PROCESS FOR THE SEPARATION OF MIXTURES OF FATTY ACIDS AND ROSIN ACIDS

A process for the separation of a mixture of fatty and rosin acids, in which a mixture of fatty acids in the form of esters, and rosin acids is neutralized by reaction with an alkali-metal or ammonium base in aqueous solution and in the presence of at least one mole (per mole of rosin acid) of an alkali-metal or ammonium aryl or alkyl-aryl sulfonate. The mixture is allowed to stand until it separates into two layers, the upper layer consisting of the fatty acid esters and the lower layer containing the alkali-metal or ammonium salts of the rosin acids, and the two layers are then mechanically separated and their constituents recovered. This process is particularly applicable for removing unsaponifiables from crude tall oil.

BACKGROUND OF THE INVENTION

This invention relates to processes for the separation of mixtures of fatty acids and rosin acids, and is particularly concerned with the separation of such mixtures known as tall oil.

Tall oil is a by-product of the wood pulp industry, and is formed when coniferous woods are treated by the sulfite process. Under the alkaline conditions of this process, fatty and resinous substances contained in the wood are brought into aqueous solution and are recovered as "skimmings." These skimmings are the sodium salts (soaps) of fatty and rosin acids mixed with various inorganic salts and with water. Acidification of the skimmings with a mineral acid, usually sulphuric acid, liberates a mixture of the free fatty acids and resin acids, together with various other materials, and this mixture is known as tall oil.

The composition of tall oil may vary within wide limits according to the variety of the wood, the location of its growth, its age, the conditions under which it is stored and treated, and the method of its manufacture. Basically, however, tall oil is a mixture of fatty acids (mostly C_{12}-C_{34} mono- and di-unsaturated fatty acids, with minor amounts of saturated acids), rosin acids (mainly abietic and dehydroabietic acid) and variable amounts of neutral, saponifiable and unsaponifiable components (which contain aliphatic and cyclic hydrocarbons, fatty alcohols and phytosterols, as well as phenolic and sulfur containing compounds), fatty acid esters, and ill-defined acidic compounds (which are insoluble in petroleum ether and are, therefore, thought to be keto and hydroxy acids).

The unsaponifiable fraction of some tall oils has been found too high to make their recovery and purification by the known art economically attractive or technically feasible.

Tall oil has been potentially available from the expanding wood pulp industry for many years, but its use has been severely limited by its variable composition, dark color and unpleasant odor. Indeed, even when whole distilled tall oil could not be used widely because the presence of one or the other of the two main components (fatty acids and rosin acids) becomes the limiting factor for specific applications, and the very recent and spectacular growth of the industry only commenced when high vacuum stills were developed which were capable of separating the fatty acids from the rosin acids.

However, although high vacuum fractionation of tall oil into its main components has been generally accepted as the only available practical method, it still suffers from a number of inherent disadvantages. Firstly, both major components are of high molecular weight, and at their boiling point (even under conditions of high vacuum), temperatures are approached which lead to the polymerization of the polyunsaturated fatty acids and to the decarboxylation of the rosin acids. Secondly, the presence, and almost inevitable formation by oxidative adornition, of hydroxy acids and other hydroxy compounds during distillation at high temperature leads to ester and esteride formation—which increases the nonvolatile fraction (pitch) and reduces the yield of distilled product. Thirdly, clean fractionation is made very difficult by the presence—if only in minor amounts—of components which form intermediate fractions which cannot readily be further refined, and, although these intermediate fractions contain large amounts of the desired compounds, they have to be disposed of as cheap mixtures. The forerun (which is composed of the lower boiling fatty acids and the more volatile unsaponifiable matter) and especially the middle cut (which often contains as much as 35% rosin acids together with 65% fatty acids, enriched in the C_{20}-C_{24} homologues and the less volatile conjugated fatty acids) are two such fractions. Finally, a modern tall oil distillation plant consists of a plurality of fractionation columns which have to be of considerable diameter and height to achieve the required fractionation and low pressure drops demanded. As the products handled are corrosive, special steels are used for most of the equipment, so that the cost of such plants is high. Accordingly, they are usually designed for large throughputs to achieve economic operation, and thus amounts of tall oil which are anything less than, for instance, 15,000 tons per year cannot be profitably handled.

It is an object of this invention to provide a method of separating mixtures of fatty acids and rosin acids, such as is found in tall oil, without fractional distillation, to provide products in high yield and of good quality.

It is equally an object to provide a process which is flexible as to the choice of crude feed and by which small quantities of crude oil can be purified economically.

SUMMARY OF THE INVENTION

In one aspect, therefore, this invention provides a process for the separation of a mixture of fatty acids and rosin acids, in which a mixture of fatty acids, in the form of esters, and rosin acids is neutralized by reaction with an alkali-metal or ammonium base in aqueous solution and in the presence of at least one mole (per mole of rosin acid) of an alkali-metal or ammonium aryl or alkyl-aryl sulfonate (wherein the aryl group or groups together contain not more than 8 carbon atoms), the thus formed mixture is allowed to stand so that it separates into two layers, the upper being an oily layer consisting of the fatty acid esters, the lower being an aqueous layer containing the alkali-metal or ammonium salts of the rosin acids, and the two layers are then mechanically separated and their constituents recovered.

Normally, the alkali-metal or ammonium salts of organic acids such as rosin acids and, in particular, fatty acids are soaps, i.e., they depress the surface tension of water and have the ability of solvating, or bringing into aqueous solution, substances otherwise insoluble in water.

The process of the invention is based upon the surprising observation that the alkali-metal or ammonium salts of fatty and rosin acids, when dissolved in water containing an alkali-metal or ammonium aryl or alkyl-aryl sulfonate as herein defined, do not behave like soaps.
DESCRIPTION OF THE INVENTION

The sulfonate salts used in the invention are those which do not themselves markedly depress the surface tension of water. Examples of such compounds which are particularly useful in the process of this invention are the salts of benzene, toluene (methyl benzene), cumene (isopropyl benzene), cymene (1-methyl-4-isopropyl-benzene) and xylene (dimethyl benzene) sulfonates, especially the sodium, potassium or ammonium salts. These products are readily available from cheap hydrocarbons or their mixtures by well known sulfonation processes.

Both the absolute amount of sulfonate and the amount relative to the free acid in the fatty ester/rosin acid mixture are factors important for the proper utilization of the process of this invention. The absolute amount of sulfonate employed is preferably that amount which will give at least a 15% w/w aqueous solution thereof. If less than 15% is employed, then there is a tendency for the rosin acid salt to behave as a soap, solvating the fatty acid ester. In extreme cases the aqueous rosin acid salt/fatty ester mixture may emulsify, in which case separation of the two components may be impossible. Indeed, in order to reduce any such tendency to a minimum it is preferred to employ at least a 20% w/w solution of the sulfonate. For all practical purposes an upper amount of 40% w/w is quite satisfactory. More can be added, without any deleterious effect, but is unlikely to make the subsequent separation much more efficient. A particularly preferred amount of sulfonate is 25% w/w.

Though the mechanism by which the sulfonates prevent solvation is not fully understood, it does seem as though they take part in complex formation with the rosin acid salt present in the mixture, and that this occurs on a mole-for-mole basis. Accordingly, it is preferred that the amount of sulfonate employed should be at least equimolecular with the amount of rosin acid salt in the mixture. If lower amounts of sulfonate are employed, then there is again a tendency for the rosin acid salt to behave like a soap, emulsifying the mixture. If greater amounts of sulfonate are employed—for example, three moles per mole of rosin acid salt—then the separation may be a little less efficient, but not markedly so. Accordingly, the process of this invention is conveniently used not more than three moles of sulfonate per mole of rosin acid salt.

The neutralization of the fatty acid ester/rosin acid mixture is conveniently effected using an alkali-metal hydroxide or carbonate such as sodium or potassium hydroxide or carbonate. Generally, the neutralization should be reasonably exact—the resulting mixture having a pH of from 7 to 8—but a slight excess of base (giving a pH of about 10) is not harmful. The neutralization step is advantageously accompanied by vigorous agitation of the reaction medium, to ensure as complete a reaction as possible.

The temperature at which neutralization is effected is not critical. However, at ambient temperature (about 25°C) the initial fatty acid ester/rosin acid mixture is somewhat viscous, and the neutralization itself proceeds rather slowly. Accordingly, the reaction is preferably effected at a temperature of from 70°C to 80°C. Higher temperatures, up to boiling point of the mixture's constituents, may be employed but they are not particularly advantageous and may lead to undesirably hydrolysis of the fatty acid ester.

After the neutralization reaction is completed the mixture is allowed to stand (preferably maintaining the temperature at from 70°C to 80°C), and separate into two layers. Separation occurs quite quickly and completely, and the layers are well defined. The top layer is an oily layer containing all the various fatty acid esters, while the bottom layer is an aqueous layer containing the rosin acid salts.

The two layers may then be mechanically separated one from another—for example, by decanting off the top layer or by draining off the bottom layer—and their constituents recovered.

The fatty acid ester layer may be washed with a little water to complete the purification, and to recover minor amounts of rosin acid salt and sulfonate salts. The aqueous layer containing the rosin acid salts is treated with a mineral acid, for example sulfuric acid. Chemically pure rosin acids separate as an upper, oily layer and may be decanted off.

The aqueouslinkedin layer (containing the arylsulfonate salt and sodium sulfate) formed by treating the rosin acid salt solution with sulfuric acid, may be recovered for reuse. The purity of the sulfonate is not critical, though it is still convenient to remove some of the sulfonate first.

It should be noted, incidentally, that an inorganic sulfate such as sodium sulfate which may arise as a byproduct in the manufacture of the alkylaryl-sulfonate salts—or, indeed is produced as a co-product is carrying out the process of the invention—is in no way deleterious to the working of the process and may be present up to and including saturation concentration. Furthermore, diaryl-sulfones, common contaminants of arylsulfonates, are also without effect.

The starting material for the process of this invention is a mixture of fatty acid esters and rosin acids. This material is conveniently prepared, in a first preliminary stage, by the partial esterification of a corresponding mixture of fatty acids and rosin acids. This reaction may be carried out in any of the conventional ways. For example, the reaction may employ an alcohol, such as methyl alcohol, as the esterification agent, and may be effected either at a low temperature in the presence of an acidic esterification catalyst or at a high temperature in the presence of a basic esterification catalyst. The reaction is thoroughly conventional, and it is believed unnecessary to describe it in any further detail.

The mixture of fatty acids and rosin acids (used to prepare the mixture of fatty acid esters and rosin acids) may be obtained from any source. However, the prime purpose of the process of this invention is the economical separation of the constituents of tall oil, and thus conveniently the fatty acid/rosin mixture is, in fact, tall oil itself.

As stated above, tall oil contains a number of types of constituents other than fatty acids and rosin acids. In particular, tall oil contains a range of unsaponifiable materials—including aliphatic and cycloaliphatic hydrocarbons, fatty alcohols, phytosterols, phenolic materials and sulfur-containing compounds—as well as small amounts of fatty acid esters. In many cases the unsaponifiable materials are present in relatively small amounts, and can be tolerated in the products of this invention. In other cases, however, this is not so. Accordingly, this invention includes, as an alternative process, the removal of these unsaponifiable compounds from tall oil by a process in which the tall oil itself is neutralized by reaction with an alkali-metal or ammonium base in aqueous solution and in the presence of at least one mole (per mole of acid) of an alkali-metal or ammonium aryl or alkylaryl sulfonate (wherein the aryl group or groups together contain not more than 8 carbon atoms), the thus formed mixture is allowed to stand so that it separates into two layers, the upper being an oily layer consisting of the unsaponified fraction, the lower being an aqueous layer containing the alkali-metal or ammonium salts of the fatty acids and the rosin acids, and the aqueous layer is removed and acidified to give a mixture of fatty acids and rosin acids.

As will be apparent, this alternative process is essentially a modification of the main process of the invention, and the various preferred features of this invention are also preferred for the alternative process. Thus, the sulfonate is sodium or potassium benzene, toluene, cymene, cymene or xylene sulfonate; the concentration of sul-
finate is in the range 20% to 35% w/w; the amount of sulfonate is at least equimolecular with the amount of free acid (fatty acid and rosin acid); the base is sodium hydroxide; the temperature for the neutralization and standing is 70° to 80° C.; and the acidification is effected using sulfuric acid.

In many cases tall oil contains, as indicated hereinabove, small quantities of fatty acid esters. For example, a typical analysis of tall oil samples from Austria, Sweden and the United States reveals the following figures for the acid value, saponification value and ester value of such tall oils:

<table>
<thead>
<tr>
<th></th>
<th>Acid value</th>
<th>Saponification value</th>
<th>Ester value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austria</td>
<td>117-127</td>
<td>149-162</td>
<td>22-35</td>
</tr>
<tr>
<td>Sweden</td>
<td>169-169</td>
<td>169-179</td>
<td>10-15</td>
</tr>
<tr>
<td>United States</td>
<td>163-170</td>
<td>168-177</td>
<td>12-17</td>
</tr>
</tbody>
</table>

Though it is difficult to express the ester value in terms of a percentage of the mixture, nevertheless the amount of ester can be said to be an appreciable proportion of the tall oil. Now, in the processes so far described, this tall oil ester fraction will be removed in the alternative process, as a component of the upper, oily layer, and discarded—which may represent the wastage of a considerable amount of fatty acid. However, if the alternative process neutralization is carried out at a high temperature of the order of 100° C. to the mixture’s boiling point—then these esters are saponified, and the resultant alkali-metal or ammonium salts are recovered in the aqueous fraction of the reaction mixture.

A typical procedure for carrying out the complete process of this invention is, therefore, as follows:

Stage A.—Removal of unsaponifiable material

One molecular proportion of sodium xylene sulfonate is dissolved in sufficient water at 70° C. to provide a 25% (w/w) solution. One molecular proportion of crude tall oil acids is then added. While keeping the temperature around 70° C., the mixture is neutralized by the careful addition of anhydrous sodium carbonate, (one half mole). A low viscosity mixture is obtained. On standing, the unsaponifiable fraction contained in the crude oil separates as an oily layer from the soap solution.

An even more complete separation of the neutral fraction may be obtained by extracting the aqueous soap solution with a hydrocarbon solvent and again separating the two phases.

Useful products may be isolated from the neutral fraction thus separated. The recovery of these from the products of normal distillation process is difficult or impossible because of chemical changes and decomposition brought about by high temperature treatment.

On acidifying the aqueous soap solution with a mineral acid, preferably sulfuric acid, the purified, mixed tall oil acids separate from the aqueous salt solution and are recovered by decantation.

It is understood that in a similar manner “skimnings,” tall oil soaps, may be purified if account is taken of the water content of the crude soap mixture in preparing the arylsulfonyl salt solution.

The aqueous solution containing the sulfonate salt and sodium sulfate is neutralized and evaporated, if necessary, to the preferred concentration. Excess sodium sulfate is removed by filtration (either from the hot solution as the anhydrous salt or from the cooled solution as the dehydrate) and the remainder is then suitable to be recycled for further treatment of crude oil. Alternatively, the remainder may be passed on to the second stage of the process.

Stage B.—Separation of fatty acids from rosin acids

1. The esterification of tall oil with alcohols (preferably methanol) is a well known reaction and need not be described here. Using methanol there is obtained a mixture of rosin acids and fatty acid methyl esters.

2. The separation of this ester/acid mixture into its components may be carried out under similar conditions to those described for the separation of neutral components from crude tall oil. The mixture is treated at 70°-80° C. with a 25% aqueous solution of the arylsulfonate salt, the amount of the sulfonate being at least one mole for each mole of rosin acid in the mixture of acids and fatty esters. Sodium carbonate or caustic soda is added to saponify completely all the acids present (pH 7-10). The mixture is stirred vigorously for a short time to complete the reaction, and then allowed to stand, maintaining the temperature between 70° and 80° C. Phase separation occurs rapidly and completely. The upper, oily phase contains all the fatty acid methyl esters, the lower, aqueous phase the soaps of the rosin acids free from any neutral material.

The fatty acid ester layer may be washed with a little water to complete the purification, and to recover minor amounts of rosin acid salt and sulfonate salt. The esters are chemically pure but usually of a dark color. On distillation, a product of low color and excellent odor is obtained. If a process of total distillation is used, all the fatty components originally present in the crude oil are recovered in the form of their esters, including the conjugated and higher boiling fractions which are normally found in the intermediate cuts associated with rosin acids.

The aqueous layer containing the rosin acid salts is treated with a mineral acid, for example sulfuric acid. Chemically pure rosin acids separate as an upper, oily layer and may be decanted off. At this stage the rosin acid product is dark in color, but an almost colorless product may be obtained by a straight short path distillation in vacuo. Such a distillation (requiring a minimum residence time) eliminates almost completely the very undesirable decarboxylation which occurs during fractional distillation.

As the high boiling residue has also been largely diminished, the yield of rosin acid product is significantly increased as compared with that obtained in a fractional distillation separation. The process of the invention may, of course, be carried out batchwise or continuously.

For many applications, methyl tall oil fatty acid esters are more desirable than the parent acids. Esters are more stable in storage, non-corrosive and can be processed readily to polymers, alkyd resins, plasticizers and stabilizers. Methyl esters are also readily converted to other esters with mono and polyhydric alcohols. If, however, the fatty acids are required, the methyl esters may be converted to the acids by hydrolysis, preferably with water under pressure at elevated temperatures. In this way methanol may be recovered for reuse.

The practice of this invention may clearly be seen in the following examples.

**EXAMPLE 1**

**Stage A**

Crude tall oil of Swedish origin having the following composition was purified and separated into its main components.

<table>
<thead>
<tr>
<th></th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rosin acids</td>
<td>40</td>
</tr>
<tr>
<td>Fatty acids</td>
<td>45</td>
</tr>
<tr>
<td>Unsap. matter</td>
<td>12</td>
</tr>
<tr>
<td>Oxidized acids</td>
<td>3</td>
</tr>
</tbody>
</table>

A solution of sodium xylene sulfonate (208 grams) was prepared in water (600 cc). While heating the solution to 80° C., 357 grams of crude tall oil was added, followed by the careful addition with stirring of 53 grams of anhydrous sodium carbonate. When this addition was completed, the pH was checked and found to be in the region of 8. The temperature was maintained, and the mixture allowed to stand for half an hour. An oily layer, containing 30 grams of unsaponifiable material, separated...
and was removed by decantation. An even more complete removal of the unsaponifiable matter was achieved by extracting the aqueous mixture with a petroleum ether solvent. After washing the solvent extract with a little water, the solvent was removed, leaving the residue of 12 grams. Total unsaponifiable matter recovered was 42 grams. To the aqueous solution 50 grams of 98% sulfuric acid was gradually added. On settling, mixed tall oil acids, freed from unsaponifiable contaminants, were isolated as an oily top layer.

Stage B

(1) By known processes, the mixed acids were esterified with methanol until all the fatty acid component in the tall oil had been converted to a mixture of methyl esters. None of the resin acid component had been so esterified.

(2) The acid value (AV) of the ester resin acid mixture was determined, and the extraction procedure of neutral material from soaps repeated using again one mole of sodium xylene sulfonate in 25% aqueous solution for each mole of resin acid present in the mixture. For this step, the previously recovered aqueous solution of sodium xylene sulfonate was employed after excess sodium sulfonate solids had been removed by filtration and the concentration of sulfonate checked to be not less than 25%.

Phase separation occurred rapidly at 75°C and the oily top layer (purified ester) was removed by decantation. It was washed once with hot water (3% by volume of the total oil volume) and the aqueous washings were combined with the soap solution. On distillation of the oil in vacuo, an almost water white product was obtained, the distillation residue amounted to 2%. The distillate contained 0.2% unsaponifiable matter and 0.5% resin material.

The aqueous rosin soap solution was acidified as previously described with sufficient sulfuric acid to reduce the pH of the mixture to 4–5. The oily layer of resin acids obtained by decantation was washed with 3% hot water, the washings being added to the aqueous solution of sulfonate salts.

The chemically pure rosin acids were finally decolorized by steam distillation in vacuo, without fractionation. The distillate was faintly yellow in color. The distillation residue amounted to 3%. The distilled product contained 0.3% unsaponifiable matter and 0.5 fatty matter.

EXAMPLE 2

Stage A

Crude tall oil of U.S. origin was purified and separated into its components. The oil had the following composition:

<table>
<thead>
<tr>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rosin acids</td>
</tr>
<tr>
<td>Fatty acids</td>
</tr>
<tr>
<td>Unsaponifiable matter</td>
</tr>
</tbody>
</table>

To a solution of 44 grams of sodium cumene sulfonate and 888 grams of water was added 80 grams of 50% w/w. caustic soda solution. The mixture was heated to boiling point and 340 grams crude tall oil gradually added. Gentle boiling was continued for half an hour with stirring to complete the hydrolysis of a small ester fraction in the oil. The low viscosity solution was then cooled to 70°C and the aqueous layer removed and extracted once with petroleum ether solvent (2000 cc.; B.P. range 100°C–120°C). On evaporation, the solvent 20 grams of unsaponifiable matter was removed.

Stage B

(1) The aqueous layer was acidified to give an oily layer of the purified acids, and these were then esterified by refluxing in methanol (340 cc.), containing a small amount (1.5 g.) of concentrated sulfuric acid as a catalyst, for one hour. The formed fatty acid ester/resin acid mixture was isolated by first neutralizing the mineral acid catalyst by the addition of an equivalent amount of sodium carbonate, then distilling off the excess of methanol and finally washing the product with water.

(2) The second step of the separation of the two main components was carried out as described in Example 1. The ester/acid mixture obtained in the previous step (330 g.) was added at 75°C to an aqueous solution (666 g.) containing sodium cumene sulfonate (222 g.). With vigorous stirring, caustic soda solution (40 g.; approximately 50% w/w.) was added carefully until a stable pH of 8 was attained in the aqueous phase. After separation of the oily layer from the soap solution it was washed with a little hot water and distilled.

The rosin acids were isolated from the soap solution as in Example 1, washed and distilled. Analysis of the ester and acid fractions showed:

<table>
<thead>
<tr>
<th></th>
<th>Fatty acids</th>
<th>Rosin acids</th>
<th>Unsaponifiable matter</th>
<th>Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester fraction, percent ......</td>
<td>99.3</td>
<td>0.5</td>
<td>0.5</td>
<td>2</td>
</tr>
<tr>
<td>Rosin acid fraction, percent</td>
<td>0.5</td>
<td>99.2</td>
<td>0.3</td>
<td>3</td>
</tr>
</tbody>
</table>

EXAMPLE 3

The same crude tall oil as used in Example 2 was purified. The preliminary removal of unsaponifiable matter was omitted.

To 340 grams of the crude oil was added 1.5 grams of concentrated sulfuric acid and the mixture was heated to 110°C. Methanol (150 g.) was introduced below the surface of the stirred mixture over a period of one and a half hours, and methanol and water were allowed to distill off. The resulting mixture, without any further treatment, was added to 900 grams of an aqueous solution containing 300 grams of dissolved mixed ortho and para sulfonate salts at 80°C. A caustic soda solution of 40 grams (approximately 50% w/w.) was carefully stirred into the mixture to neutralize all the acids (rosin acids and the sulfuric acid catalyst) until a permanent pH of 8 was attained. The ester and rosin acid fractions were isolated as previously described, and analysis thereof showed:

<table>
<thead>
<tr>
<th></th>
<th>Fatty acids</th>
<th>Rosin acids</th>
<th>Unsaponifiable matter</th>
<th>Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester fraction, percent ......</td>
<td>98.6</td>
<td>0.5</td>
<td>1.5</td>
<td>4</td>
</tr>
<tr>
<td>Rosin acid fraction percent</td>
<td>0.5</td>
<td>96.5</td>
<td>3</td>
<td>7</td>
</tr>
</tbody>
</table>

EXAMPLE 4

Distilled tall oil (referred to as "middle cut" hereinbefore) was separated into its two main components. This fraction had the following composition:

<table>
<thead>
<tr>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fatty acids</td>
</tr>
<tr>
<td>Rosin acids</td>
</tr>
<tr>
<td>Unsaponifiable matter</td>
</tr>
</tbody>
</table>

To preserve the color of this material the esterification was carried out in the presence of an oxidation inhibitor (hydro-phosphorous acid, 1% of 50% aqueous solution based on the weight of oil) and the acid catalyst used was 1.5 grams of toluene sulfonic acid. A 20-fold excess of methanol over that theoretically required was employed. The acid value (AV) of the water washed ester/rosoin acid mixture was determined, and from this figure twice the molecular amount of mixed isomer ammonium xylene sulfonate to be employed in the separation was calculated.

A sample of distilled tall oil having an acid value of 186 was thus esterified yielding 291 grams of an ester/acid mixture having an acid value of 56 from the theoretical yield of 298 grams. This was added to an aqueous solution (488 g.) containing 122 grams of dissolved ammonium xylene sulfonate. At 50°C, with agitation, an ammonium hydroxide solution (20 g. approximately 25% solution) was added until the reaction mixture was slightly alkaline.
Maintaining this temperature, the mixture was allowed to settle, and the two separate phases were worked up as previously described. As the color of the material had hardly altered from the third treatments given, neither fraction needed redistillation. Analysis showed:

<table>
<thead>
<tr>
<th>Fatty material</th>
<th>Rosin acids</th>
<th>Unsoluble matter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester fraction, percent</td>
<td>99.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Rosin acid fraction, percent</td>
<td>0.5</td>
<td>96.8</td>
</tr>
</tbody>
</table>

While the invention has been described and illustrated herein by references to various specific materials, procedures, and examples, it is understood that the invention is not restricted to the particular materials, combinations of materials, and procedures selected for that purpose. Numerous variations of such details can be employed, as will be appreciated by those skilled in the art.

What is claimed is:

1. A process for the separation of fatty acids and rosin acids, from the mixture thereof contained in tall oil or tall oil soaps comprising:
   (1) converting the fatty acid component of said mixture into fatty acid methyl esters;
   (2) neutralizing the resulting mixture of fatty acids, in the form of esters, and rosin acids by reaction at above about 25° C. with a member of the group consisting of an alkali-metal base and an ammonium base in aqueous solution and in the presence of at least one mole per mole of rosin acids of a member of the group consisting of alkali-metal and ammonium benzene, tolune, cumene, cymene and xylene sulfonates, said sulfonates being employed in an amount providing at least a 15% w/w. aqueous solution thereof;
   (3) allowing the thus-formed mixture to separate into two layers, the upper being an oily layer consisting of the fatty acid esters, the lower being an aqueous layer containing the alkali-metal or ammonium salts of the rosin acids; and
   (4) mechanically separating the two layers, and recovering the fatty acid and rosin acid constituents from the respective layers.

2. The process as claimed in claim 1, wherein the sulfonate salt is a member of the group consisting of the sodium and potassium salts.

3. The process as claimed in claim 1, wherein the sulfonate is employed in an amount to provide a 20% to 40% w/w. aqueous solution thereof.

4. The process as claimed in claim 3, wherein the amount of sulfonate is 25% w/w.

5. The process as claimed in claim 1, wherein from one to three moles of sulfonate per mole of rosin acid is used.

6. The process as claimed in claim 5, wherein one mole of sulfonate per mole of acid is employed.

7. The process as claimed in claim 1, wherein the neutralization of said mixture is effected using a member of the group consisting of sodium carbonate, potassium carbonate, sodium hydroxide and potassium hydroxide.

8. The process as claimed in claim 1, wherein said neutralization temperature is between 70° C. and 80° C.

9. The process as claimed in claim 1, wherein said aqueous layer is thereafter treated with sulfuric acid whereby the free rosin acids are liberated therefrom.

10. The process as claimed in claim 1, wherein said oily, upper layer is thereafter converted to free fatty acids by hydrolisis.

11. The process as claimed in claim 1, wherein the unsaponifiable compounds in the tall oil are first removed by neutralizing the tall oil by reaction with a member of the group consisting of an alkali-metal base and an ammonium base in aqueous solution and in the presence of at least one mole (per mole of acid) of a member of the group consisting of alkali-metal and ammonium benzene, tolune, cumene, cymene and xylene sulfonates, said sulfonates being employed in an amount providing at least a 15% w/w. aqueous solution thereof, allowing the mixture to stand so that it separates into two layers, the upper being an oily layer consisting of the unsaponified fraction, the lower being an aqueous layer containing the alkali-metal salts of the fatty acids and the rosin acids, removing the aqueous layer, and acidifying to give a mixture of fatty acids and rosin acids.

12. The process as claimed in claim 11, wherein the reaction mixture is heated to a temperature of from 100° C. to its boiling point to saponify any fatty acid esters present in the tall oil starting material.

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UNITED STATES PATENTS


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Vilbrant et al.: "Separation of Rosin and Fatty Acids" in the "Industrial and Engineering Chemistry," February 1941 (pp. 197 to 200).

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