The present invention relates to processes of fractionating tall oil in order to separate the rosin acids from the fatty acids thereof and it has particular relation to the fractionation of tall oil by liquid phase extraction of the methyl esters of tall oil fatty acids from the soaps of rosin acids by means of an appropriate solvent system.

An object of the invention is to provide a process of the foregoing type in which the fatty acid esters can be rapidly and smoothly extracted from the aqueous alcohol-rosin acid soap solution by continuous countercurrent contact in an appropriate column.

A second object of the invention is to provide a process of the foregoing type which is simple and economical and efficient in operation.

A third object is to provide a process of the foregoing type whereby hard rosin free of fatty acids may be obtained from tall oil.

A fourth object is to provide a process of the foregoing type whereby fatty acids or fatty acid esters free of rosin acids may be obtained from tall oil.

These and other objects of the invention will be apparent from consideration of the following specification and the appended claims.

Tall oil is a well known by-product of the Kraft Paper Industry. It comprises a highly complex mixture of rosin acids, polymers of rosin acids, fatty acids, sterols and other constituents. Herefore, because of the complexity of the mixture and the difficulty of separating the rosin acids from the fatty acids, these latter materials have been to a large extent wasted or employed as cheap, low-grade materials. About all that has been accomplished has been to subject the mixture to distillation whereby to obtain a fraction considerably enriched in fatty acids, a second fraction enriched in rosin acids and in some cases, a distillation residue containing some rosin acids and fatty acids and a high concentration of sterols, rosin polymers and the like. Obviously the fractionations were never sharp and clean-cut.

It has also been proposed to obtain a more complete separation of the rosins and fatty acids into portions of higher commercial value by subjecting the tall oil to an esterification reaction with a lower alcohol such as methanol, as a result of which operation, the fatty acids are selectively converted to fatty acid esters. The rosin acids could then be selectively neutralized with alkali such as sodium hydroxide. In such mixture the fatty acid esters and unsaponifiable matter could be extracted from the rosin acids soaps by the application of benzene. This latter type of process has heretofore remained of some theoretical value especially for analytical purposes, in the laboratory, but it has never, as far as is known, enjoyed any substantial degree of commercial success. This lack of success was apparently largely due to the fact that the rosin acid soaps and the esters of fatty acids tended to form emulsions with the benzene to such degree that it was practically impossible to effect satisfactory separation in a continuous countercurrent system.

The present invention involves the discovery that by proper adjustment of the various components of the mixtures of solvents and the products of esterification and neutralization of tall oil, mixtures could be obtained which would undergo ready and relatively complete separation when the mixtures were subjected to extraction with a solvent such as naphtha in countercurrent flow in an appropriate column.

For a better understanding of the invention reference may be made to the accompanying drawing in which the single figure diagrammatically illustrates a simple form of apparatus suitable for use in the practice of the invention.

Tall oil, it is to be recognized, will vary in composition dependent upon the source and the method of operation by which it is obtained. In general, the composition will be approximately as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fatty acids</td>
<td>35 to 50</td>
</tr>
<tr>
<td>Rosin acids</td>
<td>35 to 55</td>
</tr>
<tr>
<td>Unsaponifiable matter</td>
<td>6 to 12</td>
</tr>
</tbody>
</table>

In accordance with the provisions of the present invention a compound such as above described is subjected to treatment by the following stages.

I. ESTERIFICATION

In this operation a tall oil comprising rosin acids, fatty acids and the like preferably within the ranges above specified is subjected to an esterification treatment. The esterifying agents preferably is methyl alcohol or methanol but other lower aliphatic alcohols are contemplated and the reaction preferably is conducted in the presence of a catalyst such as sulfuric acid. The alcohol should be in an amount at least sufficient to esterify the free fatty acids of the mixture and it may be in considerable excess since the excess will operate as a part of the solvent system in the subsequent steps of solvent extraction. If desired, the alcohol which is in excess of that re-
required for esterification could also be evaporated. The following constitutes an appropriate example of a suitable esterification mixture:

<table>
<thead>
<tr>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligno or crude tall oil</td>
</tr>
<tr>
<td>Methanol</td>
</tr>
<tr>
<td>Commercial sulfuric acid</td>
</tr>
</tbody>
</table>

The sulfuric acid, of course, is a mere catalyst and more or less might be employed as will be understood by those skilled in the art. Preferably it will be within a range of about two to 10 parts by weight.

The reaction is effected by refluxing the mixture in a suitable apparatus. Refluxing is continued so long as methyl alcohol continues to combine and water of esterification is given off. Usually the reaction will be complete within a period of three hours or less but may be continued longer without particular harm other than the increase in the expense of operation. When the reaction is completed, the mixture should be cooled to 80° or 90° F.

The mixture is then ready for the second stage of operation (neutralization).

II. NEUTRALIZATION

The above esterified mixture in an appropriate reaction vessel is mixed with 45 parts by weight of water (preferably soft) and caustic to neutralize the sulfuric acid is added. In the particular mixture, 4.67 lbs. of caustic, e.g. caustic soda, is sufficient. The causticized mixture may be briefly agitated. Methanol is next added in order to make up an aqueous methanol solution. In the specific example contemplated herein, methanol comprised 96.13 parts by weight. Alkali (caustic soda) in an amount to neutralize the rosin acids was next added. In these specific examples, the alkali constituted 8.3 parts by weight and it was dissolved in 27.22 parts by weight of water. The alkaline solution was added slowly until the mixture was slightly on the alkaline side. In this specific instance, the pH value was 10.4. It will be apparent that the rosin acids in the final mixture are present as their soaps, the sulfuric acid is present as a sodium salt and the fatty acids are present as the methyl esters.

The soap solution

In order to prepare aqueous alcohol solutions suitable for extraction with naphtha to separate fatty acid esters from the soaps of rosin acids in accordance with the provisions of the present invention, the solids including the soaps of rosin acids, esters of fatty acids, sodium sulfate and other constituents all designated herein as solids are made up in solution in water and methyl alcohol to form a mixture which when intimately contacted by shaking or by counter-current extraction in a column will separate into clean-cut phases at once. In practically all instances the components of the mixture will fall within the range: 7 to 60% of methanol, 15 to 70% water, 20 to 65% solids made up of fatty acid esters, rosin acid soaps, solids, etc. The preferred mixture will contain methyl alcohol, 15 to 50% water and 25 to 62% solids.

In a specific example a solution was made up upon the basis of starting materials 42.09% tall oil, 34.8% methanol, 18.40% water, 3.30% sodium hydroxide and 1.41% sulfuric acid. This mixture could be flowed in intimate countercurrent contact with naphtha in a suitable column later to be described to obtain rapid and thorough extraction of the fatty acid esters and to obtain quick and efficient phase separation of the column.

In a further example a mixture was made up comprising 60% solids, 12% methanol and 28% water. This mixture was extracted at 130° F. with naphtha having a distillation range of about 90° to 115° C. and being composed of essentially heptane and octanes.

The mixture would readily separate from the naphtha in the column. This mixture is of especial value for use in the practice of the invention since the percentage of solids is high and the requirements of methanol are low.

These mixtures are particularly applicable to the use of naphtha and notably of naphtha approximating a heptane grade to extract the fatty acid esters from the soap-ester solution. This point is illustrated by the fact that a system comprising 34.8% methanol, 18.4% water, 3.3% sodium hydroxide, 4.1% sodium soap, 40.1% tall oil solids when shaken with benzene did not separate into layers even after standing for a period of 24 hours. However, when the same mixture was shaken with naphtha of heptane grade complete separation occurred within one minute and but little or no naphtha remained in the resin-soap layer. Although naphtha of hexane, heptane or octane range boiling at 90° to 115° C. is preferable the use of other liquid paraffinic petroleum naphthas is contemplated such as C5 to C9 hydrocarbons.

Extraction of the esters from the soap-ester solution

A mixture so constituted is well adapted for extraction with hydrocarbon such as petroleum naphtha and preferably of the heptane range by countercurrent operations. Preferably, the column employed for the extraction will be relatively long, for example 40 ft. or more. There would appear to be no upper limit to the height of the column other than those imposed by the economics of construction or actual operations a column of 49 ft. packed with Beri saddles has operated very satisfactorily. The soap-methyl ester solution should be fed into the top or near the top of the column and the naphtha into the column near the base. The ratio of naphtha to soap-methyl ester solution may be approximately 90 parts by volume to 70 parts by volume. Certain variations in the ratio of soap solution of methyl esters and naphtha are contemplated. For example, the naphtha may be as low as 60 parts by volume or as high as 400 parts by volume to 100 parts by volume of the solution. The column preferably is operated at a temperature within a range of 80° to 135° F. The rate of feed of the soap-methyl ester solution and naphtha should be adjusted so that adequately complete separation of the phases can occur and will separate into clean-cut phases in the column. Of course, excessive rates of feed will result in flooding. That is, excessive amounts of the soap solution will be carried backward by the naphtha or the naphtha will fail to rise satisfactorily and will be carried out in the soap solution. There should be the 90 to 400 parts by volume of naphtha channels through each other and as uniform mingling without emulsification, as is possible. These conditions can readily be observed by the operator by examination of the products from the columns. Upon the basis of a cylindrical column of 2 in. diameter, a feed of 70 cc. of the soap-methyl ester mixture to 90 cc. of naphtha per
minute is satisfactory. By appropriate increase of the column diameter, any desired feed rate can be attained.

It will be appreciated that the methyl esters are taken up by the naphtha. Also a small amount of the soaps of rosin acids are carried over into the naphtha. For complete recovery of the soaps it may be desirable to wash the methyl ester-naphtha solution with water in a second column which may be followed by the first. In such washing operation the amount of water employed will vary, dependent upon the degree of completeness of the removal of the soaps desired. Equal volumes of water and naphtha solution or methyl esters usually will be sufficient. The wash column may be operated at a temperature of 80 to 150° F. Under these conditions emulsification is avoided.

The washed naphtha solution of methyl esters may then be subjected to a number of different treatments. The naphtha, for example, may be evaporated to obtain an ester mixture having the following characteristics:

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iodine value</td>
<td>134.5</td>
</tr>
<tr>
<td>Saponification value</td>
<td>168.2</td>
</tr>
<tr>
<td>Free fatty acid</td>
<td>1.66</td>
</tr>
<tr>
<td>Unsaponifiable matter</td>
<td>18.01</td>
</tr>
</tbody>
</table>

This mixture may then be distilled over vacuum to yield a yellow methyl ester fraction and a pot residue. In the specific example the distillate constituted 60% and the pot residue constituted 39% of the methyl ester fraction which in turn represented a yield of 52% from the original tall oil. The methyl ester distillate had a free fatty acid content of 69%. It will be apparent that the methyl esters could also be subjected to saponification or hydrolysis to obtain the free fatty acids which could then be distilled as such. Also the esters, after distillation, may be subjected to such hydrolysis to obtain the free fatty acids. These acids may be employed for various purposes such as the production of resins, the production of soaps and similar purposes.

There will remain a distillation residue or pitch very rich in unsaponifiable matter that can be worked up by the technique disclosed in application Serial No. 701,900, by Roger M. Christenson and Stewart W. Glover entitled Separation of Unsaponifiable Matter from Tall Oil Residues and filed October 6, 1946 and made a part hereof to recover stilbene and the like.

The solution of rosin soaps in aqueous alcohol passing from the bottom of the first column may be subjected to acidification, e. g. with strong mineral acid such as H₂SO₄ or HCl to recover the free rosin acids which may be washed with water in order to remove salts and alcohol and then stripped of solvent thereby producing a hard dark rosin of approximately the following properties:

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid value</td>
<td>163</td>
</tr>
<tr>
<td>Rosin acid value</td>
<td>166</td>
</tr>
<tr>
<td>Unsaponifiable</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The yield of this fraction amounted to 50% of the original oil. It is well adapted for use as a paper sizing. If it is desirable to produce a lighter grade of rosin, this fraction may be subjected to vacuum distillation.

A suitable embodiment of apparatus for use in the practice of the invention is represented diagrammatically in the drawing previously described. In a container 5 for the esterification reaction, tall oil, fatty acids are esterified with methyl alcohol in the presence of a strong mineral acid such as sulfuric acid in accordance with conventional esterification technique. The mixture is conducted by line 6 to neutralizer 7 where the mixture is diluted and the rosin acids are reacted with alkali (e.g. NaOH) to form rosin acid soaps. The apparatus further comprises a column 10 of any convenient material packed appropriately with Berl saddles or other packing material. A soap solution of methyl esters, water, alcohol and rosin soaps made up as previously described is fed into the column as indicated at 11. Naphtha for extracting out the methyl esters from the soap solution is fed into the column 10 as indicated at 12. The alcohol solution of rosin acid soaps passes out at or near the bottom of the column as indicated at 13, while the solution of methyl esters of fatty acids dissolved in naphtha passes out as indicated at 14. The naphtha solution may be fed to a second column 15 near the bottom thereof for washing with water. Water is fed into the column 15 near the top thereof at 16 at an appropriate rate. The water in which is dissolved the residual soaps in the ester-naphtha solution is drawn off as indicated at 17 at the bottom of the column. The naphtha solution of esters essentially free from soaps, but still containing the unsaponifiable matter passes off at the top of the column through conduit 18 and is passed for appropriate treatment. For example, it may pass to still 19 where the naphtha is evaporated and recovered for re-use as indicated at 20. The esters may then be discharged at 21a to a pot still 21 for distillation. The residue from the pot still comprising nearly all of the unsaponifiable matter in the ester fraction may be drawn off as indicated at 22. The treatment of this pot residue does not constitute a particular feature of the present invention. However, it will be apparent that it may be subjected to various treatments to recover the various components such as the sterols or the fatty acid esters contained therein.

The rosin acid soaps in aqueous methyl alcohol drawn off as indicated at 13 and 17 are passed to acidifier 23 where mineral acid (H₂SO₄ or the like) is added at 24. Upon acidification, the mixture separates into two layers and the top rosin acid and naphtha layer passes out at 26 to still 27 for removal of naphtha or other volatile matter. If desired, the naphtha solution may be water washed prior to distillation for the removal of traces of mineral acid. Hard rosin are taken from the still. The bottom alcohol, salts and water layer passes through line 28 to still 29 for recovery of alcohol. A water solution of salts passes out as a residue at 30. The alcohol passes out at 31.

It will also be apparent that the methyl esters from column 15 may be treated with alkali such as sodium hydroxide or sodium carbonate to form soaps of the fatty acids and the soaps from which the unsaponifiable matter including the sterols of tall oil can be extracted with naphtha. Subsequently, the fatty acids can be regenerated by acidification.

For example, the esters and unsaponifiable matter from still 19 may be refluxed with sodium hydroxide in an amount of molecular equivalency of the ester content or an excess, e.g. 50% excess. The resultant soap mixture may be adjusted by addition of water and an alcohol to such concentrations that the solution can be extracted countercurrently with naphtha in a proportion of 1 to 20 volumes of naphtha per volume of soap solution. The unsaponifiable material
2,573,890

will be taken out in large measure by the naphtha and the fatty acids can be recovered by acidification of the soap solution with sulfuric acid, hydrochloric acid or the like. The amount of acid should be molar or approximately molar with respect to the total available sodium in the mixture. This can be determined by adding acid until the solution becomes neutral or slightly acid. The acids can then be distilled.

A highly important feature of the invention resides in the applicability of and the application of countercurrent technique in the contactig of the soap-ester solutions with naphtha in column 10. By the employment of the principles of the invention, it is quite feasible to effect such countercurrent extraction of the mixture of esters of tall oil fatty acids, rosin acid soaps and unsaponifiable matter in water and methyl alcohol with naphtha without any tendency to emulsify. Satisfactory separations of phases are therefore obtained at comparatively rapid rates of flow. By application of countercurrent technique of contacting the solutions, highly satisfactory removal of the unsaponifiable matter and methyl esters from the rosin acids is obtained even by use of very low volumes of naphtha.

In order to demonstrate the economies of countercurrent technique as compared with batchwise extractions, a number of experimental runs were conducted. A solution of tall oil fatty acid esters, rosin acid soaps and unsaponifiable matter of tall oil in water and methanol and comprising: 34.8 methanol, 1.41% sulfuric acid; 18.4 water, 3.3% sodium hydroxide; 43.1 tall oil solids (as sodium sulfate) was prepared.

Extractions were conducted as hereinafter described. The rosin acid soaps were then exhaustively extracted with naphtha of heptane grade and the percentage of unsaponifiable matter and methyl esters thus taken out was determined.

One portion of the solution was extracted batchwise with naphtha of heptane average molecular weight in a proportion of 5 volumes in a single application. The resultant rosin soap solution was found still to contain 1.86 percent of unsaponifiable matter and methyl esters.

In a second batchwise extraction, equal volumes of naphtha of heptane grade and soaps of rosin acids were contacted. The resultant rosin acid soap solution contained 1.97 percent of unsaponifiable matter and methyl esters.

In a third batchwise extraction, a rosin acid soap solution of the above constituency was extracted with naphtha in two separate operations. The volume of naphtha in each instance being equal to the volume of the soap solutions. The resultant rosin acid soap solution as obtained contained 1.86 percent of unsaponifiable matter and methyl esters.

In a fourth batchwise extraction, the rosin acid soap solution was contacted with naphtha in a batchwise operation with three volumes of naphtha divided into three equal portions. The resultant rosin acid soap solution contained 1.81 percent of unsaponifiable matter and methyl esters.

In contradistinction to a countercurrent operation, the solution of tall oil, fatty acid esters, rosin acid soaps and unsaponifiable matter of the foregoing constituency was contacted countercurrently in the column 10 with naphtha in a proportion of 1.25 volumes of naphtha per volume of the solution. The resultant rosin acid soap solution contained 1.2 percent of unsaponifiable matter and methyl esters.

The results of these runs are tabulated as follows:

<table>
<thead>
<tr>
<th>Mode of Extraction</th>
<th>Ratio of Naphtha</th>
<th>No. Applications</th>
<th>Per Cent Naphtha Extractibles in Rosin Acid Soap Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch</td>
<td>5:1</td>
<td>1</td>
<td>1.85</td>
</tr>
<tr>
<td>Do</td>
<td>5:1</td>
<td>1</td>
<td>1.85</td>
</tr>
<tr>
<td>Do</td>
<td>5:1</td>
<td>2</td>
<td>1.31</td>
</tr>
<tr>
<td>Counter-current</td>
<td>1.25:1</td>
<td>1</td>
<td>1.29</td>
</tr>
</tbody>
</table>

From these examples it will be apparent that a single countercurrent extraction is more effective than three applications by batch technique using two and one-half times as much naphtha.

Obviously the countercurrent technique admits of the use of much smaller apparatus and requires much less application of heat in the distillation of the naphtha from the recovered fractions.

If desired the techniques as previously described herein may also be applied to the fractionation of the mixed fatty acids and rosin acid material obtained from the distillation of tall oil. For example, if crude tall oil is fractionated distillately, the first main fraction consisting mostly of fatty acids and a second fraction consisting largely of rosin acids are obtained. This second fraction contains enough fatty acids and unsaponifiable matter to give it properties undesirable for most applications. It is either a very viscous material or a partially crystallized mass and is not comparable to hard, brittle wood rosin. By the application of the technique described for the fractionation of tall oil and constitute a part of this invention, it is possible to separate the fatty acids and unsaponifiable matter from the rosin concentrate constituting the second fraction to yield a hard, brittle rosin.

In a specific example, tall oil was subjected to distillation in accordance with conventional technique to obtain a first fraction having a high content of fatty acids and a low content of rosin acids. There was also obtained a second fraction comprising as its major component rosin acids admixed with some fatty acids and unsaponifiable matter. In the specific example the rosin acids constituted 60% of this second fraction.

In order to separate the fatty acids and unsaponifiable matter from this second fraction, it was subjected to an esterification operation by refluxing 30 parts of the distilled fraction with 16.5 parts of methanol and 1 part of concentrated sulfuric acid. The parts as herein given are by weight. The mixture was cooled to room temperature and diluted with 8.3 parts of methanol. The resultant solution was then reacted with 3 parts of sodium hydroxide dissolved in 6.9 parts of soft water to convert the free rosin acids into sodium salts without splitting the fatty acid methanol esters. The techniques of esterification and neutralization have already been described. The resultant solution of methyl esters, rosin acid soaps and unsaponifiable matter, when made up to the desired concentration as previously described, could be extracted countercurrently with paraffinic hydrocarbons to separate the methyl esters of fatty acids and unsaponifiable matter. To this end, the fatty acid methyl esters and unsaponifiable matter were extracted from the rosin soaps in the solution by
containing the neutralized mixture with mixed heptanes and octanes. The naphtha extract solution was water washed to remove entrained rosin acid soaps and the naphtha was evaporated to recover the fatty acid methyl esters and unsaponifiable matter.

The wash water containing traces of rosin soap from the washing of the combined naphtha extracts, was added to the extracted soap solution and the total mixture was acidified with acids, e.g. mineral acids such as diluted sulfuric acid. The resin layer which was separated was water washed and evaporated to yield a hard resin with a brittle, K color grade and having an acid value of 172.4 and which had a ball and ring softening point of 168° F. After briefly heating the resin to 300° C. and cooling the product of K color grade, 170.1 acid value and 169° F. ball and ring softening point was obtained. This fraction was clear and brittle. The yield of resin was 61.3% based upon the starting material. It was a high grade resin with very little plasticizing acids.

The mixture of fatty acid methyl esters and unsaponifiable matter obtained by extraction of the solution of esters, soaps and unsaponifiable matter with naphtha constituted 40.3% based upon the starting material. It had a Gardner color of 9.5 and was essentially free of rosin acids.

The fatty acid esters could easily be hydrolyzed to obtain the free acids by treating them in accordance with conventional technique, e.g. Twitchellling, high pressure splitting or saponification followed by acidification.

Although the present invention is described with reference to certain embodiments thereof, it will be apparent to those skilled in the art that it is not so limited but that various modifications can be made therein without departure from the spirit of the invention or the scope of the appended claims.

We claim:

1. In a process of fractionating tall oil to separate the resin acids from the fatty acids, the steps which comprise esterifying the fatty acids with lower aliphatic alcohol, diluting the mixture with water, neutralizing the rosin acids with sodium hydroxide, making up 1 volume of the resultant mixture of rosin acid soaps and fatty acid esters into a solution containing 25 to 62.5% solids, 20 to 62.5% of a lower alcohol and 15 to 70% water, and countercurrently contacting the resultant solution with 1 to 20 volumes of naphtha by continuously introducing the solution into an upper portion of a vertically elongated extraction zone and continuously introducing the naphtha into a lower portion of the same zone and drawing off a naphtha solution of esterified fatty acids above the point of introduction of the solution and drawing off a solution of water and lower aliphatic alcohol containing the rosin acid soaps below the point of introduction of the naphtha.

2. The steps as defined in claim 1 in which the naphtha is of heptane grade.

3. The steps as defined in claim 1 in which the alcohol is methyl.

4. A process of separating the resin acids and fatty acids of tall oil, which process comprises esterifying the fatty acids with methanol, diluting the mixture with water, neutralizing the acid components of the mixture with caustic soda and making up the resultant mixture of fatty acid esters and rosin acid soaps with water and methyl alcohol in the proportion of 28% water and 12% methyl alcohol and 60% solids and countercurrently extracting the resultant solution with naphtha of heptane grade at a temperature within a range of 80° to 135° F. by continuously introducing the solution into an upper portion of a vertically elongated extraction zone and continuously introducing the naphtha into a lower portion of the same zone and drawing off a naphtha solution of esterified fatty acids above the point of introduction of the solution and drawing off a solution of water and lower aliphatic alcohol containing the rosin acid soaps below the point of introduction of the naphtha.

5. In a process of fractionating tall oil to separate the resin acid from the fatty acid, the steps which comprise esterifying the fatty acids with methyl alcohol, diluting the mixture with water, neutralizing the rosin acids with sodium hydroxide, making up the resultant mixture of rosin acid soaps and fatty acid esters as a solution in a mixture of water and methyl alcohol, the mixture comprising 7 to 60% by weight of methyl alcohol, 15 to 70% by weight of water and 20 to 65% by weight of solids comprising the fatty acid esters and rosin acid soaps, then intimately contacting the resultant mixture in counter-current flow with naphtha at a temperature of about 80° to 135° F., by continuously introducing the solution into an upper portion of a vertically elongated extraction zone and continuously introducing the naphtha in desired proportion into a lower portion of the same zone and drawing off a naphtha solution of esterified fatty acids above the point of introduction of the solution and drawing off a solution of water and lower aliphatic alcohol containing the rosin acid soaps below the point of introduction of the naphtha, separating the naphtha as a separate phase and evaporating off the naphtha to obtain the fatty acid esters.

6. The steps as defined in claim 5 in which the naphtha is of heptane grade.

7. In a process of fractionating tall oil to separate the resin acids from the fatty acids, the steps which comprise esterifying the fatty acids with methyl alcohol, diluting the mixture with water, neutralizing the rosin acids with sodium hydroxide, making up the resultant mixture of rosin acid soaps and fatty acid esters as a solution in water and methyl alcohol, the mixture containing 10 to 40% methyl alcohol, 15 to 50% water and 25 to 62% solids, then intimately countercurrently contacting the resultant solution with naphtha at a temperature of about 110° to 130° F. by continuously introducing the solution into an upper portion of a vertically elongated extraction zone and continuously introducing the naphtha into a lower portion of the same zone and drawing off a naphtha solution of esterified fatty acids above the point of introduction of the solution and drawing off a solution of water and lower aliphatic alcohol containing the rosin acid soaps below the point of introduction of the naphtha in order to extract out the fatty acid esters in the naphtha and evaporating off the naphtha to obtain the esters.

8. The steps as defined in claim 7 where the naphtha is of heptane grade.

9. A process as defined in claim 7 in which the naphtha is employed in a range of 60 to 200 parts by volume per 100 parts by volume of the solution.

10. In a process of fractionating tall oil to separate it into portions one of which is essentially rosin acids, a second of which is essentially...
fatty acids and a third of which is essentially unsaponifiable matter of tall oil, the steps which comprise selectively esterifying the fatty acids of the tall oil with methyl alcohol, diluting the mixture with water, neutralizing the rosin acids remaining with sodium hydroxide, making up the resultant mixture of rosin acids soaps, fatty acid esters and unsaponifiable matter as a solution in water and methyl alcohol, the mixture containing 10 to 40% methyl alcohol, 15 to 50% water and 25 to 62% tall oil solids, then intimately countercurrently, contacting the resultant solution with naphtha at a temperature of about 110 to 130°F. by continuously introducing the solution into an upper portion of a vertically elongated extraction zone and continuously introducing naphtha into a lower portion of the same zone and drawing off a naphtha solution of esterified fatty acids above the point of introduction of the naphtha in order to extract out the fatty acid esters in the naphtha and evaporating off the naphtha to obtain the esters, then treating the fraction comprising the methyl esters and the unsaponifiable matter with alkali to form soaps of fatty acids, extracting the solution with naphtha to remove unsaponifiable matter and acidifying the fatty acid soaps remaining in solution in order to recover the fatty acids.

11. The steps as defined in claim 10 where the naphtha is of heptane grade.

12. A process as defined in claim 10 in which the fatty acids recovered are further distilled in order to obtain substantially pure fatty acids.

13. In a process of separating the fatty acids from the rosin acids and unsaponifiables of tall oil, the steps of (I) making up a mixture comprising upon the basis of starting materials (a) 42% tall oil in the form of a product obtained by esterifying the fatty acids therein with methanol and with H₂SO₄ as a catalyst, and neutralizing the rosin acids and sulfuric acid (b) 38% methanol (c) 18% water (d) the rest being alkali and sulfuric acid combined as salts and alkali combined as rosin acid soaps, then (II) countercurrently extracting the resultant solution with paraffinic naphtha averaging about 7 carbon atoms per molecule at a temperature of 80 to 135°F.

ROGER M. CHRISTENSON.
RALPH E. HARPT.

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The following references are of record in the file of this patent:

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<table>
<thead>
<tr>
<th>Number</th>
<th>Name</th>
<th>Date</th>
</tr>
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<tbody>
<tr>
<td>1,736,802</td>
<td>Schultze</td>
<td>Nov. 26, 1929</td>
</tr>
<tr>
<td>2,348,970</td>
<td>Gayer et al.</td>
<td>May 16, 1944</td>
</tr>
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<td>2,348,971</td>
<td>Gayer et al.</td>
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<tr>
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<td>Freeman</td>
<td>July 1, 1947</td>
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