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PROCESS FOR REFINING TALL OIL

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This invention relates to the refining of crude tall oil.

Tall oil is a dark-colored and ill-smelling mixture produced by the acidification of sulfate soap obtained in the sulfate pulp process and comprising chiefly fatty acids of the oleic and linoleic series, rosin and a certain amount of unsaponifiable material; a typical sample of tall oil contains about 43% rosin, 41% fatty acids, and 16% unsaponifiable material. Due to the extensive working of the sulfate pulp process, tall oil is available in large quantities, and were it not for its undesirable odor and color, could advantageously be used in the manufacture of soap and like materials on account of its high fatty acid content. However, the color and odor of tall oil has up to the present time prevented any important industrial application thereof.

U. S. Patent 2,111,259 describes a process for refining tall oil which involves dissolving the tall oil in gasoline and then agitating the gasoline solution with furfural; the furfural separates from the gasoline solution after agitation, and removes with it a large part of the odoriferous and coloring materials of the tall oil. However, furfural is the only solvent discovered up to this time that is capable of effecting the removal of the odoriferous and coloring materials from tall oil to an extent such that the tall oil is at all acceptable commercially.

It is the object of this invention to provide a process of refining tall oil whereby a product free of undesirable color and odor is obtained.

I have now discovered that substantially all the undesirable color and odor may be effectively removed from crude tall oil by contacting a solution of crude tall oil with an organic solvent containing an —OH radical, and which is substantially immiscible with the tall oil solution. After contact with the tall oil solution, the organic solvent used in accordance with my invention is permitted to separate therefrom, carrying with it substantially all the odoriferous and coloring material in the tall oil. Refined tall oil may be recovered from the solution thereof in any suitable manner, such as by evaporation of the solvent; the refined oil has a light yellow to a light brown color and is free of any undesirable odors; such a product represents therefore, a suitable industrial source of rosin and free fatty acids. Some of the organic solvents used in accordance with my invention I have found to be superior to furfural, in that the refined tall oil produced has an improved color and odor over that produced by a furfural extraction; in that respect, therefore, my invention possesses a decided advantage over the process of the above mentioned United States patent.

My invention is also applicable to refining esters of tall oil. Thus, for example, the tall oil may be treated with an alcohol to esterify the rosin and the fatty acids, and the esterified tall oil then treated in accordance with the process of my invention. It may be desirable to react tall oil with one of the lower monohydric alcohols, such as methanol, whereby the fatty acids, but not the rosin, are esterified; the partially esterified tall oil may then be treated as above described. The latter process has the advantage that after the partially esterified tall oil has been refined, the fatty acid esters may be easily separated from the rosin in any desirable manner, e. g., by distillation. This separation may be accomplished, if desired, before the partially esterified tall oil is refined; the fatty acid esters thus obtained may then be treated in accordance with my invention. My invention may also be used to refine mixtures formed by esterifying the fatty acids in tall oil with an alcohol of the type that will result in esters of high vapor pressure and esterifying the rosin in the tall oil with an alcohol of the type that will result in rosin esters of low vapor pressure as described in my copending application, Serial No. 217,974, filed July 7, 1938; these mixtures may be treated as such, or the fatty acid esters recovered therefrom may be processed in accordance with this invention.

The organic solvent used to extract the odoriferous and coloring material from the tall oil is one containing an —OH radical and which is substantially immiscible with the tall oil solution. I have found that such organic solvents remove substantially all the odoriferous and coloring material from the tall oil, but do not dissolve any substantial amounts of either the rosin, the fatty acids in the tall oil, or the solvent in which the tall oil is dissolved. As examples of solvents which I have found to be particularly suitable for use in the practice of my invention, the following may be mentioned: ethylene chlorhydrin, α or β dichlorhydrin, ethylene glycol, diethylene glycol, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, ethylene glycol monophenyl ether and mesityl oxide. While the formula of mesityl oxide as ordinarily written indicates it is a ketone, actually, according to Cohen's "Organic Chemistry"

—(1928) part 2, page 39, it exists predominantly in the enolic form so that it may be considered for the purposes of this invention as an organic solvent having an —OH radical. It is to be understood that other organic solvents of the above type having an —OH radical and which are substantially immiscible with a tall oil solution may be used.

In carrying out the process of my invention, tall oil is first dissolved in a suitable solvent, preferably a petroleum solvent such as gasoline, solvent naphtha, or heptane. The proportions of tall oil and solvent may vary to some extent; I have found, however, that for every 10 parts of tall oil between 70 and 100 parts of solvent, preferably 100 parts of solvent, is most advantageous. It may be desirable to subject tall oil either before or after it is dissolved to a bleaching treatment, since refined tall oil of somewhat improved color is thereby obtained; this may be accomplished by neutralizing the tall oil acids with an alkali and then passing chlorine therethrough, or in any other suitable manner.

The solution of tall oil is then contacted with a suitable amount of an organic solvent having an —OH radical, and which is substantially immiscible with the tall oil solution. The amount of organic solvent employed may vary widely depending upon the particular solvent; preferably, however, the amount of solvent is approximately equivalent to the amount of tall oil. More effective removal of the odoriferous and coloring materials from the tall oil may be accomplished by contacting the tall oil solution with successive batches of the organic solvent and separating the tall oil solution from each batch of solvent before contact with the next batch; thus, for example, the tall oil solution may be successively contacted with two or three or even more batches of organic solvent. The contact of the tall oil solution with the organic solvent may be effected in any suitable manner, for example, by agitation or counter-current flow. The total time of contact should be sufficient to cause substantially all the odoriferous and coloring material to be extracted by the organic solvent; between 5 and 10 minutes is ordinarily satisfactory. The temperature of the extraction may be any desirable temperature, but for purposes of convenience, I prefer to operate at room temperatures; however, it may be desirable to carry out the extraction at a somewhat elevated temperature to increase the miscibility of the tall oil solution and organic solvent so that more uniform contact is effected, and then to cool the mixture prior to separating the refined tall oil from the organic solvent.

When the organic solvent has been contacted with the tall oil solution for a sufficient time, the mixture may be permitted to settle, whereby two layers are formed. The top layer comprises the refined tall oil solution, and the bottom layer comprises the organic solvent containing the odoriferous and coloring materials. These layers may be separated in any suitable manner; e. g., the tall oil solution may be decanted from the organic solvent. Refined tall oil may then be recovered by evaporating the solvent, whereby a product is obtained having an amber-like color and free of any undesirable odors; the solvent may be condensed and reused. In some cases it may be desirable to utilize the tall oil solution directly, in which event, of course, the solvent need not be evaporated. The organic solvent contained in the bottom layer may be recovered for reuse by evaporation thereof from the residue comprising the odoriferous and coloring material; this residue may be used as desired or discarded. If the organic solvent after recovery possesses any undesirable odor due to the presence of some odoriferous material dissolved therein, it may be treated in any suitable manner to remove the odoriferous material; e. g., by blowing air therethrough.

As hereinabove discussed, the process of my invention is also applicable to the refining of esterified tall oil, partially esterified tall oil; i. e., tall oil in which the fatty acids only are esterified, fatty acid esters obtained from the tall oil, and mixtures of fatty acid esters of high vapor pressure and rosin esters of low vapor pressure formed in accordance with the process of my above-mentioned copending application. When operating in accordance with these phases of my invention, the process is substantially as outlined above, except, of course, for the preliminary esterification steps. The use of the term "tall oil composition" in the claims is intended to include not only tall oil but also esterified tall oil, tall oil in which the fatty acids only have been esterified, fatty acid esters obtained from tall oil and ester mixtures obtained in the practice of the process of my aforementioned application.

If desired, the refined tall oil product may be treated with bleaching earths; i. e., fuller's earth, activated bentonite, etc., in order to further decolorize or deodorize the product. However, in most cases, this treatment is entirely unnecessary since the tall oil produced in accordance with my invention is of sufficient purity to permit its use without further treatment.

The following examples are illustrative of my invention. Amounts are given in parts by volume.

Example I

10 parts of crude tall oil were dissolved in 80 parts of gasoline and the insoluble material formed filtered off. To the filtrate were then added 5 parts of ethylene chlorhydrin. The mixture was agitated for 5 minutes and permitted to separate into two layers. The top layer comprising the solution of tall oil in gasoline was decanted off, again agitated with an additional 5 parts of ethylene chlorhydrin for 5 minutes, and the mixture permitted to separate. The tall oil solution was then decanted from the ethylene chlorhydrin; this solution, when tested with a Lovibond tintometer, gave a reading of 4.4 red and 35 yellow, as compared to 19.0 red and 110 yellow for the solution of crude tall oil in gasoline. When a sample of the same crude tall oil was refined in the same manner, except that furfural was used in place of ethylene chlorhydrin, the Lovibond reading was 6.5 red and 35 yellow. The gasoline was then evaporated from the tall oil solution, whereby a refined tall oil was obtained having an amber color, and substantially free of undesirable odors. The ethylene chlorhydrin was recovered from the odoriferous and coloring material by evaporation.

Example II

10 parts of crude tall oil were dissolved in 80 parts of heptane and the insoluble material thus formed filtered off. To the filtrate were then added 5 parts of diethylene glycol, the mixture agitated for 5 minutes and permitted to separate into two layers. The top layer comprising the solution of tall oil in heptane was decanted off, again agitated with an additional 5 parts of di-

ethylene glycol for 5 minutes and the mixture permittted to separate. The tall oil solution was then decanted from the diethylene glycol; this solution gave a Lovibond reading of 5.2 red and 35 yellow, as compared to 19.0 red and 110 yellow for the solution of the crude tall oil in heptane. When a sample of the same crude tall oil was refined in the same manner, except that furfural was used in place of diethylene glycol, the Lovibond reading was 6.5 red and 35 yellow. Refined tall oil was recovered by evaporating the heptane from the solution thereof. The diethylene glycol was recovered from the odoriferous and coloring material by evaporation.

Example III

10 parts of crude tall oil were dissolved in 80 parts of heptane and the insoluble material formed filtered off. To the filtrate were then added 5 parts of diethylene glycol monoethyl ether. The mixture was agitated for about 5 minutes and permitted to separate into two layers. The top layer comprising the solution of tall oil in heptane was decanted off, again agitated with an additional 5 parts of diethylene glycol monoethyl ether for 5 minutes, and the mixture permitted to separate. The tall oil solution was then decanted from the diethylene glycol monoethyl ether; this solution gave a Lovibond reading of 5.5 red and 35 yellow, as compared to 19.0 red and 110 yellow for the solution of crude tall oil in heptane. When a sample of the same crude tall oil was refined in the same manner, except that furfural was used in place of diethylene glycol monoethyl ether, the Lovibond reading was 6.5 red and 35 yellow. Refined tall oil was recovered by evaporating the heptane from the solution thereof. The diethylene glycol monoethyl ether was recovered from the odoriferous and coloring material by evaporation.

Example IV

10 parts of tall oil were dissolved in 80 parts of heptane and the insoluble material formed filtered off. To the filtrate were then added 5 parts of ethylene glycol. The mixture was agitated for about 5 minutes and permitted to separate into two layers. The top layer comprising the solution of tall oil in heptane was decanted off, again agitated with an additional 5 parts of ethylene glycol for 5 minutes, and the mixture permitted to separate. The tall oil solution was then decanted off from the ethylene glycol. Refined tall oil was recovered by evaporating the heptane from the solution thereof; the refined product had a pale amber color and no objectionable odors. The ethylene glycol was recovered from the odoriferous and coloring material by evaporation.

Example V

10 parts of crude tall oil were dissolved in 80 parts of heptane and the insoluble material formed filtered off. To the filtrate were then added 5 parts of ethylene glycol monophenyl ether. The mixture was agitated for 5 minutes and permitted to separate into two layers. The top layer comprising the solution of tall oil in heptane was decanted off, again agitated with an additional 5 parts of ethylene glycol monophenyl ether for 5 minutes, and the mixture permitted to separate. The tall oil solution was then decanted from the ethylene glycol monophenyl ether. Refined tall oil was recovered by evaporating heptane from the solution thereof; the refined product had a pale amber color and no objectionable odors. The ethylene glycol monophenyl ether was recovered from the odoriferous and coloring material by evaporation.

Example VI

10 parts of fatty acid esters obtained by esterifying crude tall oil with methyl alcohol, neutralizing the rosin with alkali and separating the esters by distillation from neutralized rosin were dissolved in 80 parts of gasoline and the insoluble material formed filtered off. To the filtrate were added 5 parts of mesityl oxide. The mixture was agitated for about 5 minutes and permitted to separate into two layers. The top layer comprising the tall oil solution in gasoline was decanted off, again agitated with an additional 5 parts of mesityl oxide for 5 minutes, and permitted to separate. The tall oil solution was then decanted from the mesityl oxide and refined tall oil recovered therefrom by evaporating the gasoline, whereby a product was obtained having an amber color and free from undesirable odors.

From the above description it will be seen that my invention provides a process for refining tall oil in which a large number of common and inexpensive solvents may be utilized with advantage. It will, therefore, be of great assistance to industries engaged in the production and utilization of by-products of tall oil.

Since certain changes may be made in carrying out the above process without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

Having described my invention, what I claim as new and desire to secure by Letters Patent is:

1. A process for refining crude tall oil which comprises contacting a solution of crude tall oil in a petroleum hydrocarbon solvent with successive batches of ethylene chlorhydrin under conditions such that the ethylene chlorhydrin is substantially immiscible with the tall oil solution, and recovering refined tall oil from the solution thereof.

2. A process for refining crude tall oil compositions which comprises contacting a petroleum hydrocarbon solution of a crude tall oil composition with an organic solvent for removing odoriferous and coloring material therefrom, said solvent being immiscible with said tall oil solution and selected from the group consisting of ethylene chlorhydrin, α dichlorhydrin, β dichlorhydrin, ethylene glycol, diethylene glycol, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, ethylene glycol monophenyl ether and mesityl oxide, and separating the organic solvent from the tall oil solution.

3. A process for refining crude tall oil compositions which comprises agitating a petroleum hydrocarbon solution of a crude tall oil composition with an organic solvent for removing odoriferous and coloring material therefrom, said solvent being immiscible with said tall oil solution and selected from the group consisting of ethylene chlorhydrin, α dichlorhydrin, β dichlorhydrin, ethylene glycol, diethylene glycol, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, ethylene glycol monophenyl ether and mesityl oxide, permitting the mixture to separate into two layers, recovering a refined tall oil composition from the layer comprising the tall oil solution.

4. A process for refining crude tall oil which comprises dissolving about 10 parts of crude tall oil in between about 70 and about 100 parts of petroleum hydrocarbon solvent, subjecting the solution to a bleaching treatment, filtering off insoluble material, mixing and agitating the filtered solution with successive batches of an organic solvent for removing odoriferous and coloring material therefrom, said organic solvent being immiscible with said tall oil-petroleum hydrocarbon solution and selected from the group consisting of ethylene chlorhydrin, α dichlorhydrin, β dichlorhydrin, ethylene glycol, diethylene glycol, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, ethylene glycol monophenyl ether and mesityl oxide, the total amount of said organic solvent used being approximately equivalent to the amount of crude tall oil in said tall oil-petroleum hydrocarbon solution, after each period of agitation separating the tall oil-petroleum hydrocarbon solution and organic solvent and recovering refined tall oil from the tall oil-petroleum hydrocarbon solution separated from the last batch of organic solvent.

5. A process for refining crude tall oil which comprises contacting a crude tall oil-petroleum hydrocarbon solution with ethylene chlorhydrin under conditions such that the ethylene chlorhydrin is substantially immiscible with said tall oil-petroleum hydrocarbon solution and separating the ethylene chlorhydrin from said tall oil-petroleum hydrocarbon solution.

6. A process for refining crude tall oil which comprises contacting a crude tall oil-petroleum hydrocarbon solution with diethylene glycol under conditions such that the diethylene glycol is substantially immiscible with said tall oil-petroleum hydrocarbon solution and separating the diethylene glycol from said tall oil-petroleum hydrocarbon solution.

7. A process for refining crude tall oil which comprises contacting a solution of crude tall oil in a petroleum hydrocarbon solvent with successive batches of diethylene glycol under conditions such that the diethylene glycol is substantially immiscible with the tall oil solution and recovering refined tall oil from the solution thereof.

8. A process for refining crude tall oil which comprises contacting a crude tall oil-petroleum hydrocarbon solution with diethylene glycol monoethyl ether under conditions such that the diethylene glycol monoethyl ether is substantially immiscible with said tall oil-petroleum hydrocarbon solution and separating the diethylene glycol monoethyl ether from said tall oil-petroleum hydrocarbon solution.

9. A process for refining crude tall oil which comprises contacting a solution of crude tall oil in a petroleum hydrocarbon solvent with successive batches of diethylene glycol monoethyl ether under conditions such that the diethylene glycol monoethyl ether is substantially immiscible with the tall oil solution and recovering refined tall oil from the solution thereof.

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