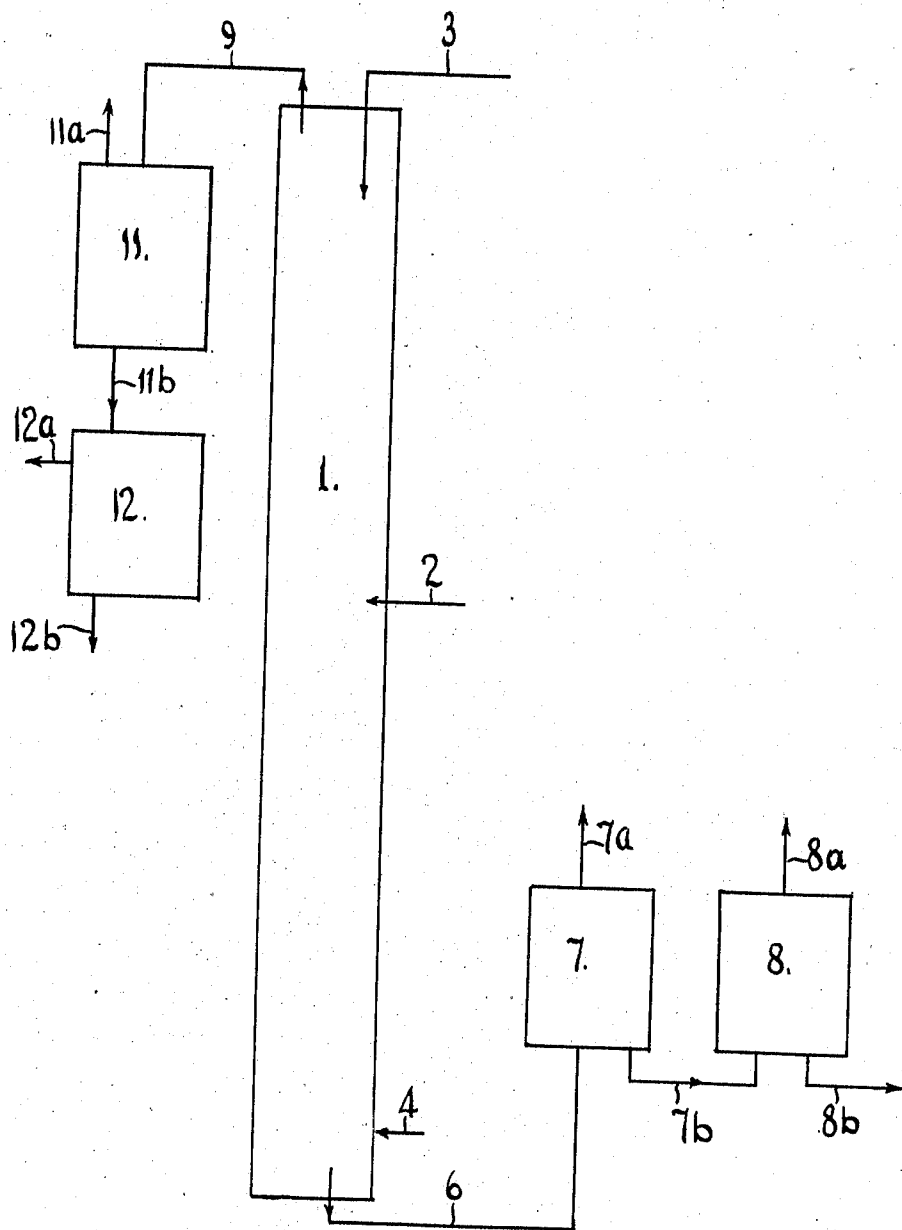


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FRACTIONATION OF TALL OIL

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FRACTIONATION OF TALL OIL

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1

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 furfural, or other polar solvents (or solvent and about 1 to 15 per

2

cent of water), selectively to dissolve the major portion of the rosin acids and a hydrocarbon solvent designed to retain in solution substantially all the esters of the free fatty acids and the sterols;

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 esterify the fatty acids of 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 I

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

or the like may be employed. 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:

EXAMPLE 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 44 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 Table I may be substituted for methyl alcohol.

EXAMPLE 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.

EXAMPLE 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 polar solvent having a selective affinity for the rosin acids and tall oil with a petroleum naphtha as an auxiliary solvent in which the fatty acid esters are preferentially retained, the whole mixture of esterified tall oil, polar solvent and naphtha forming an immiscible system. The following constitutes a partial list of polar solvents contemplated for use in conjunction with naphtha:

TABLE II

5	Furfuryl alcohol	Monomethyl ether of diethylene glycol "Methyl Carbitol"
	Formic acid	Ethyl acetate
	Ethylene glycol diformate	Ethyl-N-methyl carbamate
	Glycol diacetate	Methyl furate
	Methyl malonate	Methoxy acetaldehyde
	Methyl alcohol	Cinnamaldehyde
	Propylene glycol	Acetonyl acetone
	Monomethyl ether of ethylene glycol "Methyl Cellosolve"	Acetamide
	Monobutyl ether of diethylene glycol	Beta-methoxy ethyl carbonate
10	Beta hydroxy propionitrile	Ethyl lactate
	Beta ethoxy ethyl glycolate	Trimethyl phosphate
	Ethyl levulinate	2-Nitro 1-butanol
	Triacetin	Acetic anhydride
	Methyl oxalate	Methyl acetoacetate
	Ethylene glycol	Formic acid ester of the mono-
	Methyl lactate	methyl ether of ethylene glycol
15	Monomethyl ether of diethylene glycol "Carbitol"	Ethyl maleate
	Phenol	Methyl cyanoacetate
	Methyl levulinate	Furfural
		Formamide
		Ethylene glycol diacetate

Naphtha as designated herein comprises any liquid hydrocarbon or mixture of hydrocarbons which is immiscible with furfural or other polar solvent being used and preferably is composed of the paraffinic types of hydrocarbon.

A suitable embodiment of apparatus for use in the separation of the partially esterified tall oil into its components is shown in the single figure of the drawing. In the drawing like numerals refer to like parts throughout.

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 Examples A, B and C) may be introduced into the mid-section of the column at 2. Furfural, preferably saturated with water, is added at the top of the column as indicated at 3. Other polar solvents or polar solvent-water mixtures may be used in place of furfural if it is so desired. 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 furfural in which a concentrate of the rosin acids is selectively dissolved. This solution comprising primarily the solvent and the rosin acid concentrate conveniently is subjected to distillation in a still 7 in order to remove the furfural and naphtha in which it is dissolved. Recovered solvent passes out of the still 7a. The rosin acid concentrate is then passed through line 7b to a second still 8 in order to distill the acids. The distillate passes off at 8a. Some dark rosin will be retained in the still as a residue which may be withdrawn as indicated at 8b for use as such or for subsequent treatment in a further process not constituting a part of the herein claimed invention.

Most of the esters of the fatty acids pass out through line 9 at or near the top of the column in solution in the naphtha which is immiscible with the furfural and passes to a still 11 for removal of the solvent mixture. Solvent is recovered as indicated at 11a. The resultant fraction containing esters can then be drawn off through line 11b for distillation in a still 12 of appropriate type in which the esters are distilled and passed off at 12a leaving a residue which is taken off as indicated at 12b highly enriched in the sterol components.

It is to be understood that the various components of the tall oil as thus obtained are of high technical value. The distilled rosin acids 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 neces-

sary. 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 sterols of the raffinate are suitable for further treatment and purification.

The operation of the column with wet furfural and naphtha as a selective solvent system is illustrated by the following examples:

EXAMPLE D

Methylated tall oil prepared in accordance with the procedure outlined in Example A was subjected to fractionation in the apparatus illustrated in the drawing. The rosin acid content of the tall oil was 44 per cent. The feed solution to the column consisted of 65 per cent by weight of methylated tall oil and 35 per cent by weight of naphtha.

Fifty parts by volume of the feed solution was pumped into the middle portion of the column through line 2 and intimately contacted with 212 parts by volume of furfural saturated with water and naphtha at 80° F. introduced at the top of the column through line 3. It also intimately contacted 78 parts by volume of naphtha introduced at the bottom of the column through line 4 as a reflux. The temperature of the column was maintained at 85 to 86° F. The temperature may vary within broad limits, the upper limit being below that of complete miscibility of the system and the lower limit being that in which no solid phase or crystals are produced. Of course, the amount of water present in the furfural feed may be increased, if it is so desired, as the temperature of operation is increased. The extract and raffinate were freed of solvent by distillation under diminished pressure. A raffinate or naphtha soluble portion highly enriched in methyl esters was obtained in a yield of 48.5 per cent based upon the esterified tall oil. This portion contained only 2.9 per cent of rosin acids calculated as abietic acid. This raffinate, or naphtha soluble portion, upon distillation yielded a light yellow methyl ester distillate and a residue rich in sterols.

The yield of furfural soluble extract was 51.5 per cent and had a rosin acid content of 84.7 per cent calculated as abietic acid. The extract, as obtained after removal of the solvent, is a dark, semi-solid mass. In order to obtain a hardened rosin of light color, the extract was subjected to vacuum distillation whereby the following fractions were obtained:

1. A forerun amounting to 15.5 per cent and probably consisting of methyl esters, free fatty acids and other impurities. This fraction would well act as a softener or plasticizer for the rosin if it were not removed by distillation.
2. A hard rosin comparable to commercial W. G. grade rosin in a yield of 69.5 per cent.
3. A hard, brittle residue in a yield of 15 percent.

It is to be understood that the yields obtained will vary depending upon the composition of the starting material and the efficiency of the operation of extraction.

EXAMPLE E

Separation of mono- and diglycerides of tall oil with furfural and naphtha

In this separation the mono- and diglycerides as obtained in Example B were subjected to

countercurrent extraction in the apparatus illustrated. In this separation 33 parts by volume of a mixture consisting of 67 percent of the partially esterified tall oil and 33 percent of naphtha was fed to the middle of the column. Simultaneously, 67 parts by volume of furfural saturated with water at 80° F. (5 or 10° F. variation contemplated) was fed in at the top of the column and 45 parts by volume of naphtha was fed in at the bottom. The column was maintained at 84° F. or thereabouts. A 64.7 per cent yield of naphtha soluble raffinate with a rosin acid content of 16.2 per cent compared to a rosin acid content of 34.8 percent in the original esterified mixture was obtained.

It is to be understood that the proportions of the partially esterified tall oil and the solvents indicate ratios of flow in the column. The actual rate of flow in volumes per minute, of course, will vary dependent upon various factors but particularly upon the size of the column. In any event, there appears to be no practical lower limit to the rate of feed other than those imposed by the economics of operation. On the other hand, the upper limit is imposed by the capacity of the apparatus. The feed, of course, should be sufficiently slow to permit adequate separation of the solutions at the top and bottom of the column. If the feed is too fast, the phases at the outlets will be partially intermingled and separation will be inadequate.

EXAMPLE F

Separation of partially butylated tall oil with wet furfural and naphtha

One part by weight of partially butylated tall oil prepared in accordance with the procedure outlined in Example C and being of a rosin acid content of 37.4 per cent was thoroughly mixed with three parts by weight of wet furfural (4 per cent water) and 1 part by weight naphtha and the layers separated. Subsequently, the solvent was distilled off. The yield of the naphtha soluble butyl ester concentrate was 67.0 per cent containing 22.2 per cent of rosin acids calculated as abietic acid. The dark furfural soluble extract portion amounted to 33 per cent and had a rosin acid content of 61.4 per cent calculated as abietic acid.

As previously indicated, other polar solvents than furfural can be employed with naphtha to effect separation of rosin acids of tall oil from fatty acid esters obtained by esterifying the tall oil with an alcohol. In many instances these solvents can also be saturated or partially saturated with water in order to effect more complete separation of the rosin acids and the fatty acid esters. In order to demonstrate the use of other solvents than furfural, a series of extractions were conducted. In these extractions methylated tall oil prepared in a manner similar to that described in Example A was subjected to extraction. The polar solvent, the naphtha and the methylated tall oil were simply thoroughly agitated together at about 77° F. and allowed to separate into layers. The layers were then run or drawn off. The top layer comprised the naphtha containing a fraction of the tall oil highly enriched in the methyl esters together with sterols and other constituents. The bottom layer comprised polar solvent in which was dissolved a fraction of the tall oil highly enriched in the rosin acids. Some fatty acid esters and other constituents were also present. The ratios of solvents to the methylated tall oil, the

yields and the compositions of the fractions in the various extractions are tabulated as follows:

centrate of the fatty acid esters and a minor portion of rosin acids, the other phase comprising

Batch separations of methylated tall oil

Polar Solvent	Ratio Polar ¹ Solv. Me tall oil	Ratio Naphtha ² Me Tall Oil	Per cent Yield Raff.	Per cent Yield Extract	Per cent Rosin Acid Raff.	Per cent Rosin Acid Ext.	Per cent Rosin Acid Orig.	Spread
Dry furfural.....	2.68	.786	47.2	52.8	34.4	42.7	38.8	8.3
Wet furfural (satd.) 77° F.....	2.68	.786	53.8	46.2	29.4	49.8	38.8	20.4
Me Acetoacetate.....	2.68	.786	69.0	31.0	38.9	38.4	38.8	0.5
Acetonyl Acetone 5% H ₂ O.....	2.81	.786	50.2	49.8	25.8	52.0	38.8	26.2
Me Cellosolve 5% H ₂ O.....	2.68	.786	64.8	35.2	28.6	57.7	38.8	29.1
Do.....	5.62	.786	34.8	65.2	18.9	49.4	38.8	30.5
Me Acetoacetate.....	5.36	.786	49.0	51.0	37.1	40.4	38.8	3.3
Ethyl Acetoacetate 5% H ₂ O.....	3.62	.786	12.6	87.4	33.4	45.5	40.3	12.1
Ethyl Lactate 10% H ₂ O.....	2.68	.786	36.2	63.8	34.8	48.0	40.3	13.2
Ethylene Glycol Diacetate.....	2.68	.786	25.6	74.4	37.3	39.3	40.3	2.0
Trimethyl Phosphate.....	2.68	.786	35.8	64.2	27.8	48.0	40.3	20.2
Methyl carbitol.....	2.68	.786	27.5	72.5	23.2	55.5	40.3	32.3
Carbitol.....	2.68	.786	31.0	69.0	26.9	53.8	40.3	26.9
Methyl Lactate.....	2.68	.786	32.0	67.4	34.0	53.6	40.3	19.6
Methyl Alcohol.....	2.68	.786	71.2	28.8	30.7	55.8	40.3	25.1

¹ Parts by wt. Polar solvent to 1 Part methylated Tall Oil.

² Parts by wt. naphtha to 1 Part methylated Tall Oil.

The mode of extraction was the simplest possible. Obviously, column extraction as described in Example D could be employed with these same solvents. The esters of Example B or C could be employed in lieu of methyl esters.

In any of the examples (D, E, F, or the others) wide variation in the ratio of solvents is permissible. The polar solvent may be employed in a ratio as high as 20 or more parts by volume per part of esterified tall oil, indeed the upper limit is imposed primarily by the practical difficulty of handling large volumes of liquid. The naphtha ratio may vary in like manner. Appropriate limits would be from about 0.5 volume to 10 volumes per volume of tall oil esters. Usually the naphtha soluble or ester fraction will constitute 25 to 75% of total esterified tall oil. An approximately 50 per cent yield would constitute a good average.

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 separating rosin acids from tall oil comprising preferentially esterifying the fatty acids in tall oil with an open chain alcohol containing 1 to 5 carbon atoms and consisting of carbon, hydrogen and oxygen, then extracting off a concentrate of the rosin acids by contacting the ester mixture simultaneously with naphtha and a polar solvent immiscible with naphtha to obtain two liquid phases, one comprising naphtha containing in solution a concentrate of the fatty acid esters and a minor portion of rosin acids, the other phase comprising polar solvent containing in solution a concentrate of rosin acids containing a minor amount of fatty acid esters, separating the solutions and recovering the solvents.

2. A process of separating the rosin acids from tall oil, comprising preferentially esterifying the fatty acids in tall oil with an open chain alcohol containing 1 to 5 carbon atoms and consisting of carbon, hydrogen and oxygen, then extracting off a concentrate of the rosin acids by contacting the ester mixture simultaneously with naphtha and a polar solvent immiscible with naphtha to obtain two liquid phases, one comprising naphtha containing in solution a con-

polar solvent containing in solution a concentrate of rosin acids containing a minor amount of fatty acid esters separating the solutions and recovering the solvents.

3. A process of separating rosin acids from tall oil comprising preferentially esterifying the fatty acids in tall oil with an open chain monohydric alcohol containing 1 to 5 carbon atoms and consisting of carbon, hydrogen and oxygen, then extracting off a concentrate of the rosin acids by contacting the ester mixture simultaneously with naphtha and a polar solvent immiscible with naphtha to obtain two liquid phases, one comprising naphtha containing in solution a concentrate of the fatty acid esters and a minor portion of rosin acids, the other phase comprising polar solvent containing in solution a concentrate of rosin acids containing a minor amount of fatty acid esters, separating the solutions and recovering the solvents.

4. A process of separating rosin acids from tall oil comprising preferentially esterifying the fatty acids in tall oil with a polyhydric open chain alcohol containing 1 to 5 carbon atoms and consisting of carbon, hydrogen and oxygen, then extracting off a concentrate of the rosin acids by contacting the ester mixture simultaneously with naphtha and a polar solvent immiscible with naphtha to obtain two liquid phases, one comprising naphtha containing in solution a concentrate of the fatty acid esters and a minor portion of rosin acids, the other phase comprising polar solvent containing in solution a concentrate of rosin acids containing a minor amount of fatty acid esters, separating the solutions and recovering the solvents.

5. A process of separating rosin acids from tall oil comprising preferentially esterifying the fatty acids in tall oil with methyl alcohol, then extracting off a concentrate of the rosin acids by contacting the ester mixture simultaneously with naphtha and a polar solvent immiscible with naphtha to obtain two liquid phases, one comprising naphtha containing in solution a concentrate of the fatty acid esters and a minor portion of rosin acids, the other phase comprising polar solvent containing in solution a concentrate of rosin acids containing a minor amount of fatty acid methyl esters, separating the solutions and recovering the solvents.

6. A process of separating rosin acids from tall oil comprising preferentially esterifying the fatty acids in tall oil with an open chain alcohol con-

taining 1 to 5 carbon atoms and consisting of carbon, hydrogen and oxygen, then extracting off a concentrate of the rosin acids by thoroughly contacting the ester mixture simultaneously with naphtha and furfural the furfural containing about 1 to 15% of water to obtain two liquid phases, one comprising naphtha containing in solution a concentrate of the fatty acid esters and a minor portion of rosin acids, the other phase comprising furfural containing in solution a concentrate of rosin acids containing a minor amount of fatty acid esters, separating the solutions and recovering the solvents.

7. A process of separating rosin acids from tall oil comprising preferentially esterifying the fatty acids in tall oil with methyl alcohol, then extracting off a concentrate of the rosin acids by contacting the ester mixture simultaneously with naphtha and a furfural to obtain two liquid phases, one comprising naphtha containing in solution a concentrate of the fatty acid esters and a minor portion of rosin acids, the other phase comprising furfural containing in solution a concentrate of rosin acids containing a minor amount of fatty acid esters, separating the solutions and recovering the solvents.

8. A process of separating rosin acids from tall oil comprising preferentially esterifying the fatty acids in tall oil with an open chain alcohol containing 1 to 5 carbon atoms and consisting of carbon, hydrogen and oxygen, then extracting off a concentrate of the rosin acids by contacting the ester mixture simultaneously with naphtha and a water-polar solvent mixture immiscible with naphtha to obtain two liquid phases, one comprising naphtha containing in solution a concentrate of the fatty acid esters and a minor portion of rosin acids, the other phase comprising aqueous polar solvent containing in solution a concentrate of rosin acids containing a minor amount of fatty acid esters, separating the solutions and recovering the solvents.

9. A process of separating rosin acids from tall oil comprising preferentially esterifying the fatty acids in tall oil with an open chain alcohol containing 1 to 5 carbon atoms and consisting of carbon, hydrogen and oxygen, then extracting off a concentrate of the rosin acids by contacting the ester mixture simultaneously with naphtha and a furfural-water mixture containing about 1 to 15% of water to obtain two liquid phases, one comprising naphtha containing in solution a concentrate of the fatty acid esters and a minor portion of rosin acids, the other phase comprising aqueous furfural containing in solution a concentrate of rosin acids containing a minor amount of fatty acid esters separating the solutions and recovering the solvents.

10. A process of separating rosin acids from tall oil which comprises heating tall oil in naphtha with an open chain alcohol containing 1 to 5 carbon atoms and consisting of carbon, hydrogen and oxygen until the fatty acids of the tall oil are esterified, discontinuing the esterification before substantial esterification of the rosin acids occurs, then extracting off a concentrate of the rosin acids from the fatty acid esters by contacting the ester mixture simultaneously with naphtha and a polar solvent immiscible therewith to obtain two liquid phases, one comprising naphtha containing in solution a concentrate of the fatty acid esters and a minor portion of rosin acids, the other phase comprising polar solvent containing in solution a concentrate of rosin acids containing a minor amount of fatty

acid esters, separating the solutions and recovering the solvents.

11. A process of separating rosin acids from tall oil which comprises heating tall oil in naphtha with an open chain alcohol containing 1 to 5 carbon atoms and consisting of carbon, hydrogen and oxygen until the fatty acids of the tall oil are esterified, discontinuing the esterification before substantial esterification of the rosin acids occurs, then extracting off a concentrate of the rosin acids from the fatty acid esters by contacting the ester mixture simultaneously with naphtha and furfural to obtain two liquid phases, one comprising naphtha containing in solution a concentrate of the fatty acid esters and a minor portion of rosin acids, the other phase comprising furfural containing in solution a concentrate of rosin acids containing a minor amount of fatty acid esters, separating the solutions and recovering the solvents.

12. A process of separating rosin acids from tall oil which comprises heating tall oil in naphtha with an open chain alcohol containing 1 to 5 carbon atoms and consisting of carbon, hydrogen and oxygen until the fatty acids of the tall oil are esterified, discontinuing the esterification before substantial esterification of the rosin acids occurs, then extracting off a concentrate of the rosin acids from the fatty acid esters by contacting the ester mixture simultaneously with naphtha and a furfural-water mixture containing about 1 to 15% of water to obtain two liquid phases, one comprising naphtha containing in solution a concentrate of the fatty acid esters and a minor portion of rosin acids, the other phase comprising aqueous furfural containing in solution a concentrate of rosin acids containing a minor amount of fatty acid esters, separating the solutions and recovering the solvents.

13. A process of separating rosin acids from tall oil which comprises heating tall oil in naphtha with a monohydric open chain alcohol containing 1 to 5 carbon atoms and consisting of carbon, hydrogen and oxygen until the fatty acids of the tall oil are esterified, discontinuing the esterification before substantial esterification of the rosin acids occurs, then extracting off a concentrate of the rosin acids from the fatty acid esters by contacting the ester mixture simultaneously with naphtha and a furfural-water mixture containing about 1 to 15% of water immiscible therewith to obtain two liquid phases, one comprising naphtha containing in solution a concentrate of the fatty acid esters and a minor portion of rosin acids, the other phase comprising aqueous furfural containing in solution a concentrate of rosin acids containing a minor amount of fatty acid esters, separating the solutions and recovering the solvents.

14. A process of separating a mixture of esters of fatty acids of tall oil and resin acids of tall oil said esters being of an open chain alcohol containing 1 to 5 carbon atoms and consisting solely of carbon, hydrogen and oxygen which process comprises intimately contacting said mixture simultaneously with naphtha and a polar solvent immiscible with naphtha to obtain two liquid phases, one comprising naphtha containing in solution a fraction rich in fatty acid esters and poor in rosin acids, the other comprising polar solvent containing in solution a fraction rich in rosin acids and poor in esters of fatty acids, separating off the phases and recovering the solvents.

11

15. A process as defined in claim 14 in which the polar solvent is wet furfural.

16. A process as defined in claim 14 in which the polar solvent is admixed with water.

17. In a process of separating rosin acids from tall oil which comprises heating tall oil in naphtha with a monohydric open chain alcohol containing 1 to 5 carbon atoms and consisting solely of carbon, hydrogen and oxygen in the presence of a mineral acid as a catalyst of esterification until the fatty acids of the tall oil are esterified, discontinuing the esterification before substantial esterification of the rosin acids occurs, washing out the mineral acid with water, then extracting off a concentrate of the rosin acids from the fatty acid esters by contacting the ester mixture simultaneously with naphtha and a furfural water mixture containing about 1 to 15% of water to obtain two liquid phases, one comprising naphtha containing in solution a concen-

12

trate of the fatty acid esters and a minor proportion of rosin acids, the other phase comprising aqueous furfural containing in solution a concentrate of rosin acids containing a minor amount of fatty acid esters, separating the solution of rosin acids in aqueous furfural from the solution of fatty acid esters and evaporating off the furfural.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,166,812	Gayer et al.	July 18, 1939
2,354,812	Jenkins	Aug. 1, 1944