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FRACTIONATION OF TALL OIL

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This invention relates to the fractionation of tall oil. More particularly the invention relates to a process of separating a fraction, including the saturated fatty acids from tall oil, by partially oxidizing the tall oil and thereafter subjecting the resulting oxidized material to solvent extraction.

Tall oil is a by-product of the manufacture of kraft paper by the sulfate process from pine or fir wood and is generally considered to be a mixture of fatty acids, rosin acids, and unsaponifiable materials. Generally speaking, a typical crude tall oil contains about 35% to 50% rosin acids, about 40% to 50% fatty acids, and about 5% to 10% sterols, and other nonsaponifiables. Of the fatty acid fraction, saturated acids may comprise about 6% to 8% of the total, oleic acid about 44% to 52%, and linoleic acid about 45% to 50%.

Various methods of fractionating tall oil into a fatty acid fraction and a rosin acid fraction have been proposed and used. Generally speaking, however, these fractionation methods have not resulted in isolation of a fraction which is substantially completely free of saturated fatty acids. In other words, one fraction separated contains substantially all of the saturated acids, and, in some cases, the sterols present in the original material. In some instances, the presence of saturated fatty acids and/or sterols is undesirable as these materials tend to cause compositions containing tall oil to exhibit comparatively high thermoplasticity. In formulating a composition in which thermoplasticity is an undesirable characteristic it is, therefore, advantageous to eliminate or substantially reduce the quantity of saturated fatty acids and sterols present.

While we do not intend to be limited to any theories expressed herein, it is believed that prior methods of fractionation in which tall oil was subjected to solvent extraction failed to result in substantially complete separation of saturated fatty acids and sterols because of the similar degrees of polarity of the fractions desired to be obtained. It would seem to follow that these prior fractionation methods which, generally speaking, rely upon the use of a mixture of polar and nonpolar solvents fail to effect substantially complete separation of these fractions.

We have found that tall oil may be subjected to oxidizing conditions to partially oxidize the material and thereby increase the polarity of the unsaturated and oxidizable fatty acids. Following the oxidation, the oxidized material is subjected to solvent extraction.

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In accordance with our invention the oxidation of the tall oil may be carried out in any suitable oxidizing equipment, and the conditions of oxidation may vary depending upon the particular extraction system to be used as more fully described hereinafter. Advantageous results may be obtained by passing air through the tall oil while maintaining an elevated temperature of between about 60° C. to about 150° C. Particularly advantageous results may be obtained at temperatures of between about 70° C. to about 100° C. The most advantageous manner of determining the degree of oxidation to be desired is by measuring the viscosity of the material subjected to oxidizing conditions. Generally speaking, we have found it advantageous to subject tall oil to oxidizing conditions until the viscosity of the material is between about 15 seconds and 250 seconds at 25° C. by the Gardner-Holdt method. When material is oxidized to a viscosity less than about 15 seconds, the polarity of the unsaturated and oxidizable acids is such that the desired fractionation by solvent extraction cannot be obtained. When a viscosity greater than 250 seconds is reached, the desirable characteristics of certain fractions may be destroyed. Generally speaking, in the practice of our invention, tall oil is oxidized under such conditions as to obtain a product having an increase in refractive index over that of the starting material of about .0040.

In accordance with one embodiment of our invention the oxidized tall oil is mixed with a nonpolar solvent. While any of the well-known nonpolar hydrocarbon solvents such as the higher boiling aliphatic hydrocarbons, for example a mixed octane fraction, aromatic hydrocarbons, for example benzene, toluene, xylene, and commercial mixtures of straight chain and aromatic hydrocarbons may be used, we have obtained the desired results by means of a petroleum naphtha. Generally speaking, higher boiling solvents such as those boiling between about 150° to about 300° F. are preferred as these may be easily removed from their extracts. When this method of fractionation is followed, the fraction insoluble in the nonpolar solvent is substantially completely free of saturated acids.

In another embodiment of our invention the oxidized tall oil is dissolved in a polar solvent and thereafter extracted with a nonpolar solvent. In this embodiment of our invention, as well as in the other embodiments mentioned

hereinbelow where polar solvents are utilized, a wide variety of polar solvents may be employed. The polar solvents may contain a hydroxyl group such as methyl alcohol, ethylene glycol, propylene glycol, and glycerine. They may contain hydroxy esters such as betahydroxy ethyl acetate. They may contain a carboxyl group such as formic acid and acetic acid. They may contain an aldehyde group such as benzaldehyde. They may contain a carbonyl group such as acetone. They may be ethers, for example dimethoxy tetraglycol. All of these are well-known polar solvents and have been employed in various solvent extraction processes in which polar solvents are utilized. Generally speaking, we have obtained particularly advantageous results in the practice of our invention when furfural is used as the polar solvent.

When the oxidized tall oil is first dissolved in a polar solvent and then extracted with nonpolar solvent, the polar solvent fraction is then freed of solvent and the resulting material is substantially completely free of saturated fatty acids.

In still the third embodiment of our invention the fractionation of the oxidized tall oil may be carried out by partition chromatographic separation. In accordance with this particular embodiment of our invention a suitable column is provided and charged with an adsorbent material such as finely divided dehydrated silica which has been impregnated with an equal weight of polar solvent and then mixed into a slurry with nonpolar solvent which had been previously saturated with polar solvent. This slurry is charged to the column, and the adsorbent and nonpolar solvent separate to obtain the desired partition column. When the nonpolar solvent has settled to the level of the adsorbent, a mixture of oxidized tall oil and nonpolar solvent is added. When the tall oil has passed down to the level of the adsorbent, more nonpolar solvent is added to develop the column. Generally speaking, three bands develop within the column. The first band passes through the column rapidly and is collected at the discharge end. The column may then be broken up to separate the two remaining bands and each is eluted from the adsorbent by means of a suitable solvent such as acetone or other low boiling oxygen-containing solvents. The resulting fractions include a partially oxidized unsaturated fatty acid and resin acid fraction which is substantially completely free of saturated fatty acids and sterols.

In order to more fully understand our invention, reference may be had to the following specific examples which are given by way of illustration and not by way of limitation.

Example I

A crude tall oil which had an acid number of 165 and a rosin acid number of 82 was oxidized in a constant temperature oil bath using a two-liter three-necked flask fitted with a motor-driven stirrer and having an air-dispersing inlet. The stirrer was driven at the rate of about 1,000 R. P. M. and a constant rapid air flow was maintained by means of a flow meter. Oxidation was carried out in this manner at a temperature between 80° and 120° C. until the tall oil had a viscosity of 234 seconds (Gardner-Holdt). This viscosity was reached in 21 hours. A 23.5 gram sample of the oxidized oil was treated with 120 cc. of "Skellysolve B" (a petroleum naphtha boiling between 63° C. and 70° C.) and a residue of 5.3 grams was obtained. The residue had an acid number of 176.4 and a rosin acid number of 90.5 while the soluble fraction had an acid number of 148.3 and a rosin acid number of 56.4. The soluble fraction had 5.26% of saturated acid precipitate when cooled in acetone which was fatty acid in nature. The residue gave a small resinlike precipitate when analyzed for saturated acids.

Example II

A 26.4 gram sample of tall oil oxidized in accordance with the method set forth in Example I was completely dissolved in 130 cc. of furfural. The resulting solution was then extracted twice with "Skellysolve B," first with 100 cc. and then with 150 cc. The material recovered from the furfural extract had an acid number of 152 and a rosin acid number of 77. The material from the naphtha extract had a rosin acid number of 51.0. The latter gave a heavy saturated acid precipitate at —25° C. while the furfural extract material remained clear in a similar solution.

Example III

A partition chromatographic separation was run using 352 grams of granular silica impregnated with 353 grams of furfural which had been saturated with "Skellysolve E" (a petroleum naphtha boiling between 100° C. and 132° C.). A 51 gram sample of oxidized tall oil obtained in a manner similar to that set forth in Example I was dissolved in "Skellysolve E" which had been saturated with furfural. This solution was then poured onto the column. Sufficient "Skellysolve E" was then added to develop the column. Four fractions were taken from the column, two fractions of the material coming through the column and two fractions of the material being eluted from bands on the columns by means of acetone. The first fraction taken from the column contained 21.5 grams and had an acid number of 158 and a rosin acid number of 45 and contained a considerable amount of saturated acids. The second fraction taken from the column contained 6.7 grams, had an acid number of 182 and a rosin acid number of 85. This fraction contained some saturated acids but less than fraction 1. Fraction 3, which was the first fraction eluted from the column, contained 5 grams and had an acid number of 138 and a rosin acid number of 90. Fraction 4, which was the second fraction eluted from the column, contained 8.3 grams and had an acid number of 148 and a rosin acid number of 92.5 and was free from saturated acids.

An analysis of the above specific examples will indicate that following oxidation of the tall oil a partially oxidized unsaturated fatty acid fraction which is substantially completely free of saturated fatty acids may be obtained by solvent extraction.

It is to be understood, of course, that other modifications may be made in the practice of our invention. For example, if desired, the crude tall oil may be partially refined prior to oxidation. For example, any tar or pitch which may be present may be precipitated from the tall oil by means of a n phtha solution. It is also possible to use a refined tall oil from which the resin acids have been substantially completely removed. In another modification of our invention, when utilizing a polar-nonpolar solvent extraction system, a counter-current may be made through a packed tower between naphtha and a

furfural solution. Of course, polar solvents other than furfural may be employed in this modification and nonpolar solvents other than naphtha may be used. The removal of furfural and naphtha from the fractions described above may be accomplished by various methods such as vacuum distillation and, if desired, by means of steam stripping. The separation of furfural from the extraction containing the same is advantageously carried out by stripping with superheated steam.

In determining the various materials present in the fractions set forth in the specific examples given above, the following analytical procedures were followed. The acid numbers were determined by dissolving the sample in ethanol and titrating with approximately 0.2 N alcoholic KOH to a phenolphthalein end point. The rosin acid numbers were obtained by dissolving the sample in exactly 25 cc. of 4% p-toluenesulfonic acid in alcohol, refluxing for two hours, and titrating with approximately 0.2 N alcoholic KOH to a phenolphthalein end point. A blank determination was also run, and the difference represented the amount of rosin acids present in the sample. The saturated acids were determined by dissolving the sample in acetone and cooling to −25° C. The precipitate was removed by filtration and weighed. Viscosity measurements were made with the Gardner-Holdt bubble tubes in a bath kept at 25° C.

The unsaturated fatty acid fraction obtained in accordance with the process of our invention may be advantageously employed in compositions for use in various fields wherein thermoplasticity is undesirable. For example, many plastic compositions manufactured from tall oil or tall oil fractions are undesirable for use in warm climates or under extreme summer conditions, even in cooler regions. The increased resistance to deformation under high temperatures exhibited by plastic compositions containing the fraction free of saturated fatty acids obtained in the process of our invention is believed to result from substantially complete removal of unsaturated fatty acids and sterols from tall oil.

While we have described our invention with reference to certain particular embodiments and with reference to certain specific examples, it is to be understood that the invention is not limited thereby. Therefore, changes, omissions, substitutions, and/or additions may be made without departing from the spirit of the invention as defined in the appended claims which are intended to be limited only as required by the prior art.

We claim:

1. A method of fractionating tall oil to obtain a fraction substantially completely free from saturated fatty acids which comprises oxidizing tall oil until a product having a viscosity of between about 15 to about 250 seconds at 25° C. is obtained, removing saturated fatty acids from the resulting material by means of a nonpolar solvent, and recovering an oxidized saturated-fatty-acid-free tall oil fraction as residue.

2. An oxidized saturated-fatty-acid-free fraction of tall oil obtained by the process of claim 1.

3. A method of fractionating tall oil to obtain a fraction substantially completely free from fatty acids which comprises oxidizing tall oil until the material has a viscosity of between about 15 to about 250 seconds at 25° C., dissolving the oxidized material in a polar solvent, extracting the resulting solution with a nonpolar solvent to remove saturated fatty acids therefrom, and recovering an oxidized saturated-fatty-acid-free tall oil fraction from said polar solvent.

4. A method of fractionating tall oil to obtain a fraction substantially completely free from saturated fatty acids which comprises oxidizing tall oil until the viscosity of the material is between about 15 seconds and 250 seconds at 25° C., forming a partition chromatographic separation column including a layer containing adsorbent material impregnated with a polar solvent and a layer including a nonpolar solvent, passing oxidized tall oil through said column, and separately eluting said remaining bands from said column to obtain a fraction of oxidized tall oil which is substantially completely free from saturated fatty acids.

5. A method of fractionating tall oil to obtain a fraction substantially completely free from saturated fatty acids which comprises oxidizing tall oil until a product having a viscosity of between about 15 to about 250 seconds at 25° C. is obtained, removing saturated fatty acids from the resulting material by means of a petroleum naphtha, and recovering an oxidized saturated-fatty-acid-free tall oil fraction as residue.

6. A method of fractionating tall oil to obtain a fraction substantially completely free from fatty acids which comprises oxidizing tall oil until the material has a viscosity of between about 15 to about 250 seconds at 25° C., dissolving the oxidized material in furfural, extracting the resulting solution with a petroleum naphtha to remove saturated fatty acids therefrom, and recovering an oxidized saturated-fatty-acid-free tall oil fraction from said furfural.

7. A method of fractionating tall oil to obtain a fraction substantially completely free from saturated fatty acids which comprises oxidizing tall oil until the viscosity of the material is between about 15 seconds and 250 seconds at 25° C., forming a partition chromatographic separation column including a layer containing granular silica impregnated with furfural and a layer including a petroleum naphtha, passing oxidized tall oil through said column, and separately eluting said remaining bands from said column to obtain a fraction of oxidized tall oil which is substantially completely free from saturated fatty acids.

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