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TALL OIL TREATMENT

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3 Claims. (Cl. 260—97.5)

This invention relates in general to the production of valuable products from tall oil, and more particularly to a process of separating tall oil into ts main constituents; i. e. fatty and resinic acids. The present invention is especially directed to the recovery of valuable products from tall oil without subjecting the same to any extensive degree of hydrogenation or esterification, my copending application Serial No. 309,703, now Patent No. 2,305,498, of which this is a division, being directed to a similar process during which the tall oil is subjected to hydrogenation to varying extents; my copending application Serial No. 425,348 filed concurrently herewith being directed to a similar process in which the tall oil is esterified to varying extents; and my copending application Serial No. 425,347 filed concurrently herewith being directed to a similar process in which the tall oil is both esterified and hydrogenated to varying extents.

"Tall oil" or "talloel," which literally means "pine oil," is the resinous and fatty by-product obtained chiefly in the production of paper pulp from resin-bearing woods by the so-called sulphate process. In the sulphate process wood is digested with an alkaline liquor containing sodium sulphate, during which process tall oil accumulates in the form of its sodium soap on the surface of the waste liquor. The main constituents of this oil, after acidification, comprise resinic acids and fatty acids, the latter consisting mainly of oleic, linoleic and linolenic acids, each of which is a valuable commodity in substantially pure form. Various processes have been proposed in an attempt to effect separation of tall oil into its main constituents, i. e. fatty acids and resinic acids. One process comprises esterifying the fatty acids in tall oil with a low boiling alcohol and separating the resulting fatty ester from the free rosin acids by distillation or by alkali extraction. Another known process comprises esterifying the fatty acids with a polyhydric alcohol and distilling off the resinic acids. According to another process, both the fatty acids and the resinic acids are esterified with a polyhydric alcohol and the resin esters are then catalytically split and the liberated resinic acids distilled off. While the foregoing and other known processes have been employed with varying degrees of success, they all exhibit certain disadvantages, primarily in that only partial separation is effected. Moreóver, the fatty acid fraction obtained by these processes, consisting mainly of a mixture of oleic, linoleic and linolenic acids, is not particularly suitable for a wide variety of industrial uses. Usually having an iodine value of about 120 to 130, this fatty acid fraction (or its esters) shows some drying properties, but these drying properties are not pronounced enough for a drying oil of good quality. On the other hand, this fatty acid fraction is too highly unsaturated to find extensive application in some of the largest fat-consuming industries, namely the soap industry and in the manufacture of specialties for the textile and tanning trades, the bulk of fats used in these industries being of a more highly saturated type.

The general object of this invention is to obviate the foregoing and other disadvantages.

A specific object of the invention is to provide an improved and more efficient process for separating tall oil into fractions having more valuable properties than the original tall oil.

A further object of the invention is to provide an improved process for separating tall oil into its constituents and recovering therefrom the more saturated fatty acids so that the same can be adapted to a wide industrial use.

Still another object is to recover from tall oil a more highly unsaturated fraction suitable for many technical applications.

Other objects will in part be obvious and will in part appear hereafter.

The foregoing and other objects are accomplished according to the broader aspects of the invention whereby tall oil is dissolved in a suitable solvent and subjected to temperatures sufficiently low to effect precipitation of a certain fraction of, or all of, the fatty acids therein. In general, if lower temperatures are employed, a larger proportion of the more unsaturated fatty acids, such as linoleic acid, will be precipitated, and conversely, if higher temperatures are employed, a larger proportion of these more unsaturated fatty acids are retained in solution, and only the more saturated fatty acids, such as oleic acid, are precipitated. Thereafter, the said precipitated fraction is removed by filtration or centrifuging or by any other known means of separating an insoluble solid from a liquid. The resinic acids alone or in admixture with the more highly unsaturated fatty acids remaining in the solvent may be recovered by distilling off the solvent.

The tall oil employed in accordance with the process of the present invention may be in the crude or distilled state and it may be subjected to some slight degree of hydrogenation and/or esterification before being subjected to the chilling and separating steps. However it is not intended to cover in this application the treatment of tall oil which has been subjected to any considerable degree of hydrogenation and/or esterification, this subject matter being disclosed and claimed in my copending applications above referred to. Accordingly, the filtrate obtained upon separation of the precipitated fatty acids will also contain fatty acids of the more highly unsaturated type, mostly linoleic and linolenic acids. These higher unsaturated fatty acids may

then be separated from the rosin by esterification followed by alkali extraction of the rosin, or by methods disclosed in my copending applications, Serial Nos. 217,974 and 303,535, filed July 7, 1938, and November 9, 1939, respectively. Alternatively, the mixture of rosin acids and higher unsaturated fatty acids may be used as such in the preparation of other products such as drying oils, which is to form the subject matter of another application.

This invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others thereof, which will be exemplified in the process hereinafter disclosed, and the scope of the invention will be indicated in the claims.

In carrying out the process of the invention, the first step involves the dissolving of tall oil in a suitable solvent therefor which is characterized by the property of retaining the resinic acids or derivatives thereof in solution at low temperatures and permitting the fatty acids to precipitate out at low temperatures. Examples of such solvents include, inter alia, petroleum hydrocarbons, such as, gasoline, kerosene, heptane, mineral spirits, etc.; aromatic hydrocarbons, such as benzene, toluene, xylene, etc.; alcohols, such as ethyl alcohol, methyl alcohol, isopropyl alcohol, etc.; ketones, such as acetone, ethyl methyl ketone, cyclohexanone, etc.; chlorinated hydrocarbons, such as ethylene dichloride, trichlorethylene, etc.

After the tall oil has been dissolved in a suitable solvent, the temperature of the solution is decreased to obtain the desired degree of precipitation of fatty acids thereof. By actual experiment, a temperature range of about 5° C. to —70° C. will accomplish this result. It is obvious, of course, that temperatures outside of this range may also be operative to carry out the objects of the invention. The degree of cooling will be varied according to the nature of the solvent used and according to the form in which the fatty and resinous materials occur. The degree of cooling will be further varied according to the product desired, lower temperatures being required when it is desired to remove a larger portion of the fatty acids, particularly the more highly unsaturated fatty acids such as linoleic, from the solution. The precipitated fatty acids are removed from the solvent solution by any suitable means including centrifuging and filtration. The precipitated products after removal are preferably washed with a suitable solvent, e. g. the same solvent as used in the process, and preferably at substantially the same temperature at which the precipitating operation was carried out.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following examples, which are given merely to illustrate the invention and are not to be construed in a limiting sense.

Example I

100 gms. of distilled tall oil (having a rosin content of 32%) were dissolved in 650 ml. of acetone and cooled to —60° C. for 1 hour. The oleic acid fraction which crystallized out was then filtered off and washed with 350 ml. of fresh acetone which had previously been cooled to —60° C. 40 gms. of fatty acids were obtained which consisted chiefly of oleic acid having an iodine value of 80 and being practically free from rosin.

From the filtrate the solvent was distilled off and the residue consisting mainly of rosin, linoleic and linolenic acids was esterified by heating 50 gms. of it with 5.5 gms. of anhydrous glycerol at such a rate that the temperature gradually rose and reached 280° C. at the end of the sixth hour. The product thus obtained had excellent film-forming properties and was suitable for use in the manufacture of varnishes as a substitute for linseed oil and ester gum.

Example II

100 gms. of distilled tall oil were dissolved in 700 ml. of ethyl alcohol. The solution was maintained at —60° C. for two hours, and the crystallized fatty acids were filtered and washed with fresh alcohol which had previously been cooled to —60° C. The filter cake was freed from any residual alcohol by vacuum distillation. 42 gms. of rosin-free fatty acids were obtained having an iodine value of 71.5 and an unsaponifiable content of 1.8%.

To the above filtrate there was added 0.35 gm. of sulphuric acid and the mixture was refluxed for four hours. The sulphuric acid was then neutralized with an equivalent quantity of caustic soda and the excess alcohol was recovered by vacuum distillation. The residue was then dissolved in 200 ml. of commercial heptane and caustic soda of 12% strength was added with rapid stirring in an amount 10% in excess of that needed to neutralize the rosin acids. The rosin soap which settled to the bottom of the vessel was then drawn off and was washed once with 100 ml. of heptane. The solution of the ethyl esters in heptane was then washed with water until the last traces of soap had been removed and finally the heptane was distilled off to recover the ethyl esters of the highly unsaturated fatty acids.

The rosin soap was then dissolved in water and split with sulphuric acid to recover the rosin in a free state.

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.

It is also to be understood that the following claims are intended to cover all the generic and specific features of the invention herein described, and all statements of the scope of the invention, which as a matter of language might be said to fall therebetween.

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

1. A process of treating tall oil to separate a fatty fraction therefrom which comprises dissolving the tall oil in ethanol, decreasing the temperature of the solution to effect precipitation of a fatty fraction and removing the precipitated fraction from the remaining solution.

2. A process of treating tall oil to separate fatty acids therefrom which comprises dissolving the tall oil in ethanol, decreasing the temperature of the solution to effect precipitation of fatty acids and removing the precipitated fatty acids from the remaining solution.

3. A process of treating tall oil to separate oleic acid therefrom which comprises dissolving the tall oil in ethanol, decreasing the temperature of the solution to effect precipitation of oleic acid and removing the precipitated oleic acid from the remaining solution.

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