

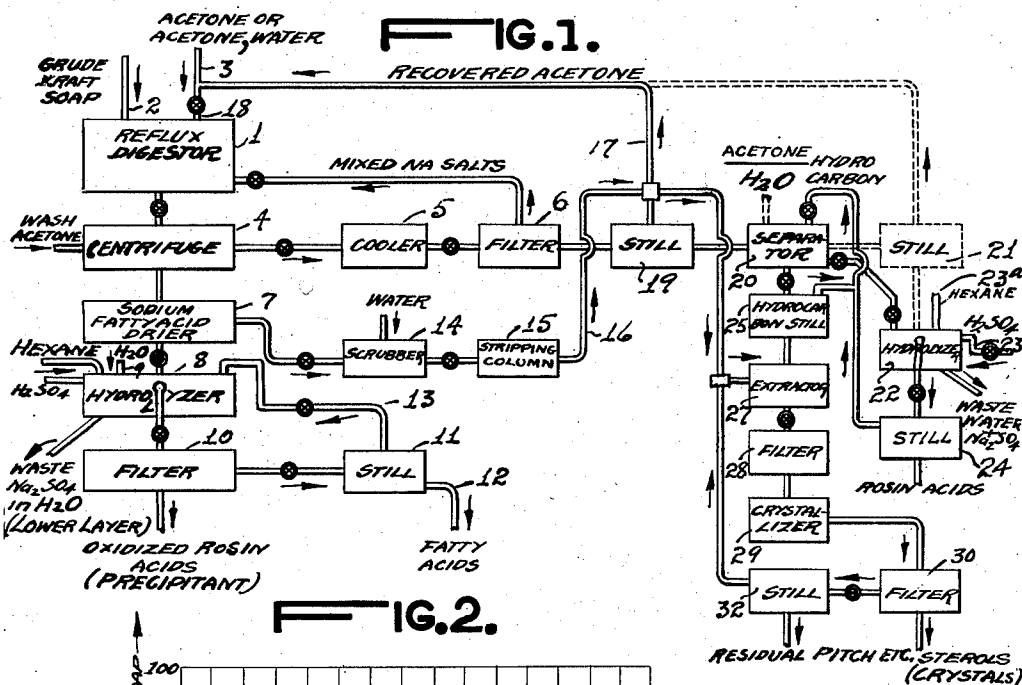
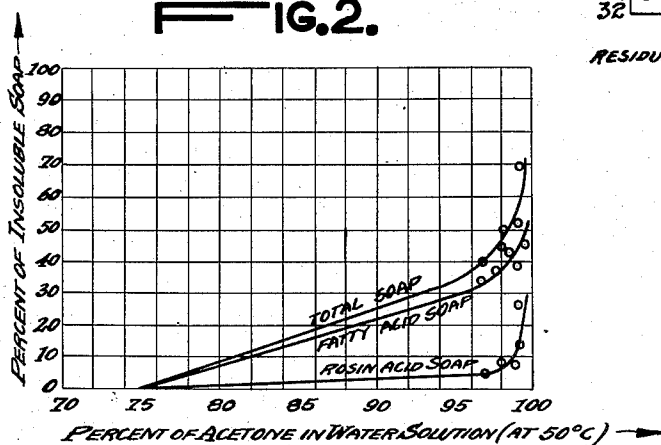
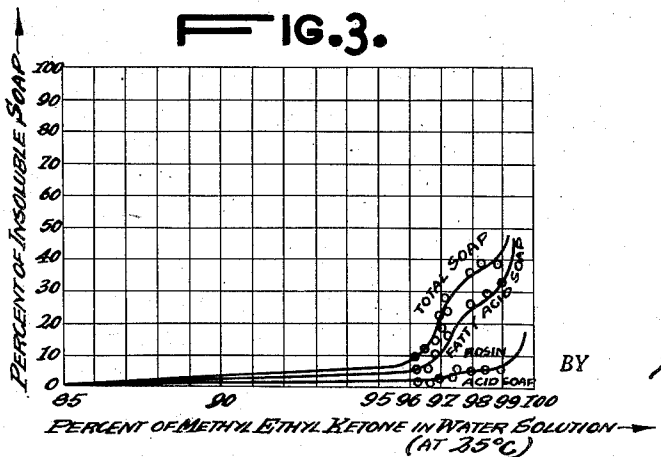
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PROCESS FOR THE SEPARATION OF FATTY ACID AND ROSIN ACID
SODIUM SALTS AND STEROLS FROM MIXTURES THEREOF

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PROCESS FOR THE SEPARATION OF FATTY ACID AND ROSIN ACID SODIUM SALTS AND STEROLS FROM MIXTURES THEREOF

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13 Claims. (Cl. 260—97.5)

The present invention arises from the discovery by us that the constituents of mixtures of fatty acid and rosin acid sodium salts can be separated by the selective solvent action of certain ketone-water mixtures, such as acetone-water mixtures and methyl ethyl ketone-water mixtures; also that fatty acid soaps may be separated by the same means from mixtures thereof with rosin soap and unsaponifiable material, including sterols.

This application contains in part subject matter in our application filed March 28, 1940, Serial No. 326,398.

A practical and industrially important application of this invention is in the separation and recovery from crude kraft soap (or crude tall oil soap as it is also called) of fatty and sodium salts, rosin acid sodium salts, and unsaponifiables including sterols.

While the process has general application, the same will be described in connection with the treatment of crude kraft soap.

Crude kraft soap consists of various evaporated and salted-out components of waste black liquid obtained from the treatment of coniferous wood by the soda-sulfate process, an example being "Wetso" of West Virginia Pulp & Paper Company, which has the following approximate composition:

	Percent
Sodium salts of fatty acids.....	36.30
Sodium salts of rosin acids.....	34.10
Unsaponifiables	3.75
Sterols	.85
Water	25.00
The rosin content may contain about 2% oxidized rosin.	

In the drawing, Figure 1 represents a flow diagram of a water-acetone solution method for the separation of constituents of crude kraft soap. Figures 2 and 3 represent the solubility of various soaps in a ketone at constant temperature.

EXAMPLE I

In carrying out one phase of the invention we first reduce the water content of the aforesaid kraft soap by evaporation, spray-drying or other suitable or convenient means, to 5% or less water content. This concentrated kraft soap is then placed in a reflux digester 1 through a pipe 2 and to said kraft soap is added, by way of pipe 3, sufficient acetone to make a 97% acetone-3% water mixture with the water contained in said kraft pulp mill soap, or there may be added to

said kraft soap acetone plus some water to make up the necessary 97-3 mixture. The said mixture in the digester is preferably subjected to a temperature of about 50° C. or some other temperature slightly below the boiling point of acetone for about 15 minutes. At the end of this period, a very substantial proportion of the sodium salts of the fatty acids separates out in the form of a precipitate, while the other substances go or remain in solution. If any oxidized rosin has been present in the kraft soap, this too will separate out with the sodium salt of the fatty acid in the form of a precipitate.

While the precipitate may then be recovered, as by filtering, we prefer that the material be placed in a centrifuge 4 which separates the liquid component from the precipitate, the former being conveyed to a cooler 5, the latter to a drier 7.

The liquid component, which is subjected to cooling contains in solution sodium salt of rosin acid, sterols and other unsaponifiables, as well as a small amount of sodium salt of fatty acids which has not precipitated out. Upon cooling to about 70° F. or by increasing the concentration of acetone, a proportion of the second fraction of fatty acid sodium salts precipitates out together with a small amount of rosin acid sodium salts, the sterols and unsaponifiables remaining in solution by virtue of the acetone. These small quantities of mixed sodium salts are returned to the digester, or may be re-worked separately.

Now, with respect to the material in the drier 7, the same comprises the sodium salts of fatty acids and substantially all of the sodium salts of oxidized rosin originally present in the waste liquid. After drying, the latter material is transferred to the hydrolyzer 8 to which is added sulfuric acid by way of pipe 9.

The effect of the sulfuric acid is to convert the sodium salts of the fatty acids to free fatty acids. After the hydrolyzing action or at some convenient point in this reaction, some ligroin, hexane or other suitable hydrocarbon is added to retain the oxidized rosin in solid condition. In the hydrolizer, then, there are oxidized rosin protected by the ligroin from going into solution, sodium sulfate, and free fatty acid. The oxidized rosin, ligroin and the free fatty acids are transferred to a filter 10 where the oxidized rosin is separated from the ligroin and free fatty acid. The sodium sulfate from the hydrolyzer is drawn off.

After the separation of the oxidized rosin from the ligroin and free fatty acid, the latter two

substances are transferred to a still 11 where the ligroin is distilled off and returned to the hydrolyzer 8 by way of pipe 13 while the free fatty acid is recovered through the pipe 12. The latter may contain a greater or less amount of rosin acid depending upon the care with which the operation has been carried out and other factors.

At drying operation 7, traces of acetone are driven off by heat to the scrubber 14, and from there treated in the stripping column 15, from whence such acetone is returned to the digester 1 by way of pipes 16, 17 and 18.

Reverting to the liquid component derived from the filter 6: as stated, the latter comprises in dissolved condition sterols and other unsaponifiables as well as sodium resinates. This material is transferred to the still 19 where the acetone and some water are driven off, leaving the material substantially free of acetone and deprived of more or less of its water content. The mass remaining after such distillation is placed in a separator 20 and there is added sufficient ligroin, hexane or the like, together with acetone, preferably in substantially equal proportions, and sufficient with the remaining water, to form a homogeneous solution of the entire mixture. Water is then added to cause separation into two layers, the top layer being a hydrocarbon solution of the pitch, sterols and other unsaponifiables, and the bottom layer being a water-ketone solution of sodium resinates. The two layers are separated from each other by decantation or other separatory operation, the rosin acid soap layer being transferred to still 21 where the acetone is distilled out and conveyed back to pipe 3. The water solution of rosin acid soap is delivered directly to a hydrolyzer 22 where sulfuric acid is added through pipe 23, and hexane through pipe 23a. This acid converts the sodium salt of rosin acid to the free rosin acid and sodium sulfate. The mixture is allowed to settle, forming two layers. The top layer, being a hexane solution of rosin acids is then transferred to a still 24, where the hexane is distilled off and returned to the separator 20, as indicated. There then emanates from the still 24 free rosin acid which is removed.

Reverting now to the hexane pitch, sterols and unsaponifiables portion from the separator 20, the said material is transferred to a still 25 where the hexane is driven off and conveyed back to the separator 20 for re-use, the remaining pitch, sterols and unsaponifiables being transferred as a dark viscous mass to extractor 27 receiving hot acetone, preferably anhydrous. The hot acetone dissolves all small amounts of sodium resinate which, although soluble in 97% acetone containing a small amount of water (3%) are insoluble in anhydrous acetone, so that when the material is transferred to filter 28, the insoluble substances will be separated from the hot acetone-soluble pitch, sterols and unsaponifiables. The latter are placed in crystallizer 29 where, upon chilling of the acetone to a low temperature, preferably below 70° F., the sterols crystallize out. The crystallized sterols, remaining pitch, unsaponifiables and acetone are placed in filter 30 where the crystallized sterols are separated from the dissolved pitch, unsaponifiables and acetone. The latter material is placed in a still 32 where the acetone is distilled off and returned into circulation while the unsaponifiables, loosely called "pitch" remain behind and are removed from the still. The last-named mass of material can be hydrolyzed and otherwise

treated to obtain certain desirable or useful products, but this is no part of the present invention.

The sterols, ordinarily pure white in color, are sometimes contaminated with sodium salt of rosin acid or sodium abietate; the latter may be removed as follows:

The mixture of sterols and sodium abietate is dissolved in water to form an emulsion, and hydrolyzed with a slight excess of hydrochloric acid. The sterols and abietic acid are extracted by means of hot hexane, and then recovered from the hexane solution by distilling off the solvent. The residue is then dissolved in anhydrous acetone, the solution chilled to crystallize out the sterols, and filtered. The acetone filtrate contains the abietic acid which can be recovered by distilling off the solvent.

As an illustration of the yields obtained by the above example of our process of separation and recovery, in an actual operation, starting with the composition—

	Per cent
Sodium salts of fatty acids.....	36.30
Sodium salts of rosin acids.....	34.10
Unsaponifiables, and pitch.....	3.75
Sterols	.85
Water	25.00
Some sodium salts of oxidized rosin acids.	

we succeeded in recovering (based upon 100 grams of the original composition—

	Grams
Free fatty acids having melting point between 18-18.50° C., acid No. 200, refractive index 1.484.....	30.2
Oxidized rosin acid.....	.9
Free rosin acid.....	27.0
Sterols (mainly in the form sitosterols)	.81
Residual material.....	8.59

A preliminary separation of the oxidized rosin content of the starting material may be effected by subjecting the latter to an acetone-water solution in the proportion of 75% acetone and 25% water, whereby solution of the materials with the exception of the sodium salts of oxidized rosin will be secured. The oxidized rosin being first removed, the solution may be passed to digester 1 and acetone added to provide a 97-3 acetone-water content. This, as has been shown, causes the sodium salts of the fatty acids to precipitate out. On the other hand, if acetone is added so as to raise the acetone-water ratio to 99.5-.5, both the fatty acid sodium salts and the rosin acid sodium salts precipitate out, leaving the unsaponifiables, including the pitch and sterols, in solution.

There are three main classifications into which the rosin acids may be divided. Henceforth they shall be referred to as follows:

- Type A—Hexane soluble abietic acid.
- Type B—Hexane insoluble rosin acid.
- Type C—Rosin acid, the sodium salt of which is soluble in anhydrous acetone and hexane. This type has previously been referred to as "pitch."

EXAMPLE II

Treat with anhydrous acetone

961.2 grams of spray dried soap was washed with three successive portion of 1½ gallons of anhydrous acetone for each wash at a temperature of 50° C. The insoluble soap was filtered out and then dried until free of acetone. It was then dissolved in hot water, and hydrolyzed by the addition of dilute sulfuric acid.

Hexane was then added to extract the resulting mixture of fatty and rosin acids. The hexane solution was decanted, filtered, and then heated to distill off the solvent. 672 grams (70.0% yield) of brown "mixed acids" was obtained. On analysis it was found to contain 57.2% fatty acid and 42.8% abietic acid. 31 grams (3.2% yield) of light brown oxidized rosin was filtered from the hexane solution of "mixed acids."

The acetone solution from which the fatty acid soaps had been filtered was heated to distill off the acetone. The residue was dissolved in water. Hexane was then added to extract the sterols and the sodium salts of type C rosin acid, from the water solution of the sodium salts of types A and B rosin acid. The two layers formed on settling were separated. The top hexane layer was heated to distill off the solvent. The residue was then dissolved in hot acetone. The solution was chilled and sterols were crystallized and filtered out. Additional sterols were recovered by concentrating the filtrate and then crystallizing sterols from it. Yield of sterols=18.25 grams=1.9%. The filtrate was heated to distill off the acetone. A residue of 88.4 gm. (yield=9.2%) of type C sodium resinate was recovered.

The lower water layer from which the sterols and type C sodium resinate were extracted with hexane, was hydrolyzed by the addition of dilute sulfuric acid. Hexane was then added, to dissolve type A rosin acid, leaving the type B rosin acid undissolved. This type B rosin acid was separated from the hexane solution of type A rosin acid. The hexane solution containing the type A rosin acid was decanted, and then heated to distill off the solvent, leaving a residue of type A-rosin acid weighing 17.3 gm. (yield=1.8%). The hexane insoluble rosin acid (type B) was recovered as a dark brown residue, weighing 33.6 grams (yield=3.5%).

Summary of yields

	Per cent
Mixed acids	70.0
Oxidized rosin.....	3.2
Type A rosin acid.....	1.8
Type B rosin acid.....	3.5
Type C sodium abietate.....	9.2
Sterols	1.9

EXAMPLE III

Treat with anhydrous acetone and then with 97% acetone

1000 grams of spray dried soap was washed with three successive portions of 1½ gallons of anhydrous acetone for each wash at a temperature of 50° C. The insoluble soap was filtered out. The soap was then washed with six successive portions of 1¼ gallons of 97% acetone for each wash at 50° C. The soap which remained insoluble consisted very largely of the sodium salts of the fatty acids. This soap was dissolved in water and hydrolyzed by the addition of dilute sulfuric acid. Hexane was then added to extract the resulting fatty acid. A considerable volume of insoluble, light weight, brown, oxidized rosin acid was precipitated. It was filtered out and dried. Yield of oxidized rosin=23 grams=2.3%. The hexane solution of fatty acids was heated to distill off the solvent. A residue of 335 grams (yield=33.5%) of yellow fatty acids was obtained. On analysis it was found to contain 90.0% fatty acid and 10.0% rosin acid.

The 97% acetone solution of sodium resinates and sterols, from which the sodium salts of the fatty acids were filtered, was heated to distill off the solvent. The residue, a dark brown paste, was dissolved in water and hydrolyzed with dilute sulfuric acid. Hexane was added to extract the resulting (type A) abietic acid. The hexane solution was heated to distill off the solvent. A residue of clear, brown rosin acid weighing 286.0 grams was obtained (yield=28.6%). On analysis it was found to consist of 86.6% rosin acid and 13.4% fatty acid. The residue of hexane insoluble rosin acid (type B) was a very dark brown material, weighing 33.0 grams (yield=3.3%).

The original anhydrous acetone washings of the dried soap were heated to distill off the solvent. The residue was a mixture of the three types of sodium resinate and sterols. The mixture was dissolved in water. Hexane was then added to extract the sterols and type C-sodium resinate from the types A and B sodium resinate. The hexane solution was heated to distill off the solvent, leaving a residue of sterols and type C sodium resinate. The residue was dissolved in hot anhydrous acetone and then chilled to crystallize the sterols. The sterols were filtered out. Additional sterols were recovered by concentrating the acetone filtrate and then crystallizing sterols from it. Yield of sterols=19.0 gm.=1.9%. The filtrate was heated to distill off the acetone. A residue of 92 grams of type C sodium resinate was obtained (yield=9.2%) as a dark brown residue.

The water solution from which the type C sodium resinate and sterols had been extracted with hexane, was hydrolyzed with dilute sulfuric acid. Hexane was then added to extract the type A rosin acid. The hexane solution was decanted and then heated to distill off the solvent. A residue of type A rosin acid, weighing 18.0 grams (yield=1.8%) was obtained. The type B, hexane insoluble rosin acid was recovered as a dark brown residue weighing 35 grams.

Summary of yields

	Per cent
Fatty acids.....	33.5
Type A rosin acid.....	28.6
Oxidized rosin	2.3
Type B rosin acid.....	6.8
Type A rosin acid.....	1.8
Sterols	1.9
Type C sodium resinate.....	9.2

EXAMPLE IV

Treat with methyl ethyl ketone

30 grams of spray dried soap was dissolved in 300 cc. of a saturated solution of water in methyl ethyl ketone (90% ketone) at room temperature. 0.30 gram of insoluble material (yield=1.0%) was filtered out. The concentration of ketone was increased to 99% by the addition of 2250 cc. of anhydrous methyl ethyl ketone.

Upon the addition of ketone to the solution, white sodium fatty acid soaps were precipitated and then filtered out. The residue was dissolved in water and hydrolyzed with dilute sulfuric acid. Petroleum ether was added to extract the resulting fatty acids. The ether solution of fatty acids was heated to distill off the solvent. The residue was a yellow fatty acid weighing 10.81 grams (yield=36.03%). On analysis it was found to consist of 87.50% fatty acid and 12.50% abietic acid.

The methyl ethyl ketone solution from which the fatty acid soaps had been filtered was heated to distill off the ketone. The residue was dissolved in water with hexane to extract the sterols and type C sodium resinate from the water solution of the sodium soaps of types A and B rosin acid. The hexane solution was heated to distill off the solvent. The residue of sterols and type C sodium resinate was dissolved in hot acetone. The solution was chilled, sterols were crystallized and then filtered out. Additional sterols were recovered by concentrating the acetone filtrate and then recrystallizing sterols from it. Yield of sterols=0.45 gram=1.52%. The filtrate was heated to distill off the acetone. A residue weighing 1.66 grams=5.52% of type C sodium resinate was recovered.

The water solution of the sodium soaps of types A and B rosin acids was hydrolyzed with dilute sulfuric acid. Hexane was added to extract the type A rosin acid. The hexane solution was decanted and then heated to distill off the solvent. A residue of clear, light brown abietic acid, type A, was obtained, weighing 6.4 grams (yield=21.35%). The hexane insoluble type B rosin acid was recovered as a dark brown residue weighing 6.6 grams (yield=22.0%).

Summary of yields

	Per cent
Fatty acid.....	36.03
Ketone insolubles	1.00
Sterols	1.52
Type C sodium resinate.....	5.52
Type A rosin acid.....	21.35
Type B rosin acid.....	22.00

Any aliphatic ketones in which water is soluble, or, at least slightly soluble, may be employed in our process. In the examples, acetone and methylethyl ketone were specified, but in general, ketones with a structure containing up to 8 or 9 carbon atoms may be used and, as examples, we may mention di-ethyl ketone and ethyl propyl ketone. Water is generally insoluble in the higher ketones.

From the above it will be seen that a method has been provided whereby from crude kraft soap, constituting a low grade source and either with its normal water content or dried, free fatty acids, free rosin acids and sterols may be severally separated and recovered; that the foregoing method, at an intermediate stage, enables the recovery of the fatty acid sodium salts from the rosin acid sodium salt components and sterols, one from the other, to be used or further processed, and, that the method, within certain limits, is capable of being varied to meet variations of the starting product and the nature of the recovery desired.

The above described process may be employed with advantage in connection with compositions or mixtures of fatty acid sodium salts, rosin and sodium salts, pitch and sterols and other unsaponifiables obtained from sources other than waste black liquor of the soda-sulfate process.

By the use of varying ratios of acetone-water mixtures between anhydrous and 97% acetone, an insoluble product may be obtained, varying from 55% to 95% fatty acid sodium salts and 4% to 45% rosin acid sodium salts.

Again, it should be borne in mind, that the type of higher fatty acid sodium salt may vary with the characteristics of the starting material. In wood pulp cook liquor, which is given merely as one example, the sodium fatty acid salt is comprised chiefly of the sodium salts of the fatty

acids; oleic, linoleic, linolinic, ricinoleic, and possibly, depending on the specific source of the liquor, may even contain such fatty acids as stearic, palmitic and hydroxystearic.

Having described our invention, what we claim and desire to secure by Letters Patent is as follows:

1. The process of separating the constituents of kraft pulp mill soap which comprises extracting the same with a mixture of about 97% aliphatic ketone of not more than 9 carbon atoms per molecule and 3% water whereby the sodium salts of fatty acids and oxidized rosin acids are separated out as insoluble precipitate.

2. Process in accordance with claim 1 wherein the insoluble precipitate is removed; the ketone is removed from the remaining solution; then adding to the remaining solution water and a hydrocarbon selected from the group consisting of hexane and ligroin to dissolve the sodium resinates contained therein and thereby forming an aqueous and non-aqueous layers; and separating said layers.

3. Process in accordance with claim 1 wherein the insoluble precipitate is removed; the ketone is removed therefrom, and the residue is hydrolyzed with a mineral acid in the presence of water; then to said hydrolysate there is added a hydrocarbon selected from the group consisting of hexane and ligroin thereby forming an aqueous layer, and a hydrocarbon layer containing dissolved fatty acid and suspended oxidized rosins acids; removing the hydrocarbon layer and filtering the same to remove the oxidized rosin acids; removing the hydrocarbon from the filtrate by distilling the same to recover the fatty acids.

4. The process of separating and recovering the acid constituents of crude kraft soap which comprises subjecting the same to the selective solvent action of a mixture of about 97% acetone and 3% water, whereby sodium salts of fatty acids are separated out, separating the latter from the solution portion, subjecting the sodium salts of fatty acids to hydrolysis to obtain the free fatty acids.

5. The process in accordance with claim 4, wherein there is added to the hydrolyzer for solid portion water and a low boiling point hydrocarbon selected from the group consisting of hexane and ligroin in which the sterols, pitch and other unsaponifiables are soluble in which the free fatty acids are soluble and in which the oxidized rosin is insoluble.

6. The process of separating sodium salts of fatty acids, sodium salts of rosin acid, pitch and unsaponifiable matter from a mixture thereof, which comprises subjecting said mixture to the selective action of a ketone-water mixture the ketone being an aliphatic ketone of not more than 9 carbon atoms per molecule and in which water may be at least partially soluble, the proportion of water being to about 3% to separate out a major proportion of the said sodium salts of fatty acids while maintaining the remaining substances in solution, and removing the undissolved material.

7. The process of separating sodium salts of fatty acids and sodium salts of rosin acid from a mixture thereof, which comprises subjecting the mixture to the action of a lower-aliphatic ketone-water mixture, the aliphatic ketone being of not more than 9 carbon atoms per molecule in which water may be at least partially soluble, the proportion of water in said solvent mixture being about 3% to maintain substantially insoluble the

sodium salts of fatty acids, and removing the latter.

8. The process of separating the constituents of crude kraft soap to remove the sodium salts of oxidized rosin acids therefrom, which comprises extracting the crude kraft soap with a mixture of about 75% acetone and 25% water.

9. The process of treating crude kraft soap containing sodium salts of oxidized rosin acid which comprises first treating the crude kraft soap with a mixture of about 75% acetone and 25% water, to dissolve all of the components of said soap with the exception of said salts of oxidized rosin acids, separating the latter from the solution portion, adding to the latter sufficient acetone to increase the percentage of acetone in the acetone-water mixture to 97-3, whereby sodium salts of fatty acids are precipitated out, and removing the latter.

10. The process of separating sodium salts of fatty acids from sodium salts of rosin acids in mixtures thereof, which comprises dissolving the latter with a mixture of about 97% acetone and 3% water to effect separation of said component soaps, and separating the same.

11. The process of separating sodium salts of fatty acids and sodium salts of rosin acids from a mixture thereof with pitch and unsaponifiables, which comprises dissolving the pitch and unsaponifiables thereof with an acetone-water mixture

where the acetone is in excess of 97% so as to precipitate out the component soaps.

12. The process of separating sterols, pitch and other unsaponifiables from a mixture thereof, with sodium salts of rosin acids which comprises adding thereto acetone and water and a low boiling hydrocarbon selected from the group consisting of hexane and ligroin in which the sterols, pitch and other unsaponifiables are soluble so as to form two layers, in the water layer of which are the sodium salts of rosin acids and in the hydrocarbon layer of which are the pitch, sterols, and other unsaponifiables, separating said layers, distilling the hydrocarbon layer to remove the latter and leave the pitch, sterols and other unsaponifiables, treating the latter with hot acetone, thence chilling the resulting solution to crystallize out sterols, and removing the crystalline material.

13. The process of separating the constituents of substantially dry kraft pulp mill soap which comprises extracting the same by the solvent action of an aliphatic ketonic solvent of not more than 9 carbon atoms per molecule, and not less than 97% ketone concentration, and in which water may be at least partially soluble, whereby the unsaponifiable fraction is dissolved and the sodium soaps are precipitated.

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