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PROCESSING OF TALL OIL

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The invention relates in general to the production of valuable products from tall oil and more particularly to a process of separating the fatty acids from the resin acids normally present in tall oil.

"Tall oil" or "talloel," which literally means "pine oil" is the resinous and fatty by-product obtained 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 operation 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 fatty acids and resinic acids each of which are valuable commodities in substantially pure form. Various processes have been proposed in an attempt to effect a 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 by alkali extraction or by distillation. 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, the fact remains that only a partial separation is being effected thereby. The resulting fatty acids and their esters are invariably contaminated with appreciable quantities of resinic acids.

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

A specific object of the invention is to provide a process of recovering from tall oil both the fatty acids and the resinic acids each in substantially pure and uncontaminated form.

A further object of the invention is to provide an improved and more efficient process of separating the main constituents in tall oil.

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

The foregoing objects are accomplished according to the process of the invention by esterifying the fatty and resinic acids in tall oil with an alcohol of the kind that will result in esters of relatively low vapor pressure and then trans-esterifying the esters of the fatty acids by alcoholysis with an alcohol of the type that produces esters of high vapor pressure. The resulting mixture comprises relatively low boiling fatty acid esters, higher boiling resin esters, excess of low boiling alcohol used for trans-esterification of the fatty esters and high boiling alcohol liberated during trans-esterification of the fatty esters. The low boiling alcohol is then separated by distillation and the high boiling alcohol may be separated from the mixture by settling procedures, or it may be washed out with water or other suitable solvents. The fatty acid esters are finally distilled off under reduced pressure from the resin esters with or without the use of steam distillation. The fatty acid esters thus obtained are practically free from contamination with resin acids or esters thereof which remain in the still.

The 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 tall oil to be treated may be in the crude or partially or completely refined state. Any suitable relatively high boiling alcohol may be used for the first step of complete esterification of the fatty acids and resinic acids, but it is preferred to employ polyhydric alcohols such as glycerol, ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, sorbitol, mannitol, etc. While any suitable polyhydric alcohol may be used, it is highly preferred to employ glycerol for various reasons including cost and efficiency of operation. For trans-esterification of the fatty acid esters any suitable relatively low boiling alcohol having a carbon content preferably not more than five carbon atoms may be used. Examples of such alcohols include, inter alia, monohydric alcohols such as methyl, ethyl, propyl, isopropyl, etc. alcohols or any other alcohol that will produce fatty acid esters having a boiling point sufficiently low with respect to that of the resin esters to permit a complete separation of the fatty acid esters by distillation.

The first step of complete esterification of the fatty acids and the resinic acids with a high boiling alcohol may be carried out by heating the mixture of tall oil and alcohol at temperatures generally ranging from 190° C. to a temperature just below that of the boiling point of the alcohol in a closed vessel provided with a stirring device and a reflux condenser of such design that it

permits the escape of water vapors formed during the reaction but condenses the alcohol and fatty acids returning them to the reaction chamber. During the process of reaction it is of advantage for obtaining light-colored products to pass a stream of non-oxidizing gas such as carbon dioxide, nitrogen, etc., through the reaction mass, or esterification may be effected under a partial vacuum. Esterification may be carried out with or without the use of a catalyst, but it is preferred to accelerate the reaction by such catalizing agents as zinc oxide, zinc carbonate, magnesium oxide, calcium oxide, powdered tin or zinc, or the like.

The trans-esterification of the fatty acid esters is carried out by heating the esters, formed in the first step as described above, with an excess of the low boiling alcohol at its boiling point in a closed vessel provided with an efficient reflux condenser, using a suitable catalyst, such as, sulphuric acid, hydrochloric acid, naphthalene betasulphonic acid, sodium- or potassium alcoholates or the like.

The reaction mass comprises essentially relatively low boiling fatty acid esters relatively high boiling resin esters, low boiling alcohol and high boiling alcohol. The high boiling alcohol usually separates out in a separate layer and may thus be withdrawn. The low boiling alcohol may be distilled off from the mass alone, or it may be distilled off with the fatty acid esters which are preferably removed from the resinic acid esters by distillation.

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, all parts being by weight.

Example #1

100 parts of distilled tall oil (having a resinic acid content of 32.5%) is heated under rapid stirring with 13 parts of glycerol of 88% strength at such a rate that after the first hour a temperature of 200° C. is reached and that the temperature rises gradually until at the end of the seventh hour 280° C. is reached. The acid number of the mixed esters has now dropped to below 5.0. The water formed during the reaction is allowed to escape, the fatty acids and the glycerol being returned to the reaction chamby suitable reflux condensation. During the process of reaction a stream of carbon dioxide is introduced into the reacting mass by means of an inlet tube at the bottom of the vessel. After cooling 50 parts of methanol containing 3 parts of dissolved HCl gas is added and the mixture is refluxed for sixteen hours. The hydrochloric acid is then neutralized by the addition of an equivalent quantity of sodium hydroxide dissolved in methanol and the excess methanol is then distilled off at atmospheric pressure. After allowing to stand for three to four hours the glycerol which has been set free by the trans-esterification of the fatty acid esters has accumulated at the bottom of the vessel and is drawn off. The fatty acid methyl esters are then distilled off at a pressure of 2 mm. Hg between a temperature of 140° C. to 180° C.

The methyl esters thus obtained consisting of a straw-colored liquid are substantially free from rosin having an acid number of less than 2 mgs. They may be used as such for various industrial purposes or they may be split into their fatty acids according to known processes, or they may be sulfonated, phosphated or hydrogenated. The still residue consisting mainly of the glycerides of the resinic acids is a plastic mass of light-brown color, which finds application as a valuable ingredient in the manufacture of varnishes or in other industries. If desired the rosin and glycerol may be recovered by saponification or catalytic splitting of the esters.

Example #2

100 parts of distilled tall oil (having a resinic acid content of 40%) is heated with rapid stirring with 11 parts of anhydrous glycerol and with 0.3 part of zinc oxide at such a rate that at the end of one hour 190° C. is reached and that at the end of the fifth hour the temperature has risen to 260° C. The mass consisting of the mixed glycerides of the fatty and resinic acids is allowed to cool and is then refluxed with 70 parts of ethyl alcohol and 2 parts of sulfuric acid for eight hours. The sulfuric acid is then neutralized by the addition of an equivalent quantity of sodium carbonate and the excess ethyl alcohol distilled off. The liberated glycerol is allowed to settle out and is drawn off. The ethyl esters of the fatty acids are then distilled off at 1 to 2 mm. Hg between 150° to 185° C.

The expression "resinic acids" is employed herein to connote rosin acids and/or any other resin acids normally present in tall oil.

While the present invention is particularly adapted for the treatment of tall oil, it is within the purview of the invention to employ the process for separating resinic acids from fatty acids in any mixture.

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. In a process of treating tall oil to separate the fatty acid components from the resinic acid components, the steps which comprise esterifying the fatty and resinic acids with a relatively high boiling alcohol, subsequently trans-esterifying the fatty acid esters only with an alcohol having a lower boiling point than the first alcohol, and distilling off the fatty acid esters thus formed.

2. In a process of treating tall oil to separate the fatty acid components from the resinic acid components, the steps which comprise esterifying the fatty and resinic acids with a polyhydric alcohol, subsequently trans-esterifying the fatty acid esters only with a monohydric alcohol containing less than six carbon atoms, and distilling off the fatty acid esters thus formed.

3. In a process of treating tall oil to separate the fatty acid components from the resinic acid components, the steps which comprise esterifying the fatty and resinic acids with a polyhydric alcohol, subsequently trans-esterifying the fatty acid esters only with a monohydric alcohol containing less than six carbon atoms in the presence of an acid catalyst, and distilling off the fatty acid esters thus formed.

4. In a process of treating tall oil to separate the fatty acid components from the resinic acid components, the steps which comprise esterifying the fatty and resinic acids with a polyhydric alcohol, subsequently trans-esterifying the fatty acid esters only with methyl alcohol in the presence of an acid catalyst, and distilling off the fatty acid esters thus formed.

5. In a process of treating tall oil to separate the fatty acid components from the resinic acid components, the steps which comprise esterifying the fatty and resinic acids with a polyhydric alcohol, subsequently trans-esterifying the fatty acid esters only with ethyl alcohol in the presence of an acid catalyst, and distilling off the fatty acid esters thus formed.

6. In a process of treating tall oil to separate the fatty acid components from the resinic acid components, the steps which comprise esterifying the fatty and resinic acids with a polyhydric alcohol, subsequently trans-esterifying the fatty acid esters only with butyl alcohol in the presence of an acid catalyst, and distilling off the fatty acid esters thus formed.

7. In a process of treating tall oil to separate the fatty acid components from the resinic acid components, the steps which comprise esterifying the fatty and resinic acids with glycerol, subsequently trans-esterifying the fatty acid esters only with a monohydric alcohol having not more than 5 carbon atoms in the presence of an acid catalyst, and distilling off the fatty acid esters thus formed.

8. In a process of treating tal loil to separate the fatty acid components from the resinic acid components, the steps which comprise esterifying the fatty and resinic acids with glycerol, subsequently trans-esterifying the fatty acid esters only with methyl alcohol in the presence of an acid catalyst, and distilling off the fatty acid esters thus formed.

9. In a process of treating tall oil to separate the fatty acid components from the resinic acid components, the steps which comprise esterifying the fatty and resinic acids with glycerol, subsequently trans-esterifying the fatty acid esters only with ethyl alcohol in the presence of an acid catalyst, and distilling off the fatty acid esters thus formed.

10. In a process of treating tall oil to separate the fatty acid components from the resinic acid components, the steps which comprise esterifying the fatty and resinic acids with glycerol, subsequently trans-esterifying the fatty acid esters only with a butyl alcohol in the presence of an acid catalyst, and distilling off the fatty acid esters thus formed.

11. The process of separating the fatty constituents from the resinous constituents of tall oil which comprises esterifying the fatty and resinic acids with an alcohol of the type that produces esters of relatively low vapor pressure, trans-esterifying the fatty acid esters only with an alcohol of the type that produces fatty acid esters of relatively high vapor pressure with respect to that of the unaffected resinic acid esters, and separating the fatty acid esters by distillation under reduced pressure.

12. In a process of treating tall oil to separate the fatty acid components from the resinic acid components, the steps which comprise esterifying the fatty and resinic acids with a polyhydric alcohol, subsequently trans-esterifying the fatty acid esters only with a monohydric alcohol having not more than 5 carbon atoms in the presence of an acid catalyst, and distilling off the fatty acid esters thus formed.

13. The process of claim 12 in which HCl is used as the acid catalyst.

14. The process of claim 12 in which H_2SO_4 is used as the acid catalyst.

15. The process of claim 12 in which naphthalene beta-sulfonic acid is used as the acid catalyst.

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