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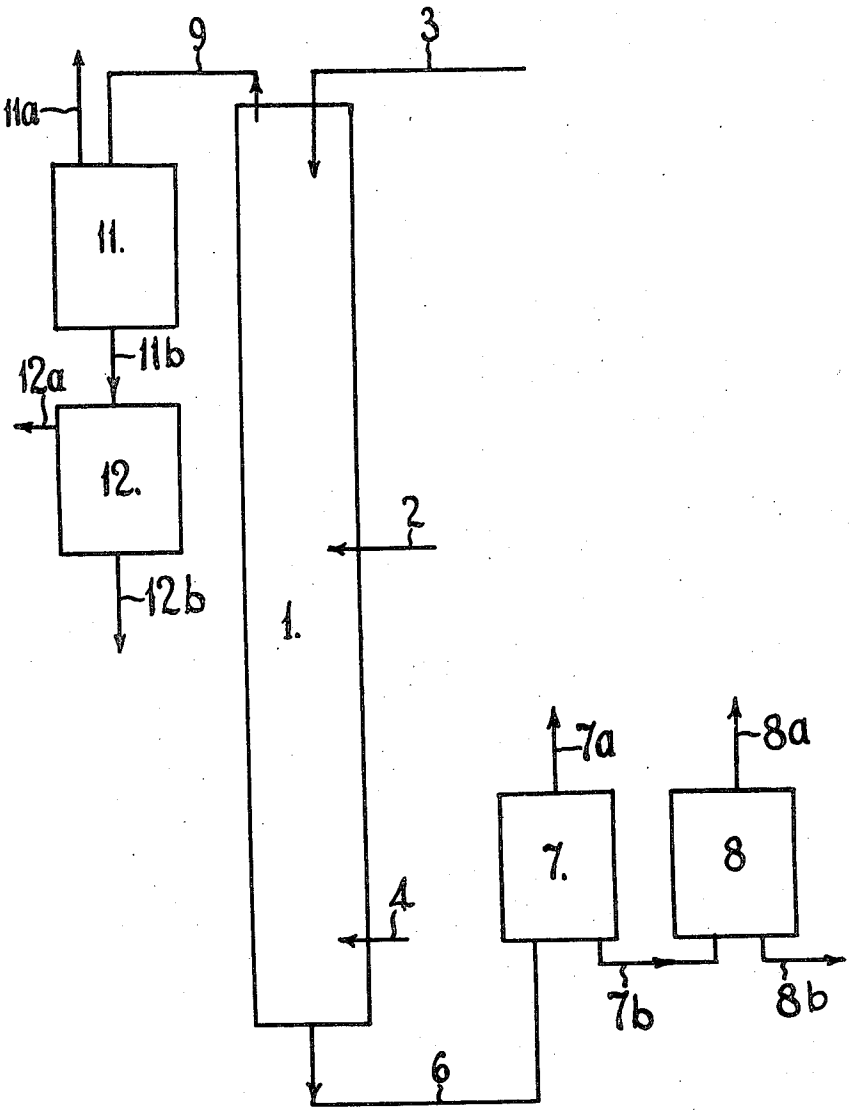

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SOLVENT FRACTIONATION OF TALL OIL

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The present invention relates to the treatment of wastes from the manufacture of paper pulp and it has particular relation to the treatment of the complex mixture of acids, sterols, and the like comprising tall oil obtained in the digestion of chips of pine wood in the preparation of paper pulp.

One object of the invention is to provide a simple, economical and efficient process of separating tall oil into its components.

This and other objects of the invention will be apparent from consideration of the following specification and the appended claims.

In the preparation of paper pulp from pine wood, the wood is cut into small chips or fragments and then cooked in a solution containing caustic. At the completion of the cooking operation, the caustic solution is drained off and subjected to evaporation. As the concentration increases, a curd-like mass termed tall oil soap is precipitated. This product is a dark, crude mixture rich in such components as soaps of free fatty acids such as the soaps of oleic acid, linoleic acid, linolenic acid and the like, soaps of rosin acids (mainly abietic acid) and its isomers, sterols, and other unsaponifiable constituents. It is obvious that many of the components of the crude mixture comprising tall oil would be, if pure, highly valuable. For example, the fatty acids would be highly useful in the preparation of synthetic resins, as soap stocks and other purposes. Rosin acids are the main components of purified rosin and as such the rosin acids of tall oil would be of value for applications to which rosin is customarily applied. The sterols in purified form would be highly valuable for use in the preparation of pharmaceuticals, wetting agents and many other purposes. However, no commercially satisfactory process of separating the tall oil into components has heretofore been available. The crude mixtures have been of but slight value and were sold by the paper companies at nominal prices.

In accordance with the provisions of the present invention, tall oil is separated into a plurality of fractions suitable for commercial use by a series of steps involving:

I. Subjecting the crude material to partial esterification with an alcohol (preferably a lower open chain alcohol) in order selectively to esterify the free fatty acids without substantial esterification of the rosin acids;

II. Intimately contacting the mixture of esters, rosin acids and sterols with a nitro alkane, selectively to dissolve the major portion of the esters,

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and a hydrocarbon solvent designed to retain in solution a concentrate of the rosin acids.

III. Removing the solvent mixtures from the fractions by such methods as distillation;

IV. Distilling off the esters or acids from the fractions to obtain the purified esters or acids as distillates and to leave still residues, which are of value in themselves.

Preparation of Esters

In order selectively to prepare esters of the fatty acids in tall oil, the latter composition may be heated (preferably in the presence of an esterification catalyst) with an alcohol (monohydric or polyhydric). Such alcohols as:

Table

Methyl alcohol	Ethylene glycol
Ethyl alcohol	Diethylene glycol
Propyl alcohol	1–2 or 1–3 propylene glycol
Isopropyl alcohol	Glycerol
n-Butyl alcohol	Pentaerythritol
Secondary butyl alcohol	

or the like may be employed. The alcohol may be in molar equivalency but an excess may be distilled during or after the reaction and does no harm. These alcohols when heated under esterification conditions with the tall oil readily react with the free fatty acids to form esters. The rosin acids under similar conditions react or condense with the alcohols much less readily than do the free fatty acids so that it is readily possible to obtain highly selective esterification. If the mixtures are heated sufficiently high for a sufficient length of time, some esterification of the rosin acids will take place but the margin of temperature and time between an adequate esterification of the fatty acids and the rosin acids is so great that no difficulty need be encountered in obtaining adequate esterification of the fatty acids before substantial esterification of the rosin acids occurs.

The following examples illustrate the esterification of the fatty acids in tall oil with a number of different alcohols:

Procedure A

Tall oil esters of methyl alcohol

In the preparation of the ester, 110 parts by volume of crude tall oil was charged into the kettle. To the tall oil 22 parts by volume of methyl alcohol and 1.9 parts by volume of concentrated sulphuric acid was added. The sulphuric acid constitutes an esterification catalyst and may be replaced by various other catalysts.

Such catalysts are well known in the art and need not be discussed in detail. The mixture was heated to 180° F. and allowed to reflux for 2.5 hours. The reflux mixture was allowed to settle and a lower layer consisting of methyl alcohol and sulphuric acid was formed and was drained away from the tall oil mixture.

Thirty parts by volume of a petroleum naphtha, e. g. iso-octane, heptane, hexane or conventional mixtures, was added to the tall oil mixture and this naphtha solution was washed with water to remove any residual mineral acid. Subsequently, 40 parts by volume of naphtha was added to the mixture to make up a solution containing 35 parts by weight of naphtha. The esterified tall oil contained 38.8 per cent of rosin acids calculated as abietic acid.

The solution of partially esterified tall oil in naphtha constitutes a starting material for subsequent fractionation into a fatty acid ester enriched raffinate and a rosin acid enriched extract by means of a suitable polar solvent. This operation will be described in subsequent examples. The other alcohols mentioned in the table may be substituted for methyl alcohol.

PROCEDURE B

Partial esterification of tall oil with glycerol

In the preparation of a mixture of mono and diglycerides of the fatty acids in tall oil 500 parts by weight of tall oil, 47.5 parts by weight of glycerol, 0.5 part by weight of litharge and 97.5 parts by weight of naphtha were heated to a temperature of 195° C. for a period of three hours during which time the water produced by the reaction was continuously removed. The litharge in the mixture was removed by filtration. The rosin acid content of the partially esterified tall oil on a naphtha free basis was 34.8 per cent calculated as abietic acid.

The naphtha solution of partially esterified tall oil constituted the starting material for subsequent fractionation by means of a polar solvent.

PROCEDURE C

Preparation of n-butyl esters of tall oil acids

In order to prepare the n-butyl esters of the free acids in tall oil 1,000 parts by weight of tall oil, 162 parts by weight of n-butyl alcohol and 0.4 part by weight of litharge were charged into an appropriate container and refluxed with continuous removal of water until the acid value corresponded to the calculated amount of rosin acids in the original tall oil. In this particular instance, the rosin acids constituted 37.4 per cent calculated as abietic acid.

Solvent fractionation of rosin acids and fatty acid esters in tall oil

In order to fractionate the partially esterified tall oil upon the basis of fatty acid esters and rosin acids, the partially esterified product as obtained in the foregoing examples may be subjected to fractionation by intimately contacting the mixture with an appropriate mixture of a nitroalkane having a selective affinity for the esters of fatty acids and lower alcohols in the esterified tall oil and petroleum naphtha as an auxiliary solvent in which the rosin acids are preferentially retained, and which is immiscible with the nitroalkane.

The application of the solvents to the esterified tall oil may be either batch-wise or counter-current. In the following examples, the application of the solvents is batch-wise, that is, the solvents and the esterified tall oil are merely thoroughly intermingled and then allowed to separate into layers and the layers separated from each other by appropriate procedure as, for example, by decantation. It is also apparent that the intermingled solutions may be separated from each other by appropriate centrifugation devices. After the solutions have been separated, the solvents may be evaporated either with or without application of vacuum as may be desired.

Example I

Methylated tall oil from Procedure A was thoroughly mixed with nitromethane and naphtha in ratios respectively:

	Parts
Tall oil	1
Nitromethane	2.6
Naphtha	.786

by weight

The mixture was then allowed to separate at a temperature of about 77° F. into layers and the layers were decanted individually. From the naphtha layer was recovered 92% of the original tall oil containing 40.3% rosin acids. From the nitromethane layer was recovered 8% of the original tall oil, having a concentration of 20.8% rosin acids. Therefore, of the original 38.8% rosin acids present only 1.8% appeared in the nitromethane fraction and 37% stayed in the naphtha phase.

Example II

Similarly, tall oil esterified by the procedure outlined in Procedure A to provide a mixture of rosin acids and methyl esters was extracted at 77° F. with nitroethane and naphtha. The ratios of the various components of the system were:

	Parts
Esterified tall oil	1
Nitroethane	2.68
Naphtha	4.29

The resultant immiscible phases were allowed to settle and were separated. The solvents were then evaporated to obtain the concentrates. The rosin acid concentrate (being the naphtha layer) contained 41.6% rosin acids and the fatty acid ester concentrate (being the nitroethane layer) contained 28.1% rosin acids. A fraction of relatively pure rosin acids could be readily distilled from the rosin acid concentrate.

In the examples the ratios of solvents to tall oil is susceptible of considerable variation. For example, the nitroalkane may be within a range of 1.5 to 10 parts per part of esterified tall oil and the naphtha may vary within a range of none to five parts per part of tall oil. The ratio of either of the solvents to tall oil may be maintained constant while the ratio of the other is varied or the ratio of both solvents may be varied simultaneously.

The temperature of 77° F. above described for the performance of the extraction of the tall oil is merely typical. Considerable variation either up or down is permissible. Of course, as the temperature is increased the various components of the esterified tall oil increases in solubility and as the temperature is lowered they decrease in solubility. The temperature obviously should be so selected that the esterified tall oil is completely soluble in the solvent system. The optimum temperatures will depend somewhat upon the ester employed and the desired proportions of the fractions.

Usually the temperature will be regulated to

obtain from 7 to 50 or 60 per cent of the esterified tall oil in the nitroalkane extract.

It will be appreciated that esters of any of the other alcohols mentioned in the table may be substituted for the methylated tall oil of Examples I and II.

The use of normal or isonitropropane or nitrobutane in place of nitromethane or nitroethane of the examples is contemplated.

A countercurrent extraction would often be more efficient and rapid than batch-wise operation. Suitable apparatus for such operation is described below. The temperatures and the ratios of solvents may correspond to those described in connection with the batch-wise operation.

The apparatus comprises a column I of conventional design formed of any suitable material such as steel or the like. Partially esterified tall oil (preferably in solution in naphtha as described in Procedures A, B and C) may be introduced into the mid-section of the column at 2. A nitroalkane is added at the top of the column as indicated at 3. Naphtha is added as a reflux as indicated at 4 near the bottom of the column. The column is provided near the bottom with an outlet line 6 which carries away the extract comprising nitroalkane in which a concentrate of the fatty acid esters is selectively dissolved. This solution comprising primarily the solvent and the fatty acid ester concentrate conveniently is subjected to distillation in a still 7 in order to remove the solvents. The concentrate is then passed through line 7*b* to a second still 8 in order to distill the esters.

Most of the rosin acids pass out through line 9 at or near the top of the column in solution in the naphtha which is immiscible with the nitroalkane and passes to a still 11 for removal of the solvent mixture. Solvent is recovered as indicated at 11*a*. The resultant fraction containing rosin acids can then be drawn off through line 11*b* for distillation in a still 12 of appropriate type.

It is to be understood that the various components of the tall oil as thus obtained are of high technical value. The distilled rosin acid concentrates are relatively clear and pure and are thus quite suitable for uses in the paint and varnish industry to which rosin is conveniently applied. The fatty acids can be recovered by appropriate hydrolysis or saponification of the esters, although for many purposes such recovery is not necessary. The esters may, for example, be employed directly in the manufacture of alkyd resins in the place of free fatty acids. In such reaction the esters are broken by interchange to form glycerides and to liberate the alcohols which can be removed from the mixture by distillation.

The forms of the invention herein disclosed are to be regarded merely as representative of the broad aspects of the invention. It will be apparent to those skilled in the art that various modifications may be made therein without departure from the spirit of the invention or the scope of the appended claims.

We claim:

1. A process of fractionating crude tall oil into useful fractions which comprises selectively subjecting the fatty acids in said tall oil to esterification with an open chain alcohol of 1 to 5 carbon atom content and extracting the resultant mixture of fatty acid esters and rosin acids with a mutually immiscible nitroalkane containing 1 to 4 carbon atoms in the alkane nucleus and a liquid paraffin hydrocarbon as selective solvents to obtain a nitroalkane phase and a hydrocarbon phase, separating the phases, evaporating the solvents from said phases to obtain a concentrate of fatty acid esters and a concentrate of rosin acids and then distilling off a portion of the rosin acids from the rosin acid concentrate to obtain a clear rosin-like product.

2. A process of fractionating a crude tall oil into useful fractions, which comprises selectively subjecting the fatty acids in the tall oil to esterification with methyl alcohol and extracting the resultant mixture of fatty acid esters and rosin acids with a mixture of mutually immiscible nitroalkane containing 1 to 4 carbon atoms in the alkane nucleus and a liquid paraffin hydrocarbon as selective solvents to obtain a nitroalkane phase and a hydrocarbon phase, separating the phases and evaporating the solvents from the phases to recover a concentrate of fatty acid esters and a concentrate of rosin acids.

3. A process of fractionating crude tall oil into useful fractions which comprises selectively subjecting the fatty acids in the tall oil to esterification with an open chain alcohol containing 1 to 5 carbon atoms and extracting the resultant mixture of fatty acid esters and rosin acids with nitromethane and a liquid paraffin hydrocarbon as selective solvents to obtain a nitromethane phase and a hydrocarbon phase, separating the phases and evaporating the solvents from the phases to obtain a concentrate of fatty acid esters and a concentrate of rosin acids.

4. A process of fractionating crude tall oil into useful fractions which comprises selectively subjecting the fatty acids in the tall oil to esterification with an open chain alcohol containing 1 to 5 carbon atoms and extracting the resultant mixtures of fatty acid esters and rosin acids with nitroethane and a liquid paraffin hydrocarbon as selective solvents to obtain a nitroethane phase and a hydrocarbon phase, separating the phases and evaporating the solvents from the phases to obtain a concentrate of fatty acid esters and a concentrate of rosin acids.

5. A process of fractionating a crude tall oil into useful fractions, which process comprises subjecting the fatty acids of the tall oil selectively to esterification with an open chain alcohol containing 1 to 5 carbon atoms and then extracting the resultant mixture of fatty acid esters and rosin acids with a nitroalkane containing 1 to 4 carbon atoms in the alkane nucleus and a liquid paraffin hydrocarbon as selective solvents to obtain a nitroalkane phase and a hydrocarbon phase, separating the phases and evaporating the solvents from said phases to obtain a concentrate of fatty acid esters and a concentrate of rosin acids.

6. A process of fractionating a crude tall oil into useful fractions, which process comprises subjecting the fatty acids of the tall oil selectively to esterification with an open chain alcohol containing 1 to 5 carbon atoms and then extracting the resultant mixture of fatty acid esters and rosin acids with a nitroalkane containing 1 to 2 carbon atoms in the alkane nucleus and a liquid paraffin hydrocarbon as selective solvents to obtain a nitroalkane phase and a hydrocarbon phase, separating the phases and evaporating the solvents from said phases to obtain a concentrate of fatty acid esters and a concentrate of rosin acids.

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