acids involves the adsorption of the fatty acids on adsorbent clay (19). It is also suggested in the description of this method that the fatty acids be partially esterified to form mono- or di-glycerides and thus decrease their polarity (18). The efficiency of separation of the resin acids from these partial esters

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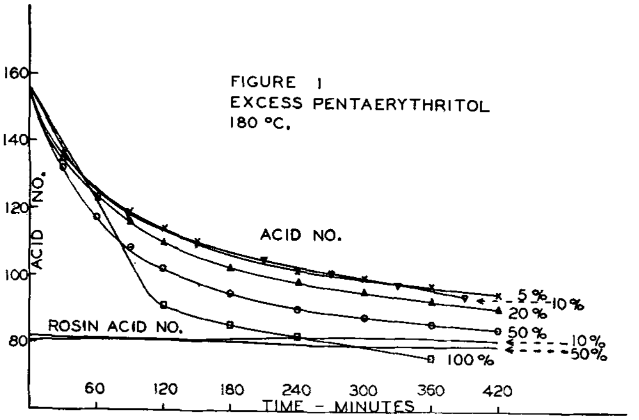


is considerably increased, it is claimed. This method was developed particularly for the isolation of resin acids or fractions containing 50-80% resin acids.

The complete esterification of tall oil to form both fatty and resin esters has frequently been described and the products have been evaluated by a number of groups in the paint and varnish industry. No further remarks need be made except to say that no practical separation of fatty esters from resin esters has been reported.

It has long been known that fatty acids will esterify much more rapidly than resin acids with low boiling alcohols such as methyl, ethyl, propyl, and butyl alcohols (16). This fact is the basis of the official method of this Society for the determination of resin acids and fatty acids in the presence of each other. For the separation of the fatty acid fraction from the resin acids a great many people have based this third general method on this same process of esterification of the fatty acids with a low boiling alcohol. The esterification is usually with ethyl or methyl alcohol with a little acid catalyst, which may later be neutralized with alkali and the mixture of esters and resin acids can then be treated in a variety of ways. One of the simplest is by selective solvent extraction whereby the esters are held in a non-polar solvent such as naphtha and the resin acids are removed by a polar solvent such as furfural (7). Also the resin acids may be separated by neutralizing them with alkali to form the soaps and then extracting the soaps with water or by completely dehydrating the solution to precipitate the resin soaps (13). Soaps other than the alkali metals can be formed directly, such as aluminum and zinc resinates, which are insoluble in the organic solvent as such and will precipitate (6). The presence of water in the mixtures of esters and alkali metal soaps must be carefully controlled in order to avoid troublesome emulsions. In another modification the mixture of fatty esters and resin acids is treated with a catalyst which causes the resin acids to isomerize to an insoluble form which then precipitates and is removed (8). In still another modification the mixture of fatty acid esters of a monohydric alcohol and resin acids was further esterified with glycerol, for example, forming, it was claimed, glyceride esters of the resin acids (20).

It was further claimed that the mixture of esters could be distilled and the lower boiling methyl esters of the fatty acids removed from the resin glycerides. Nothing was said about mixed esters being formed during the esterification with glycerol. The esters of the fatty acids have been separated from the rest of the tall oil as saturated and oleic esters by first esterifying the fatty acids, then hydrogenating the material to reduce the more unsaturated fatty acids to saturated and oleic esters (23). The mixture of esters and resin acids is then dissolved in acetone and cooled to about —18°. The fatty esters precipitate and are recovered. They are said to be, in this case, very free of resin acids. The iodine value of these esters was about 10. It is claimed that the resin acids may also be esterified at the same time and that they can still be separated in the same way from the fatty esters.

Another method which involves the esterification of tall oil calls for the esterification first of *all* of the acids, both fatty acids and resin acids, with a polyhydric alcohol, such as glycerol (21). These esters are then treated with a low boiling alcohol, such as methanol and the fatty esters trans-esterified. The methyl esters of the fatty acids are then separated from the resin acid glycerides by vacuum distillation. Another method which involves esterification of all of the acids with a polyhydric alcohol calls for the treatment of the mixed esters with Twitchell's reagent or some other saponification agent so as selectively to saponify the fatty esters (4). Zinc oxide, calcium oxide, sodium hydroxide, or concentrated sulfuric acid can be used. The fatty acids may then be removed from the resin acid esters by distillation or by extraction with aqueous alkali.

The formation of amides from the fatty acids has also been used to separate them from the resin acids (15). Diamines such as ethylene diamine have been used to form the fatty acid amides. These materials were dissolved in hot methanol and the amides precipitated when the solutions were cooled. They were removed, the solvent was then evaporated, and the resin acids recovered.

Another method has been described which involves the decarboxylation of the resin acids, for example, with phosphorus pentoxide, and other catalysts but since the resin fraction, in this case, is recovered in an inert form, this method is not considered further (2, 12). Still other methods for separation of the constituents of tall oil are more concerned with the separation of sterols and the like and are not particularly pertinent to this discussion (24).

A consideration of this considerable variety of methods for the separation of resin acids from fatty acids reveals that none of them seems to give a polyhydric ester of the fatty acids conveniently in a few steps with a clean separation of resin acids leaving the polyhydric ester usable as a drying oil substitute or extender. It was believed that if such a separation could be carried out, a drying ester could be formed directly and the resin acids could easily be removed

TABLE I

Esterification Kinetics, 180°C.[a]

t	F.A.N.	$K \times 10^4$
0	73.5	......
20	62.0	3.60
40	51.9	4.05
60	44.1	4.25
90	37.0	4.14
120	32.3	3.98
150	28.4	3.91
210	24.0	3.55
270	20.0	3.50
330	15.6	3.83
390	13.4	3.81

[a] $K = 1/t \log \frac{b\,(a-x)}{a\,(b-x)}$

by an alkaline wash or by solvent extraction, low temperature precipitation, and the like. Although it has been known for a long time that at low temperatures resin acids do not esterify at any appreciable rate, there was little evidence to indicate that at higher temperatures such a selective esterification could be achieved. In some of our contacts the opinion was expressed to us that at higher temperature, that is around 200°C. and above, the rates of esterification of both fatty acids and resin acids were about the same. No examples or discussions of this point were available in the literature. However some of those working with tall oil have known that the esterification was still selective up to 200°C., but the exact extent of the reactions at various temperatures seems not to have been investigated systematically. There have been suggestions in the patent literature that tall oil fatty acids could be esterified with some selectivity at temperatures around 200° with polyhydric alcohols but only partial esters, that is to say, mono- and di-glycerides, for example, were prepared which, of course, would not be suitable as drying oil extenders. From the data given it appeared that an appreciable fraction of the resin acids had esterified also (5).

It was the purpose of this investigation to determine the exact circumstances under which the fatty acids of tall oil could be preferentially esterified with polyhydric alcohols to form suitable drying oil substitutes which could be practically and simply separated from the resin acids. The complete esterification of tall oil has frequently been described in the literature and temperatures have been used as high as 275°C. Accordingly the comparative rates of esterification have been determined up to that temperature.

Experimental

The materials used in this study were based principally on a refined tall oil. It had an acid value of about 164 and a rosin acid value of about 86, with a fatty acid value of about 78. The pentaerythritol was a technical grade containing minor proportions of dipentaerythritol. The glycerol was a C.P. laboratory grade which was redistilled. The catalyst used was lead naphthenate containing 24% lead and was used in the proportion of 1% of the weight of the batch. The procedure follows.

TABLE II

Esterification Kinetics at 220°C.

t	F.A.N.	K X10^4	K X10^4 Corr.
0	73.5	......	......
9	51.9	18.0	14.2
19	38.8	17.8	14.4
35	28.0	17.1	12.3
50	23.6	15.3	10.3
65	20.0	14.4	9.3
80	18.2	13.3	8.2
110	14.2	12.7	7.4

The tall oil in an amount sufficient to supply one equivalent weight of fatty acids was heated in a three-necked flask equipped with a mechanical stirrer, a Stark and Dean water trap to which was connected a reflux condenser, and a gas inlet tube and thermometer. The flask was heated with a Glascol mantle as rapidly as possible to the reaction temperature. During this time inert gas, nitrogen, which was passed first through a pyrogallol solution, then through a calcium chloride drying tower, was bubbled through the tall oil at a rate of about 1.2 liters per minute. The catalyst was added when the batch reached the reaction temperature. The pentaerythritol or other polyhydric alcohol was then added as rapidly as possible. The temperature dropped a few degrees and then rose in 2 or 3 minutes to the reaction temperature. The zero time was taken as the time at which the polyhydric alcohol had completely dissolved. In the case of glycerol this was the time of the completion of addition. Small samples of between 5 and 10 ml. were taken as soon as the material was dissolved and periodically thereafter. The intervals of time between samples were chosen to get enough points to draw a smooth curve. At the higher temperatures the samples had to be taken at closer time intervals than at the lower temperatures. Samples were taken until both the acid number and the rosin acid number were dropping at about the same rate. Acid numbers and rosin acid numbers were determined on each sample in the usual way as described in the official methods of this Society.

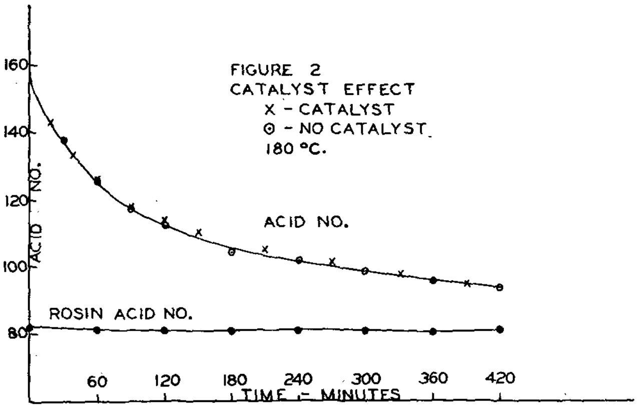


FIGURE 2
CATALYST EFFECT

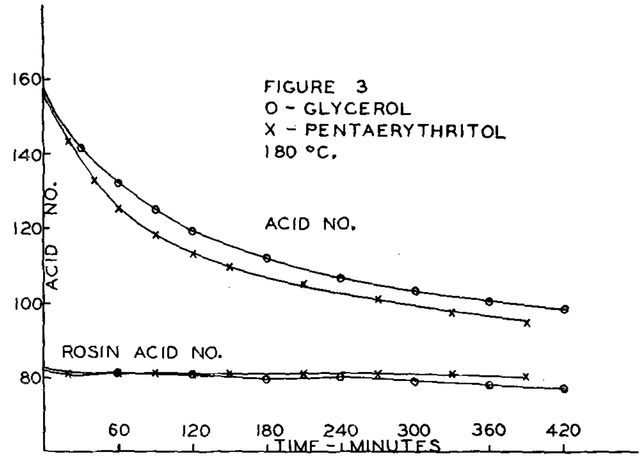
Discussion

The study of the various factors which might influence the rate and extent of selective esterification included the following: a) excess pentaerythritol, b) presence of catalysts, c) glycerol compared with pentaerythritol, and d) temperature.

Effect of Excess Pentaerythritol. It has previously been reported that the amount of excess pentaerythritol between 5 and 15% has little effect on the esterification rate (17). Some examples have been carried out in this study to cover a range of excess of pentaerythritol from 5 to 50% more than that required to esterify the fatty acids and also enough to esterify all of the acids present, here called 100% excess, since about equal amounts of fatty and resin acids were present. As shown in Figure 1 there was no significant difference in reaction rates between 5 and 10% excess pentaerythritol at 180°C. The use of 20 and 50% excess pentaerythritol showed more complete esterification of the fatty acid and with 100% excess the esterification of the resin acids continued toward completion, although at 180°C. very slowly.

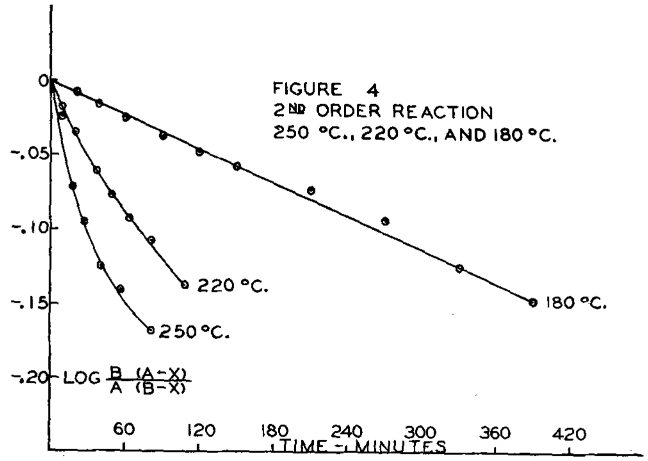
Effect of Catalysts. Out of respect for tradition lead naphthenate was used as a catalyst although it is generally recognized that it has no particular effect on the esterification rate (17). To illustrate this one esterification was carried out at 180°C., 10% excess pentaerythritol, with no catalyst added. A comparison of the curves for the two reactions one with and one without catalyst is shown in Figure 2. There seems to be no justification for the use of lead naphthenate driers as esterification catalysts.

Effect of Glycerol Substituted for Pentaerythritol. Since glycerol contains the secondary hydroxyl group, substitution of it for pentaerythritol on an equivalent basis results in a somewhat slower esterification rate. This is shown in Figure 3. The results are about as expected, and no particular comment is necessary.



Effect of Temperature. Using 10% excess pentaerythritol at 180°C. the resin acids do not appear to esterify, as shown in Figure 2. In order to provide some kinetic information on the rate of esterification at different temperatures, specific reaction rate constants were calculated at 180, 220, and 250°C. The total acid and resin acids were determined as indicated previously. The fatty acid was obtained by difference. The per cent of fatty acids at a time t was taken as the quantity (a—x), that is, the per cent of fatty acids unreacted. The initial equivalent concentration of fatty acid and of pentaerythritol was of course known, and the general equation for a second order reaction rate was set up assuming the reaction was bi-molecular. Using the relationship $1/t \log b(a-x)/a(b-x)=k$, the value for $\log b(a-x)/a(b-x)$ was plotted against time and a straight line obtained, Figure 4. The logarithm of the ratio was divided by the time t and k obtained as in Table I.

At 220°C. the resin acids begin to esterify, Figure 5. This is shown by the failure of the reaction to follow second order reaction rate kinetics. When the logarithm of the ratio $b(a-x)/a(b-x)$ is plotted against time t, the line is curved (Figure 4). The reaction rate constant is also not a true constant, nor does it become so when an attempt is made to correct the concentration of the pentaerythritol by the amount of pentaerythritol esterified by the resin acids, Table II. Apparently some side reactions occur. At 250°C. the fatty acids esterify quite rapidly while the resin acids esterify at an appreciable rate although still much more slowly (Figure 6). Again second order reaction rate calculations show that side reactions occur (Figure 4, Table III). At 275°C. the same trend continues (Figure 6).



A comparison of the rates of esterification of fatty and resin acids at each temperature is shown in Figure 7. It is clear that for complete separation of resin acids from fatty acids 180°C. is the best temperature. For practical purposes, where time is important and slightly less complete separation is tolerable, 220°C. is better as the fatty acids are quickly esterified while little of the resin acids are. There is no advantage in attempting selective esterification at 250°, and at 275° the resin acids esterify considerably faster than at 250° while the fatty acids esterify very little faster.

In an effort to get some idea of the extent of side reactions other than the esterification of resin acids a calculation was made for the presence of simultaneous reactions. The percentage of fatty ester formed had already been calculated. The percentage of resin acid at each time t was also calculated. The ratio of percentage of fatty ester to percentage of resin ester was then found for each time. In the case of the reaction at 220°C. the ratio was nearly constant, showing only a slight drift, so that little side reactions other than esterification of the two acids was occurring. At 250°C. there was a more perceptible drift, indicating a somewhat higher amount of side reactions, Table IV.

TABLE III

Esterification Kinetics, 250°C.

t	F.A.N.	K X10^4
0	73.5	......
7	44 7	35.4
17	24.7	42.0
27	19.9	35.2
40	16.3	30.0
56	14.1	25.2
82	11.8	20.6

The side reactions which occur at the higher temperatures appear to be predominantly decomposition of the pentaerythritol. In a study of esterification with tetramethylol cyclohexanol side reactions were attributed to etherification as shown by loss of hydroxyl groups not esterified (25). Pentaerythritol is said to decompose above 250°C. to form methyl acrolein, water, and formaldehyde, but it is said not to etherify, e.g., form dipentaerythritol (9). A study has been made here of the decomposition of pentaerythritol heated in solution at 180, 220, and 250°C. for six hours. It was found that in that time there was no loss of hydroxyl groups at 180° but a loss of 8% and 10% respectively at 220° and 250°C.

It is well-known that esterification is acid catalyzed and, in the absence of strong acid catalysts, is self-catalyzed by the organic acid present. As has been shown (3), the kinetics of the self-catalyzed reaction is not altogether clear-cut, even in simpler systems than this, being initially nearly second order and, after a much longer time than used here, becoming approximately third order. As indicated previously, there is no apparent catalytic effect due to the lead naphthenate, and it is presumed not to affect the reaction kinetics in this case, as shown in Figure 2.

The apparent agreement of the data with second order reaction rates at 180°C. may well be due to the resin acid acting as a catalyst. If third order kinetics are assumed in which the components are alcohol, fatty acid, and resin acid, at 180°C. the concentration of the resin acid does not change appreciably and

TABLE IV

Simultaneous Reactions

t	% F.E.	% R.E.	% F.E./% R.E.
220°C.			
19	.472	.020	23.6
35	.619	.028	22.1
50	.679	.033	20.6
65	.728	.035	20.8
80	.752	.038	19.8
110	.807	.042	19.2
250°C.			
17	.664	.057	11.64
27	.729	.075	9.73
40	.778	.080	9.73
56	.808	.091	8.89
82	.839	.112	7.50

may be considered a constant. The expression for a third order reaction

$$dx/dt = k(a-x)(b-x)(c-x)$$

where a, b, and c are respectively the concentrations of alcohol, fatty acid, and resin acid, then becomes

$$dx/dt = kc(a-x)(b-x)$$

and plotting log b(a—x)/a(b—x) against time will give as straight a line as if the reaction were second order.

It was thought that third order kinetics might occur, particularly at 180°C., in which the fatty acids were the reactants and the total acids, fatty and resin acids, acted as catalyst. Then

$$dx/dt = k(a-x)(b-x)(c-x)$$

where a, b, and c are the concentrations respectively of alcohol, fatty acid, and total acid. Calculations were made for this possibility, and the results are listed in Table V. From the reaction rate constants obtained the above assumptions could not be considered satisfactory. Similarly, reaction rate constants calculated on the basis that fatty acids only were both reactant and catalyst were not satisfactory. Above 180°C. the resin acids appear to act not only as catalyst but also as a reactant. Normal third order kinetics should then be followed, but constants calculated on the basis of total acids, fatty and resin acids, being both reactant and catalyst, were poor even at 250°C.

Separation

The separation of the esters of the fatty acids from the resin acids was carried out on a sample of refined tall oil selectively esterified at 180°C. with 10% excess pentaerythritol as follows:

An amount of sodium hydroxide equivalent to the amount of acids remaining in the partially esterified tall oil was dissolved in 100 ml. of water and in the first case was added slowly with mechanical stirring to a portion, 100 g., of the partially esterified tall oil. Another 100 ml. of water and 200 ml. of naphtha (Skellysolve C) were added to the emulsion which had formed. A water layer containing resin soaps slowly separated from the emulsion above the naphtha layer, and the soap was removed. The naphtha layer was washed several times with water. The aqueous solution of the resin soaps was acidified and the resin acids removed by extraction with ether. The ether solution was dried and the ether removed by evaporation in vacuum. The naphtha solution was acidified, and the solvent removed by evaporation in a vacuum. In a second example, in order to avoid emulsions which may be troublesome, the partially esterified material was first dissolved in naphtha (Skellysolve C) and then the solution of sodium hydroxide was added with stirring. After the aqueous solution of resin soaps was removed, the naphtha solution was washed with sodium hydroxide solution and then with water. The combined extracts were acidified and dried as before. About equal amounts of resin acids and ester were obtained. Each fraction was characterized by analysis for acid number and saponification number and the ester fraction for iodine value.

The separation of resin acids was more complete in the second case than in the first, Table VI. In the first case the ester fraction had an acid number of 46 and the resin acids fraction an acid number of 103. In the second case the ester fraction had an acid number of 21 and the resin acids fraction an acid number of 144. Theoretically the ester fraction should of course have an acid number of zero and the resin acids fraction an acid number of 164. The saponification value of both fractions was about the same—174, 174. The iodine value of the ester fraction was 140 and had been calculated to be between 135-140. The iodine values were determined by the Wijs method. The saponification numbers were determined by dissolving 1.5 g. of the sample in 15 ml. of dioxane and then adding exactly 50 ml. of 0.5 normal alcoholic potassium hydroxide. This solution was refluxed for 1 hour and titrated with 0.5 normal hydrochloric acid using thymol blue as an indicator.

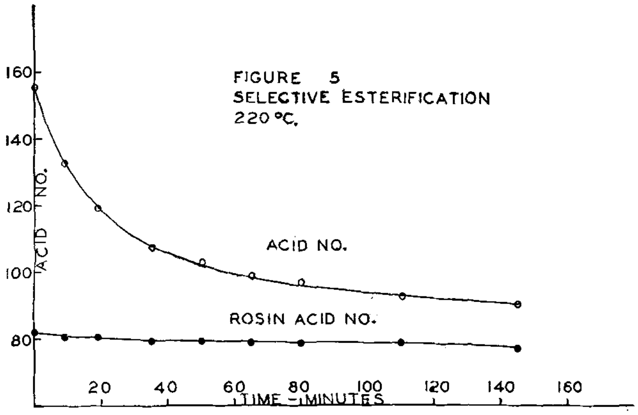


FIGURE 5
SELECTIVE ESTERIFICATION
220 °C.

Another type of ester of tall oil in which considerable interest is being expressed is the vinyl ester. Our laboratory prepared vinyl esters of tall oil some years ago, but at the time selective esterification was

TABLE V

Third Order Calculations

a = (alc.), b = (F.A.), c = (total acids)

t	F.A.N.	K X10⁴
180°		
0	73.5	......
20	62.0	7.30
40	51.9	7.94
60	44.1	7.82
90	37.0	7.35
120	32.3	6.72
150	28.4	6.22
210	24.0	5.42
270	20.0	4.94
330	15.6	4.81
390	13.4	4.55
220°		
0	73.5	......
9	51.9	10.5
19	38.8	14.5
35	28.0	20.0
50	23.6	21.6
65	20.0	24.7
80	18.2	24.9
110	14.2	31.3
250°		
0	73.5	......
7	44.7	2.44
17	24.7	5.69
27	19.9	6.02
40	16.3	6.38
56	14.1	6.23
82	11.8	6.16

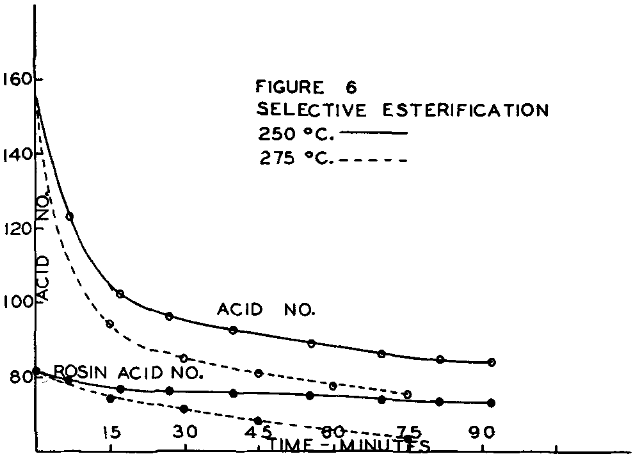


FIGURE 6
SELECTIVE ESTERIFICATION

not investigated. An indication of selectivity can be obtained by determination of acid and rosin acid numbers of available tall oil vinyl esters. Samples from two different suppliers were analyzed with the results listed in Table VII. These data indicate that the small amounts of free acids remaining in the esters are resin acids since the total and resin acid numbers are about the same. While this evidence is by no means conclusive, it is of some interest in view of the different process by which vinyl esters are produced.

TABLE VI
Product Characteristics
Separated Tall Oil Fatty Esters and Resin Acids

	Acid No.	Sap. No.	Iodine No.
1. Ester	46	......	......
Resin Acids	103	......	......
2. Ester	21	174	140
Resin Acids	144	174	......

Summary

A review of the literature has shown that there has not been described heretofore a relatively simple and inexpensive process for obtaining the polyhydric esters of tall oil fatty acids practically free of resin acids and in a form directly suitable for drying oil applications. Since for some purposes it is desirable to have the fatty esters free of resin acids or esters, a simple procedure for separation of the two should be of some interest and value.

It was believed that the difference in rates of esterification between fatty acids and resin acids should remain large at much higher temperatures than previously shown. Esterification of tall oil with the polyhydric alcohols, pentaerythritol and glycerol, as described in this paper has shown that a difference in rates of esterification persists even up to 275°C.(527°F.). At 180° in six hours the resin acids are not appreciably esterified while the fatty acid esterification is virtually complete. Esterification of the resin acids becomes evident at 220°C. and is progressively more rapid at 250° and 275°C. Lead naphthenate does not appear to be an esterification catalyst.

Some calculations have been made in an effort to describe the kinetics of the esterification. Although simple esterification has been observed to lie between second and third order, approximating the latter beyond the initial stages, at 180°C., this reaction appears to be second order. Possible reasons for this are discussed. Above 180°C. the kinetics appear to be more complex.

The resin acids of the product of selective esterification can be removed easily and almost completely from the fatty esters by washing a naphtha solution of the reaction product with aqueous alkali solution. The fatty esters have an iodine number above that of soybean oil; the resin acids are similar to a dark rosin.

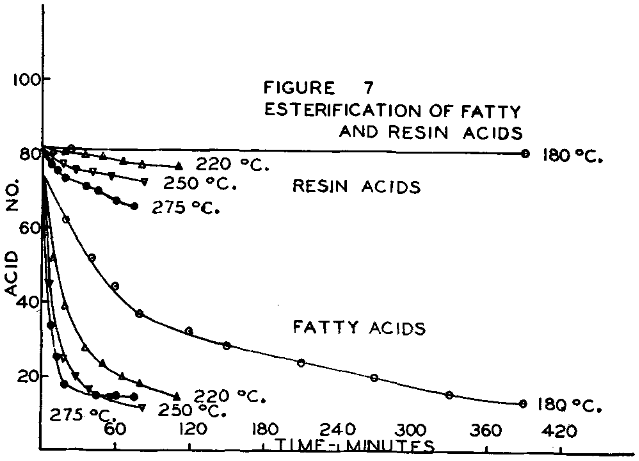


FIGURE 7
ESTERIFICATION OF FATTY AND RESIN ACIDS

TABLE VII
Analyses of Vinyl Tall Oil

	Acid No.	Rosin Acid No.
1. Crude	30.2	31.2
Refined	34.0	33.7
2. Refined	21.0	22.7

Appreciation is expressed to Frank J. Koller who checked some of the experimental data and to the Armstrong Cork Company for permission to publish this paper.

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