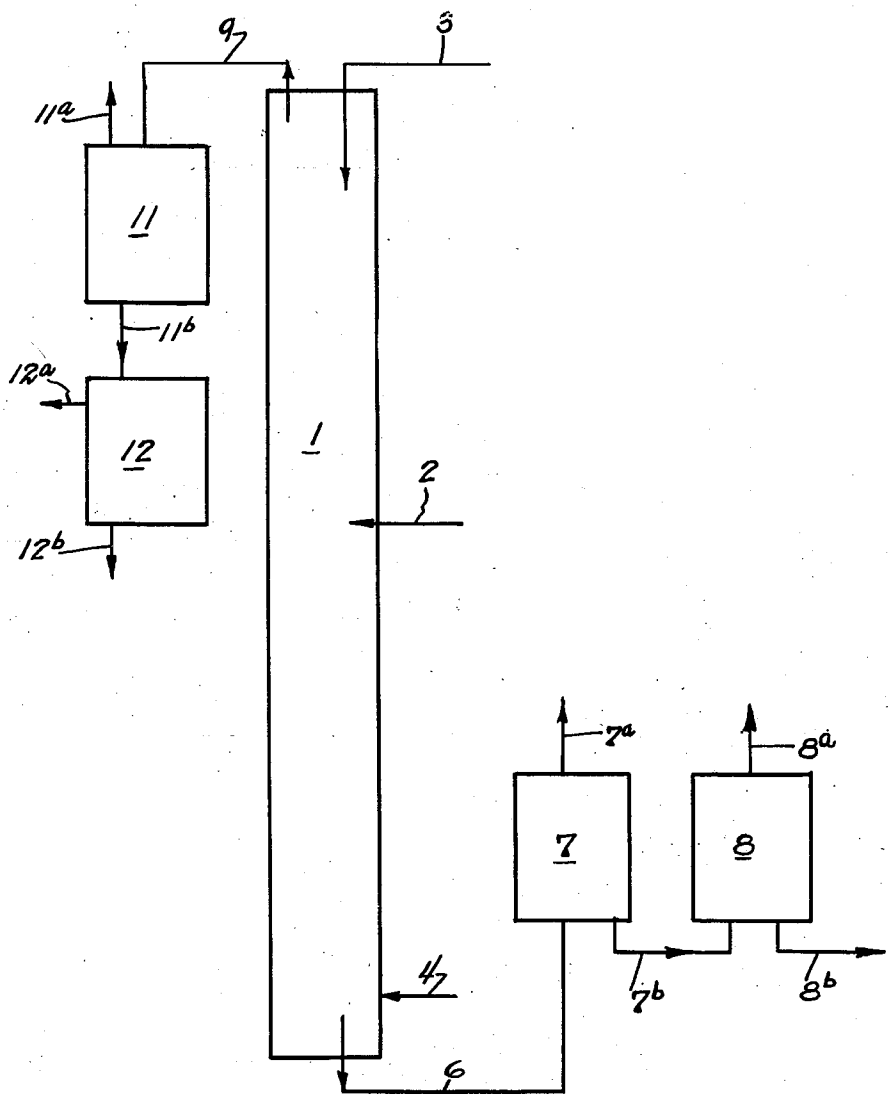
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TREATMENT OF TALL OIL

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TREATMENT 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.

A second object of the invention is to provide an economical method of obtaining light-colored esters of tall oil substantially free of both rosin acids and unsaponifiable matter.

A third object is to provide a method of concentrating the sterols and other unsaponifiable constituents into a raffinate or ester fraction of tall oil.

A fourth object of the invention is to provide a method by application of which the sterols and similar unsaponifiable constituents of tall oil can be obtained in a highly concentrated form and substantially free of rosin acids and free fatty acids characterizing tall oil.

These 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

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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 including a fraction of relatively pure unsaponifiable matter suitable for commercial use by a series of stages 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 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 raffinate or ester fractions by such methods as distillation to obtain a concentrate of fatty acid esters and unsaponifiable matter;

IV. Concentrating and recovering the unsaponifiable matter in the raffinate. The preferred mode of procedure in Stage IV comprises:

(A) Distilling the raffinate fraction to obtain a distillate of relatively pure fatty acid esters suitable for various applications and a still residue of black pitchy appearance and being greatly enriched in unsaponifiable matter.

(B) Treating the material rich in unsaponifiable matter with an alkaline substance such as sodium or potassium hydroxide to saponify the esters.

(C) Washing a water and alcohol solution of the soaps containing the unsaponifiable matter with a solvent of the unsaponifiable matter which is immiscible in the water-alcohol solution to obtain the unsaponifiable matter.

Alternatively step A (distilling the ester fraction) may be omitted and steps B and C applied directly to the raffinate from Stages I, II, and III.

Stages I, II and III are substantially the same as those described in patent application to Stephen E. Freeman and Stewart W. Gloyer, Serial No. 637,432, filed December 27, 1945, now U. S. Patent 2,423,232, and entitled Fractionation of Tall Oil. The process as described in the prior applications is susceptible of certain variations of technique. The following constitute illustrations of such variations:

PREPARATION OF ESTERS

STAGE I

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

Methyl alcohol
Ethyl alcohol
Propyl alcohol
Isopropyl alcohol
n-Butyl alcohol
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. Any excess of methyl alcohol may be used since such excess may be distilled off to any desired composition, or such excess may be washed out of the reaction mixture with water.

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

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

STAGE II

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 of tall oil, and 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 partially esterified tall oil mixture is made into a solution with naphtha or other hydrocarbon. Such hydrocarbon solvent also serves to preferentially retain fatty acid esters and unsaponifiable constitutents in the raffinate fraction upon liquid-liquid fractionation of this solution with a polar solvent. The amount of naphtha must be sufficient to maintain an immiscible system when the solution is contacted with a polar solvent and usually is within a range of 0.1 to 10 parts per part by volume of partially esterified tall oil. All of the naphtha may be introduced in the form of a solution of partially esterified tall oil; or, if preferred, a portion of it may be added to the system separately as reflux naphtha near the bottom portion of the column. The following constitutes a partial list of polar solvents contemplated for use in conjunction with naptha.

Table II

Furfuryl alcohol
Formic acid
Ethylene glycol diformate
Glycol diacetate
Methyl malonate
Methyl alcohol
Propylene glycol
Monomethyl ether of ethylene glycol
Monobutyl ether of diethylene glycol
Beta hydroxy propionitrile
Beta ethoxy ethyl glycolate
Ethyl levulinate
Triacetin
Methyl oxalate
Ethylene glycol
Methyl lactate
Monoethyl ether of diethylene glycol
Phenol
Methyl levulinate
Monomethyl ether of diethylene glycol
Ethyl acetoacetate
Ethyl-N-methyl carbamate
Methyl furoate
Methoxy acetaldehyde

Cinnamaldehyde
Acetonyl acetone
Acetamide
Beta-methoxy ethyl carbonate
Ethyl lactate
Trimethyl phosphate
2-nitro 1-butanol
Acetic anhydride
Methyl acetoacetate
Formic acid ester of the monomethyl ether of ethylene glycol
Ethyl maleate
Methyl cyanoacetate
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 1 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 and B) 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 at 7*a*. The rosin acid concentrate is then passed through line 7*b* in a second still 8 in order to distill the acids. The distillate passes off at 8*a*. Some dark rosin will be retained in the still as a residue which may be withdrawn as indicated at 8*b* 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 11*a*. The resultant fraction containing esters can then be drawn off through line 11*b* for distillation in a still 12 of appropriate type in which the esters are distilled and passed off at 12*a* leaving a residue which is taken off as indicated at 12*b* 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 necessary. The esters, for example, may 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 C

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° C. 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 amount of furfural may be varied within wide limits but is usually within 2 to 25 parts per part by volume of partially methylated tall oil. The extract and raffinate were freed of solvent by distillation under diminished pressure.

In the above Example 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.

EXAMPLE D

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 B 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.

Use of polar solvents other than furfural

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:

BATCH SEPARATION OF METHYLATED TALL OIL

Polar Solvent	Ratio [1] Polar Solv./ Me Tall Oil	Ratio [2] Naphtha/ Me Tall Oil	Percent Yield Raff.	Percent Yield Extract	Percent Rosin Acid Raff.	Percent Rosin Acid Ext.	Percent 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 Aceto-acetate	2.68	.786	69.0	31.0	38.9	38.4	38.8	0.5
Acetonyl Acetone, 5% H_2O	2.81	.786	50.2	49.8	25.8	52.0	38.8	26.2
Me Cellosolve, 6% H_2O	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 Aceto-acetate	5.36	.786	49.0	51.0	37.1	40.4	38.8	3.3
Ethyl Acetoacetate, 5% H_2O	3.62	.786	12.6	87.4	33.4	45.5	40.3	12.1
Ethyl Lactate, 10% H_2O	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	32.6	67.4	34.0	53.6	40.3	19.6
Methyl Alcohol	2.68	.785	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 C could be employed with these same solvents. The esters of Example B could be employed in lieu of methyl esters.

In any of the examples 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 0.1 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.

Distillation of solvent

STAGE III

The residual solvents dissolved in the raffinate may be eliminated by distillation, with or without application of vacuum.

Separation of unsaponifiable matter

STAGE IV

By application of the foregoing steps a raffinate containing nearly all of the fatty acid esters and only a minor proportion of the rosin acids is obtained as disclosed in Example C. It will be found that the unsaponifiable matter comprising the sterols of the original tall oil is also concentrated in this raffinate. The compositions of the original tall oil, the raffinate and the extract are tabulated for purposes of comparison as follows:

	Original	Raffinate	Extract
Yield, percent		48.5	51.5
Rosin Acids, percent	44	2.9	84.7
Fatty acid esters, percent	47	82.8	11.3
Unsaponifiables, percent	9	14.3	4.0

It is to be observed that 77 per cent of the total unsaponifiable matter is concentrated in the raffinate fraction. The sterols in the tall oil are even more sharply concentrated, for example, considering the total unsaponifiable matter of the tall oil. In the original tall oil this portion constituted 36 per cent while in the raffinate it constitutes 57 per cent and in the extract or rosin acid fraction it constitutes 5 to 10 per cent.

In accordance with the provisions of the present invention, the raffinate from the solvent extraction of the esterified tall oil may be subjected to the operations of Stage IV in order to obtain the unsaponifiable matter in relatively pure form.

For example, it may be subjected to Step A of Stage IV, distillation in order to recover most of the fatty acid ester and thus to obtain still further concentration of the unsaponifiable matter. In such process the raffinate comprising the fatty acid ester, e. g. methyl esters, and the major portion of the unsaponifiable matter is subjected to vacuum distillation preferably at a pressure of approximately 1 mm. of mercury over a distillation range of approximately 158° to 170° C. Under this pressure condition, the pot temperature is not allowed to exceed 225° C. since temperatures above this value result in substantial increase in the volatilization of the unsaponifiable matter. It will be appreciated that in the distillation of the fatty acid esters substantial variation in the pressures of distillation are permissible. For example, a range between 1 and 20 or 30 mm. of mercury is contemplated and naturally the temperature of distillation will vary in accordance with the pressures. Of course, the cuts in the distilling operation may be made at various temperatures. The lower the temperature of cut the purer will be the fatty acid ester fraction obtained, however, then more of the acid esters will tend to remain in the still pot residue.

If the distilling operation is conducted as above described, a fraction of distilled free fatty acid esters constituting 68 per cent of the raffinate distills over leaving a still residue of 31.6 per cent. The compositions of the original undistilled raffinate, the distilled ester and the still pot residue may be tabulated as follows:

	Undistilled Raffinate	Distilled Me esters	Still Residue	Loss
Yield, percent		68.0	31.6	0.4
Rosin Acid, percent	3.9	1.3	6.5	
Unsaponifiables, percent	14.3	2.9	38.5	
Me ester, percent	82.8	95.8		
Color, Gardner-Holdt	12-13	3-4	Black	
Sap. Value		185.3	118	
Iodine Value		130.4	113.8	

From the foregoing table it will be observed that the distillation has concentrated the unsaponifiable constituents into the still pot residue. Approximately 85 per cent of the unsaponifiable content of the original raffinate or ester fraction has thus been retained in this residue. This represents 65 per cent of the total unsaponifiable matter present in the original tall oil.

Saponification of esters

STEP B

The still pot residue containing a high concentration of unsaponifiable matter is pitch-like in consistency. In order to obtain the sterols in a purified form, this pitchy material is subjected to saponification with an alkali such as sodium or potassium hydroxide in water and a lower alcohol followed by extraction of the sterols with a solvent. In an actual example, the pitch was subjected to saponification with potassium hydroxide in solution in a mixture of methyl alcohol and water. The following is the composition of the saponification mixture:

1 part still residue
0.2 part potassium hydroxide (or a molecular equivalent amount of sodium hydroxide)
0.36 part methyl alcohol
1.8 parts water
(all parts are by weight)

The mixture was refluxed for two hours and then allowed to cool. In the foregoing operation (Step B) rosin acids and fatty acid esters are both substantially fully saponified.

Extraction of unsaponifiable matter

STEP C

The resultant soap solution was extracted batchwise with an appropriate solvent for the sterol, such as ethyl ether. In this extraction six applications, each of one-half the volume of the solution of soaps, were made. The yield of unsaponifiable matter thus extracted constituted 35.4 per cent by weight of the still residue representing 93.6 per cent of the total unsaponifiable matter in the residue.

It will be appreciated that in the extraction of the still pot residue soaps, various solvents may be employed. These included ethyl ether, butyl or isopropyl ether or mixed ethers such as methyl isopropyl ether or other alkyl ethers containing 4 to 10 carbon atoms, aromatic hydrocarbons, such as toluene or benzene, halogenated hydrocarbons, such as ethylene dichloride, straight chain hydrocarbons such as naphtha e. g. naphtha containing 6 to 10 carbon atoms, e. g. an average chain length of 7 or 8 carbon atoms and many other compounds having a solvent action for unsaponifiable constituents and simultaneously being relatively immiscible with the water-alcohol solution. Batch and countercurrent extractions are both admissible. Great variation in the ratio of solvent for unsaponifiable matter, e. g. 0.5 part to 10 parts by volume per part of soap solution is permissible. These solutions containing the extracted unsaponifiable constituents may be washed with water either countercurrently or batchwise for the removal of any dissolved soaps.

In the above examples in order to obtain a contration of the sterols from the unsaponifiable matter, the solvent was distilled and the unsaponifiable matter was dissolved in methyl alcohol employing approximately 15 parts by weight of the alcohol to 1 part by weight of unsaponifiable matter. When this mixture is refluxed the unsaponifiable matter goes into solution but when the mixture is cooled for several hours, e. g. 10 or 12 hours to −10° C. the sterol fraction crystallizes out. In this manner a yield of 57 per cent of the unsaponifiable matter as a sterol mixture may be obtained. This mixture comprises 80 to 85 per cent of sterols having a melting point of 120 to 130° C.

In the crystallization of the sterol fraction, methyl alcohol has been referred to. However, other alcohols such as ethyl alcohol, isopropyl alcohol or other solvents such as acetone, paraffinic naphtha, methyl acetate, ethyl acetate or a variety of other solvents may be employed. The ratio of solvent required will vary for each solvent. However, enough should be employed substantially to dissolve the unsaponifiable matter. Substantially any excess can be employed if appropriate adjustment of temperature is made.

As previously indicated, Step A of Stage IV, distillation of the fatty acid esters to provide a pitchy residue, may be omitted. In that event, the mixture of fatty acid esters enriched in unsaponifiable matter and containing only minor amounts of rosin acids will be treated with an amount of potassium or sodium hydroxide commensurate with the amount of acids and esters present in accordance with Step B of Stage IV to form soaps of the acids. The unsaponifiable matter will then be extracted from a water-alcohol solution by use of a solvent immiscible with water and alcohol, in accordance with Step C. The solvent may be evaporated from the extract of unsaponifiable matter and if desired, the sterols may be fractionated out in the manner already described.

A further alternative would involve treating the raffinate or ester fraction from the solvent fractionation of esterified tall oil to liberate the free acids. This may be done either by acid hydrolysis or by saponifying the ester fraction with sodium hydroxide or potassium hydroxide and acidifying the resultant soaps with mineral acid to liberate fatty acids. The fatty acids and unsaponifiable matter will separate as a top layer and can be decanted. The free fatty acids can then be distilled over under vacuum to leave a still residue of free acids very rich in unsaponifiable matter. The acids may be saponified with alkali and extracted in a water and alcohol solution with an immiscible solvent such as ether or naphtha to recover the unsaponifiable matter. The steps of saponifying the raffinate fraction and extracting the soap solutions are essentially the same as those already discussed in the preceding examples.

The recovery of the unsaponifiable matter of tall oil has been particularly emphasized. However it will be evident that the esters of fatty acids occurring in the raffinate obtained by solvent extraction of tall oil are extremely useful. They are distilled over in relatively pure state when the raffinate fraction is distilled. They may be employed directly in the preparation of resins and in other products. The distilled esters may also be saponified and then acidified to recover the free fatty acids. The soaps of fatty acids, after the unsaponifiable matter has been extracted, may also be acidified with a mineral acid, e. g. sulfuric acid to recover the free fatty acids nearly free of unsaponifiable matter and rosin acids.

The forms of the invention herein given are by way of illustration. It will be apparent that numerous 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 recovering unsaponifiable matter of tall oil from tall oil, which process comprises selectively esterifying the free fatty acids in tall oil with a lower alcohol, extracting the resultant mixture of esterified fatty acids, rosin acids and unsaponifiable matter with a selective polar solvent to obtain an extract of rosin acids and a raffinate containing most of the esters of fatty acids and most of the unsaponifiable matter of the tall oil and a minor amount of rosin acids, then distilling the raffinate to obtain the esters of fatty acids in purified form and to obtain a pitch-like still residue of residual esters of fatty acids, rosin acids and a high concentration of unsaponifiable matter, saponifying said acids and esters with an aqueous alcohol solution of an alkaline compound of an alkali metal to obtain solutions of soaps of tall oil and unsaponifiable matter in water and alcohol, extracting out the unsaponifiable matter from said solution with a solvent therefor which is immiscible in water and alcohol, eliminating the solvent from the unsaponifiable matter and crystallizing out the sterols in the unsaponifiable matter in a monohydric alcohol containing 1 to 3 carbon atoms in a straight chain hydrocarbon nucleus.

2. A process of recovering unsaponifiable matter of tall oil from tall oil, which process comprises esterifying the free fatty acids in tall oil with a lower alcohol, extracting the resultant mixture of esterified fatty acids, rosin acids and unsaponifiable matter with a selective polar solvent to obtain an extract of rosin acids and a raffinate containing most of the esters of fatty acids and a small amount of rosin acids and most of the unsaponifiable matter of the tall oil, then distilling the raffinate to obtain the esters of fatty acids in purified form and to obtain a pitch-like still pot residue of residual esters of fatty acids, rosin acids and a high concentration of unsaponifiable matter, saponifying said acids and esters with an aqueous alcohol solution of an alkaline compound of an alkali metal to obtain solutions of soaps of tall oil and unsaponifiable matter in water and alcohol, extracting out the unsaponifiable matter from said solution with a solvent which is immiscible in water and alcohol, eliminating the solvent from the unsaponifiable matter and crystallizing out the sterols in the unsaponifiable matter from an acetate of an alcohol containing 1 to 2 carbon atoms in the hydrocarbon nucleus.

3. A process of recovering unsaponifiable matter of tall oil from tall oil, which process comprises esterifying the free fatty acids in tall oil with a lower alcohol, extracting the resultant mixture of esterified fatty acids, rosin acids and unsaponifiable matter with a selective polar solvent to obtain an extract of rosin acids and a raffinate containing most of the esters of fatty acids and a small amount of rosin acids and most of the unsaponifiable matter of the tall oil, then distilling the raffinate to obtain the esters of fatty acids in purified form and to obtain a pitch-like still residue of residual esters of fatty acids, rosin acids and a high concentration of unsaponifiable matter, saponifying said acids and esters with an aqueous alcohol solution of an alkaline compound of an alkali metal to obtain solutions of soaps of tall oil and unsaponifiable matter in water and alcohol, extracting out the unsaponifiable matter from said solution with a solvent which is immiscible in water and alcohol, eliminating the solvent from the unsaponifiable matter.

4. A process of recovering unsaponifiable matter of tall oil from tall oil, which process comprises esterfying the free fatty acids in tall oil with a lower alcohol, extracting the resultant mixture of esterified fatty acids, rosin acids and unsaponifiable matter with a selective polar solvent to obtain an extract of rosin acids and a raffinate containing most of the esters of fatty acids and a small amount of rosin acids and most of the unsaponifiable matter of the tall oil, then distilling the raffinate to obtain the esters of fatty acids in purified form and to obtain a pitch-like still residue of residual esters of fatty acids, rosin acids and a high concentration of unsaponifiable matter, saponifying said acids and esters with a solution of an alkaline compound of an alkali metal in a mixture of about 1.8 parts by weight of water and 0.36 part by weight of a lower water soluble alcohol to obtain solutions of soaps of tall oil and unsaponifiable matter in water and alcohol, extracting out the unsaponifiable matter from said solution with naphtha containing 6 to 10 carbon atoms in the molecule, and crystallizing out the sterols in the unsaponifiable matter from acetone.

5. A process of recovering unsaponifiable matter of tall oil from tall oil, which process comprises esterifying the free fatty acids in tall oil with a lower alcohol, extracting the resultant mixture of esterified fatty acids, rosin acids and unsaponifiable matter with a selective polar solvent to obtain an extract of rosin acids and a raffinate containing most of the esters of fatty acids and a small amount of rosin acids and most of the unsaponifiable matter of the tall oil, then distilling the raffinate to obtain the esters of fatty acids in purified form and to obtain a pitch-like still residue of residual esters of fatty acids, rosin acids and a high concentration of unsaponifiable matter, saponifying said acids and esters with an aqueous alcohol solution of an alkaline compound of an alkali metal to obtain solutions of soaps of tall oil and unsaponifiable matter in water and alcohol, extracting out the unsaponifiable matter from said solution with ethylene dichloride eliminating the ethylene dichloride from the unsaponifiable matter and crystallizing out the sterols from the rest of the unsaponifiable matter in acetone.

6. A process of recovering unsaponifiable matter of tall oil from tall oil, which process comprises esterifying the free fatty acids in tall oil with a lower alcohol, extracting the resultant

mixture of esterified fatty acids, rosin acids and unsaponifiable matter with a selective polar solvent to obtain an extract of rosin acids and a raffinate containing most of the esters of fatty acids and a small amount of rosin acids and most of the unsaponifiable matter of the tall oil, then distilling the raffinate to obtain the esters of fatty acids in purified form and to obtain a pitch-like still residue of residual esters of fatty acids, rosin acids and a high concentration of unsaponifiable matter, saponifying said acids and esters with an aqueous alcohol solution of an alkaline compound of an alkali metal to obtain solutions of soaps of tall oil and unsaponifiable matter in water and alcohol, extracting out the unsaponifiable matter from said solution with an ether.

7. A process of recovering unsaponifiable matter of tall oil from tall oil, which process comprises esterfying the free fatty acids in tall oil with a lower alcohol, extracting the resultant mixture of esterified fatty acids, rosin acids and unsaponifiable matter with a selective polar solvent to obtain an extract of rosin acids and a raffinate containing most of the esters of fatty acids and a small amount of rosin acids and most of the unsaponifiable matter of the tall oil, then distilling the raffinate to obtain the esters of fatty acids in purified form and to obtain a pitch-like still residue of residual esters of fatty acids, rosin acids and a high concentration of unsaponifiable matter, saponifying said acids and esters with an aqueous alcohol solution of an alkaline compound of an alkali metal to obtain solutions of soaps of tall oil and unsaponifiable matter in water and alcohol, extracting out the unsaponifiable matter from said solution with a solvent which is immiscible in water and alcohol, said solvent being ethylene dichloride, elminating the solvent from the unsaponifiable matter.

8. A process of recovering unsaponifiable matter of tall oil from tall oil, which process comprises esterifying the free fatty acids in tall oil with a lower alcohol, extracting the resultant mixture of esterified fatty acids, rosin acids and unsaponifiable matter with a selective polar solvent to obtain an extract of rosin acids and a raffinate containing most of the esters of fatty acids and a small amount of rosin acids and most of the unsaponifiable matter of the tall oil, then distilling the raffinate to obtain the esters of fatty acids in purified form and to obtain a pitch-like still residue of residual esters of fatty acids, rosin acids and a high concentration of unsaponifiable matter, saponifying said acids and esters with an aqueous alcohol solution of an alkaline compound of an alkali metal to obtain solutions of soaps of tall oil and unsaponifiable matter in water and alcohol, extracting out the unsaponifiable matter from said solution with a solvent which is immiscible in water and alcohol, comprising a single benzene nucleus containing 1 to 2 methyl groups as side chains, eliminating the solvent from the unsaponifiable matter.

9. A process of recovering unsaponifiable matter of tall oil from tall oil, which process comprises esterifying the free fatty acids in tall oil with a lower alcohol, extracting the resultant mixture of esterified fatty acids, rosin acids and unsaponifiable matter with a selective polar solvent to obtain an extract of rosin acids and a raffinate containing most of the esters of fatty acids and a small amount of rosin acids and most of the unsaponifiable matter of the tall oil, then distilling the raffinate to obtain the esters of fatty acids in purified form and to obtain a pitch-like still residue of residual esters of fatty acids, rosin acids and a high concentration of unsaponifiable matter, saponifying said acids and esters with an aqueous alcohol solution of an alkaline compound of an alkali metal to obtain solutions of soaps of tall oil and unsaponifiable matter in water and alcohol, extracting out the unsaponifiable matter from said solution with a solvent which is immiscible in water and alcohol, washing the resultant solvent of unsaponifiable matter with water to remove soaps contained therein, and eliminating the solvent from the unsaponifiable matter.

10. A process as defined in claim 3 in which the polar solvent is furfural.

11. A process as defined in claim 3 in which the polar solvent is furfural containing 1 to 15 per cent of water.

12. A process as defined in claim 9 in which the polar solvent is furfural containing 1 to 15 per cent of water.

13. A process as defined in claim 3 in which the distillation is effected at a temperature within the range of 158 to 225° C. and under a vacuum of 1 to 30 mm. of mercury whereby to remove the fatty acid esters without substantial volatilization of the unsaponifiable matter.

14. A process as defined in claim 9 in which the distillation is effected at a temperature within a range of 158 to 225° C. and under a vacuum of 1 to 30 mm. of mercury whereby to remove the fatty acid esters without substantial volatilization of the unsaponifiable matter.

15. In a process of recovering unsaponifiable matter of tall oil from a mixture thereof with rosin acids and fatty acids of tall oil, the steps which comprise selectively esterifying the fatty acids of said mixture with a lower aliphatic alcohol of 1 to 4 carbon atoms in the molecule, then contacting the resultant mixture of rosin acids, unsaponifiable matter and esters of fatty acids with a solvent system comprising two intimately mixed but distinct liquid phases, one comprising a polar solvent and the other comprising a non-polar solvent but partially miscible with the polar solvent to obtain selective solution of the rosin acids in the polar solvent phase and selective solution of a mixture of said esters and unsaponifiable matter in the non-polar solvent phase, separating the phases, evaporating the non-polar solvent from the mixture of esters and unsaponifiable matter, distilling a fraction of esters from the recovered mixture, then saponifying with alkali, the residual fatty acid esters and any retained rosin acids in the distillation residue, dissolving the mixture of soaps and unsaponifiable matter in a solution of water and a lower water-soluble aliphatic alcohol, the water and alcohol being in the respective proportions of 1.8 and 0.36 parts by weight and extracting out the unsaponifiable matter with a solvent of unsaponifiable matter of tall oil which is immiscible with water and alcohol, said solvent being selected from a class consisting of aliphatic ethers of 4 to 10 carbon atoms, naphthas containing 6 to 10 carbon atoms, ethylene dichloride, toluene and benzene, and distilling the solvent from the unsaponifiable matter.

16. In a process of recovering the unsaponifiable matter of tall oil from a pitch-like mixture of rosin acids, esters of fatty acids and unsaponifiable matter obtained as a still residue

from the distillation of a concentrate of fatty acid esters constituting the raffinate fraction from the extraction with a selective polar solvent, of a mixture of esters of fatty acids, unsaponifiable matter and rosin acids, resulting from the selective esterification of the fatty acids of tall oil with a lower alkyl alcohol containing 1 to 4 carbon atoms, the steps which comprise saponifying the free acids and the esters in said mixture with alkali dissolved in water and a lower alcohol and extracting out the unsaponifiable matter from the solution with a solvent of unsaponifiable matter which is insoluble in the aqueous mixture.

17. The steps as defined in claim 16 in which the solvent of unsaponifiable matter is selected from a class consisting of alkyl ethers of 4 to 10 carbon atoms, naphthas containing 6 to 10 carbon atoms, ethylene dichloride, benzene and toluene.

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