

April 9, 1974

D. L. MITCHELL ET AL

3,803,114

PROCESS FOR PRODUCING UNSAPONIFIABLES-FREE TALL OIL PRODUCTS

Filed March 10, 1972

16 Sheets-Sheet 1

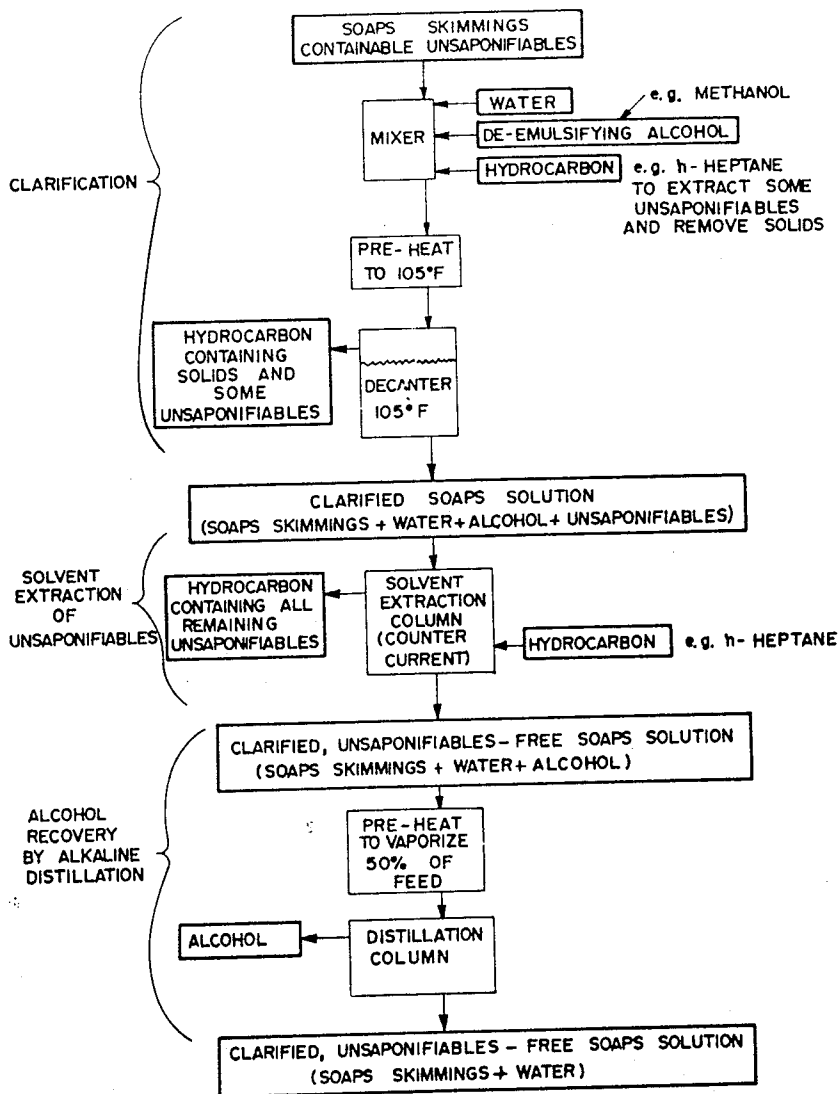


FIG. 1.

April 9, 1974

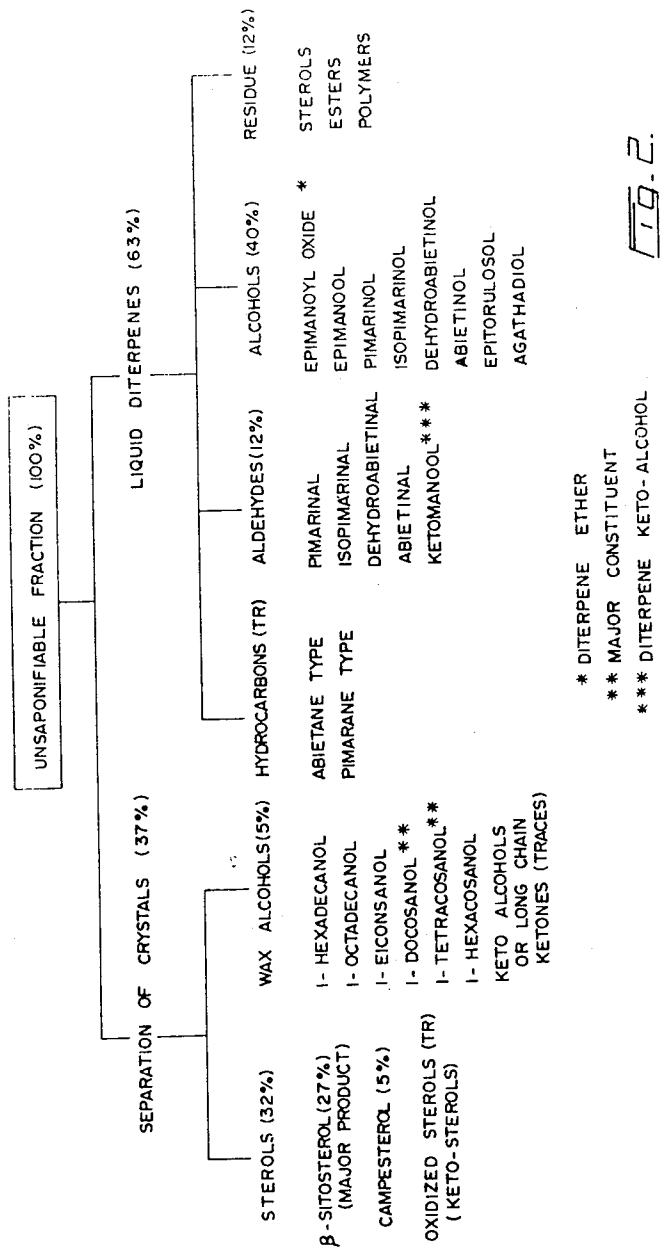
D. L. MITCHELL ET AL

3,803,114

PROCESS FOR PRODUCING UNSAPONIFIABLES-FREE TALL OIL PRODUCTS

Filed March 10, 1972

16 Sheets-Sheet 2



April 9, 1974

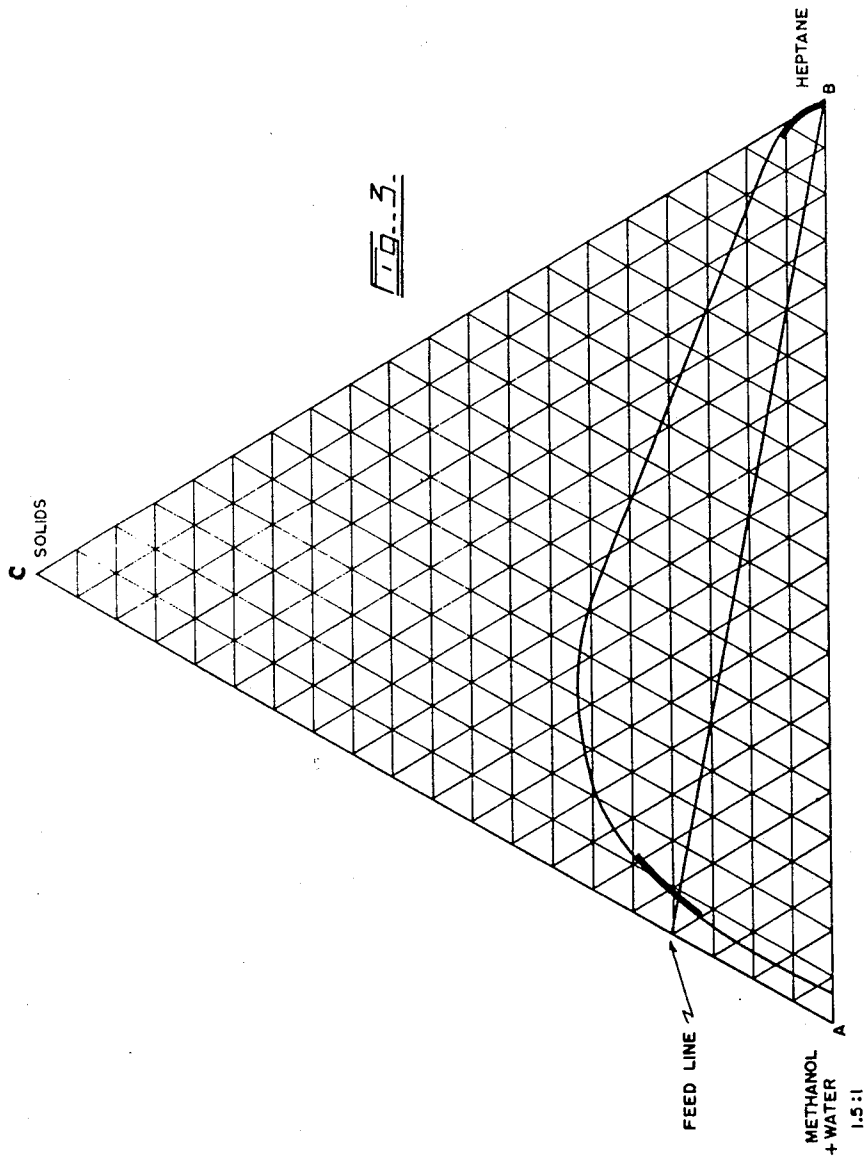
D. L. MITCHELL ET AL

3,803,114

PROCESS FOR PRODUCING UNSAPONIFIABLES-FREE TALL OIL PRODUCTS

Filed March 10, 1972

16 Sheets-Sheet 3



April 9, 1974

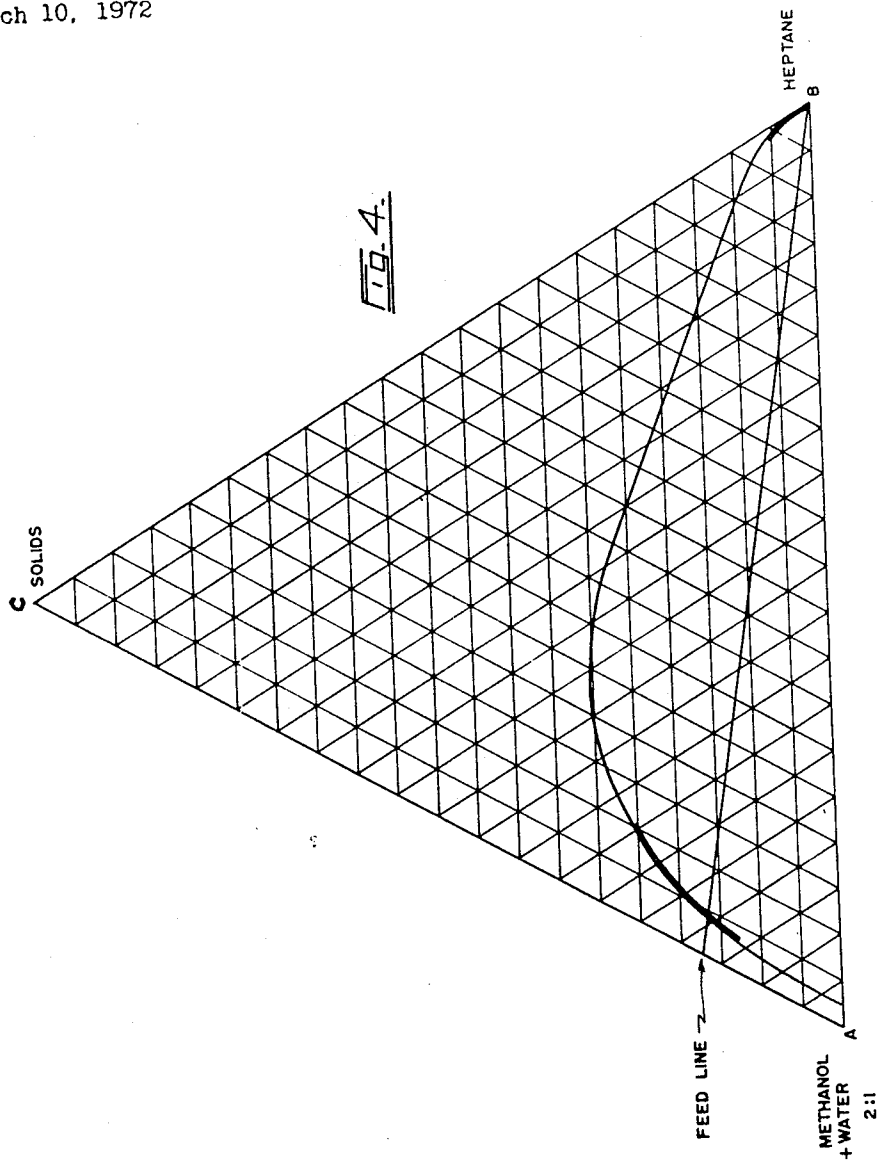
D. L. MITCHELL ET AL

3,803,114

PROCESS FOR PRODUCING UNSAPONIFIABLES-FREE TALL OIL PRODUCTS

Filed March 10, 1972

16 Sheets-Sheet 4



April 9, 1974

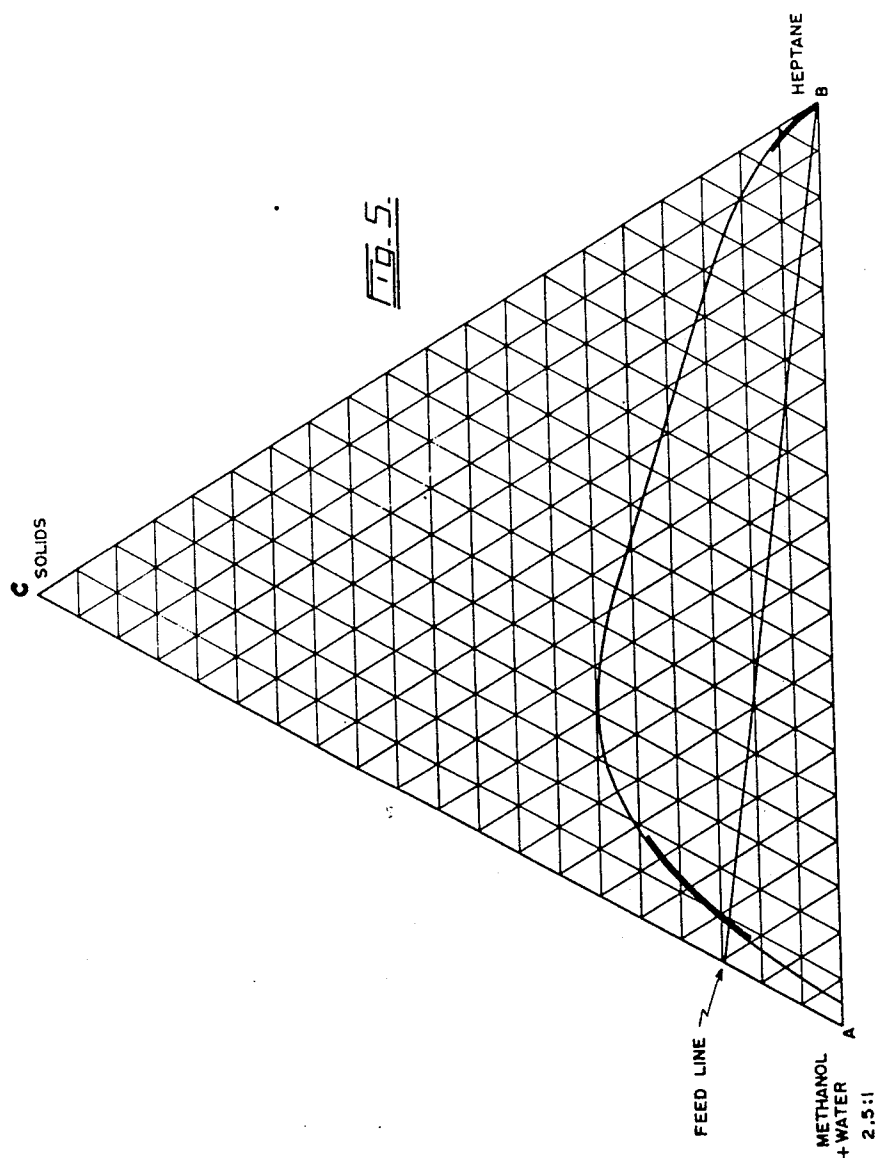
D. L. MITCHELL ET AL

3,803,114

PROCESS FOR PRODUCING UNSAPONIFIABLES-FREE TALL OIL PRODUCTS

Filed March 10, 1972

16 Sheets-Sheet 5



April 9, 1974

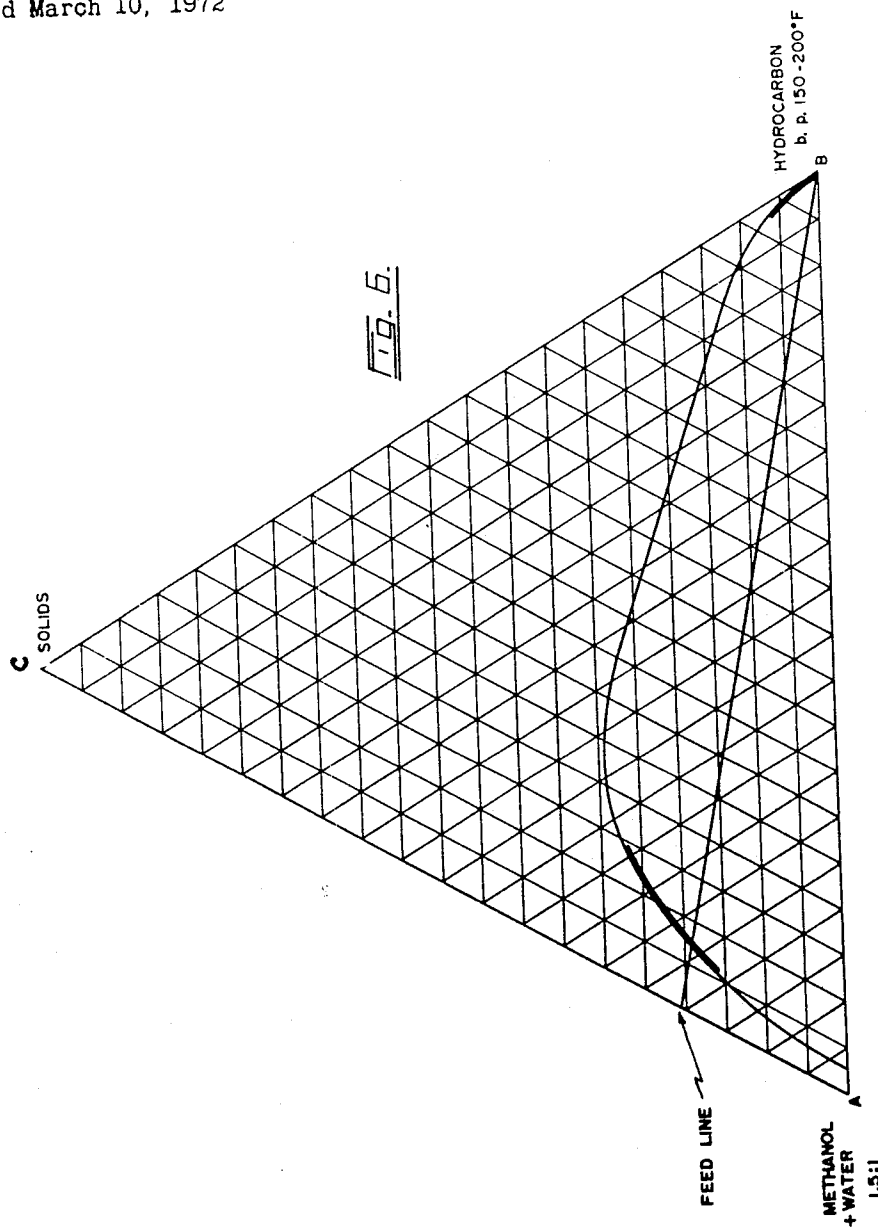
D. L. MITCHELL ET AL

3,803,114

PROCESS FOR PRODUCING UNSAPONIFIABLES-FREE TALL OIL PRODUCTS

Filed March 10, 1972

16 Sheets-Sheet 6



April 9, 1974

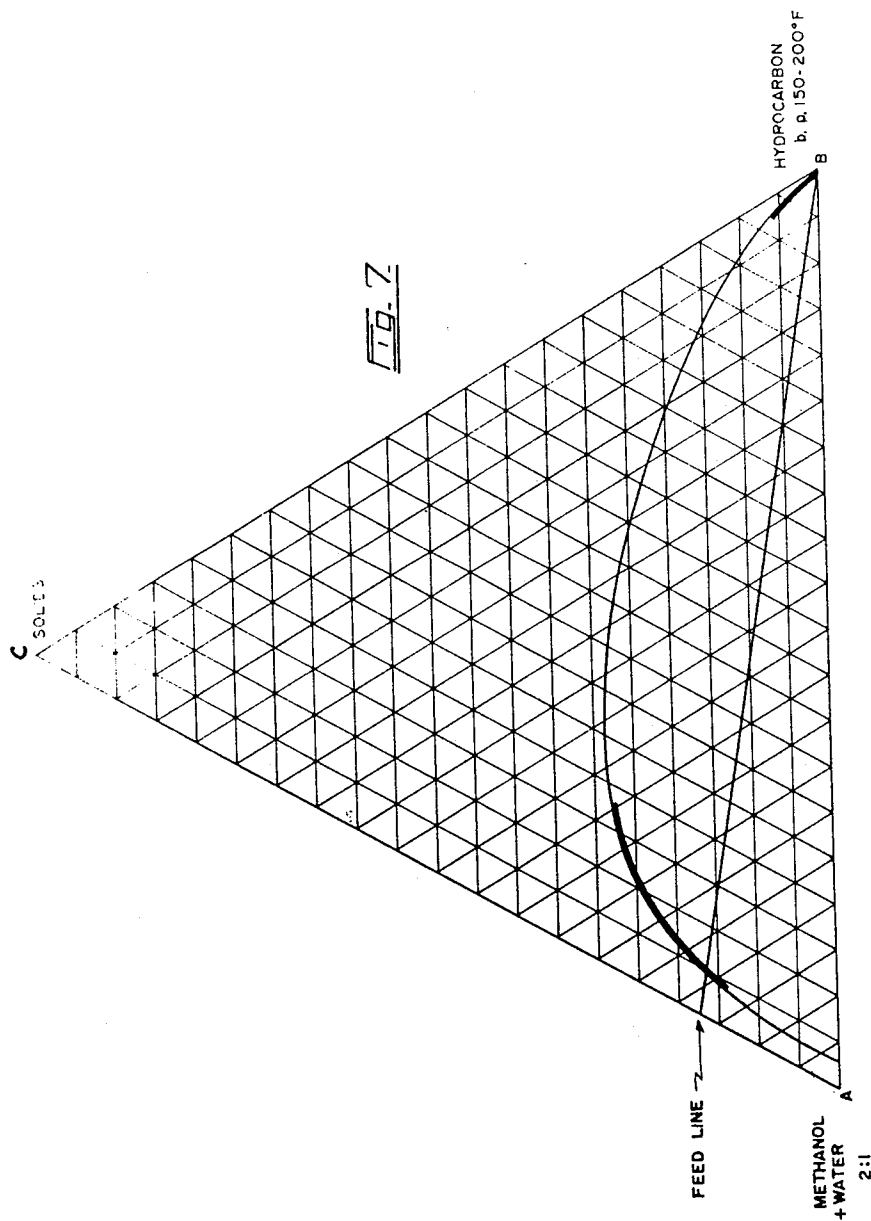
D. L. MITCHELL ET AL

3,803,114

PROCESS FOR PRODUCING UNSAPONIFIABLES-FREE TALL OIL PRODUCTS

Filed March 10, 1972

16 Sheets-Sheet 7



April 9, 1974

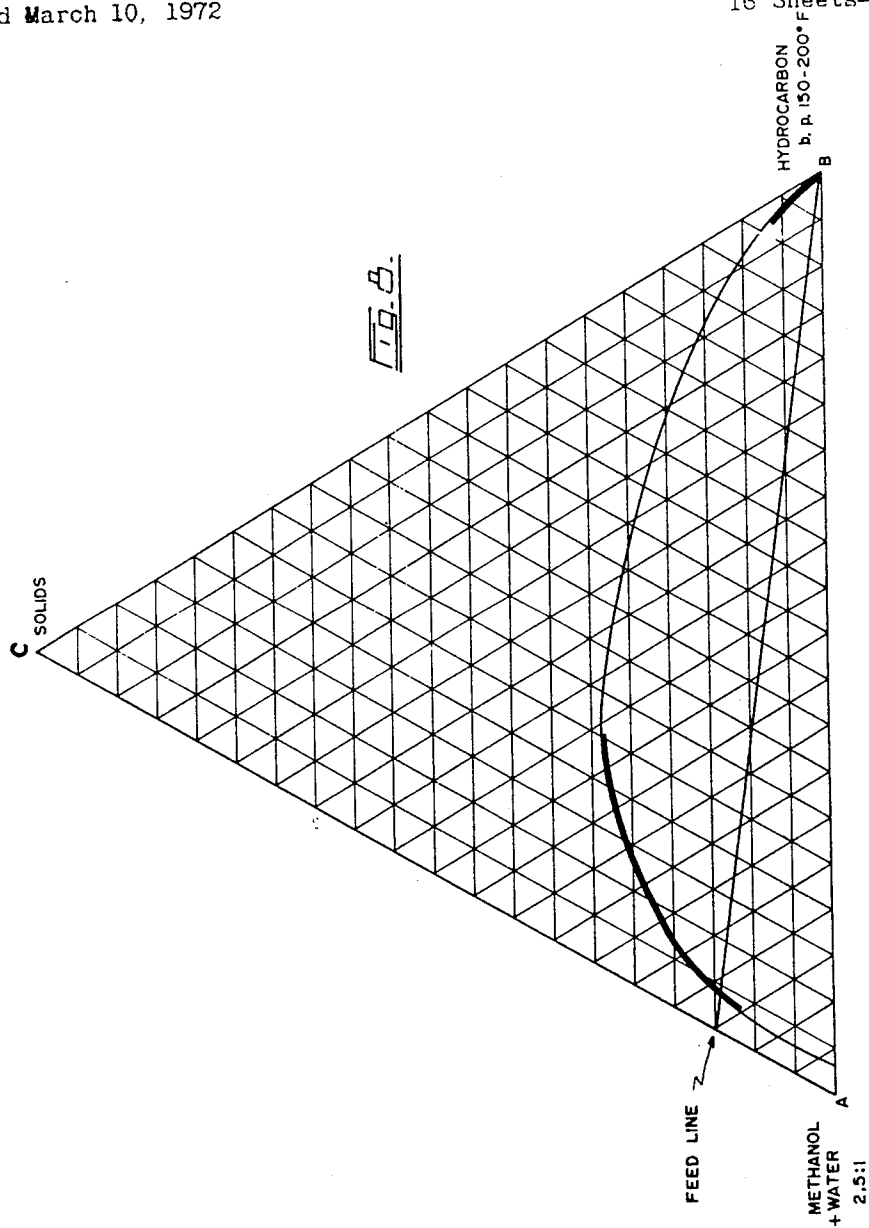
D. L. MITCHELL ET AL

3,803,114

PROCESS FOR PRODUCING UNSAPONIFIABLES-FREE TALL OIL PRODUCTS

Filed March 10, 1972

16 Sheets-Sheet 8



April 9, 1974

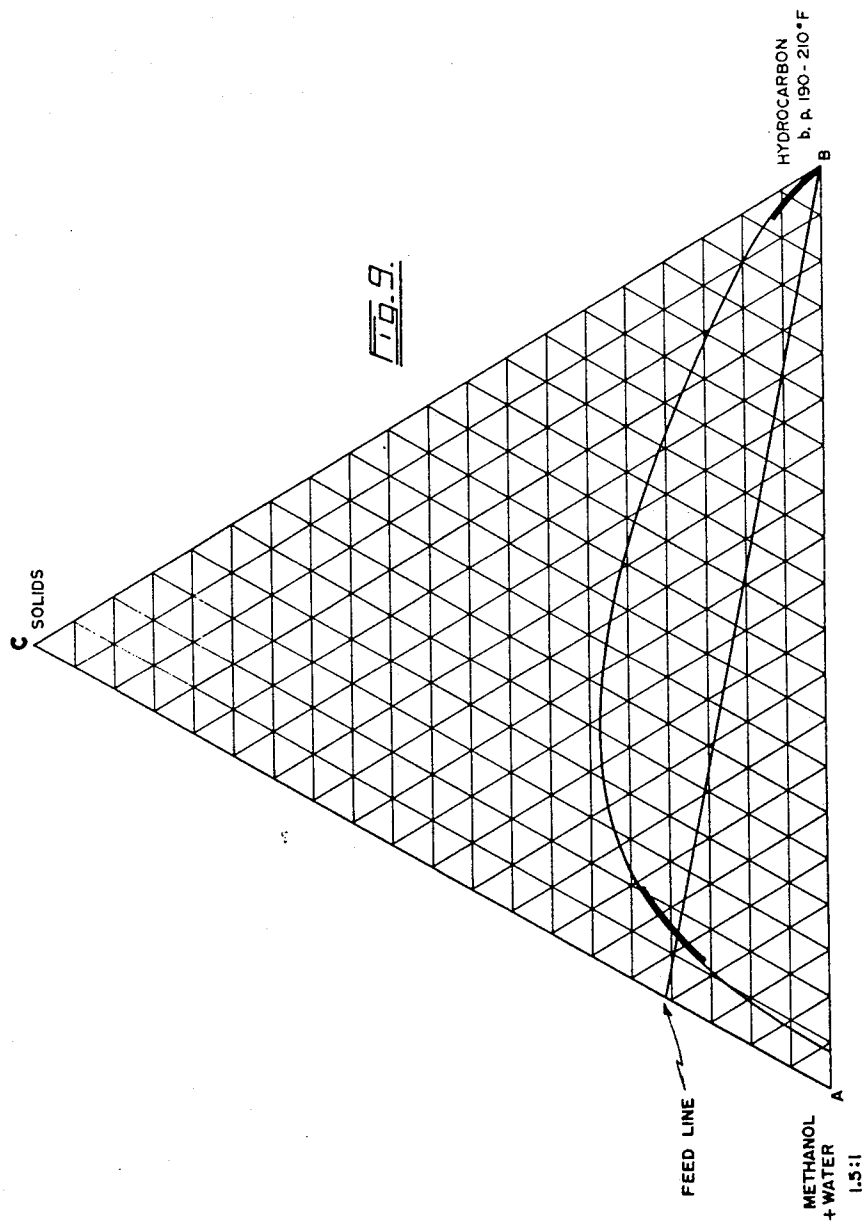
D. L. MITCHELL ET AL

3,803,114

PROCESS FOR PRODUCING UNSAPONIFIABLES-FREE TALL OIL PRODUCTS

Filed March 10, 1972

16 Sheets-Sheet 3



April 9, 1974

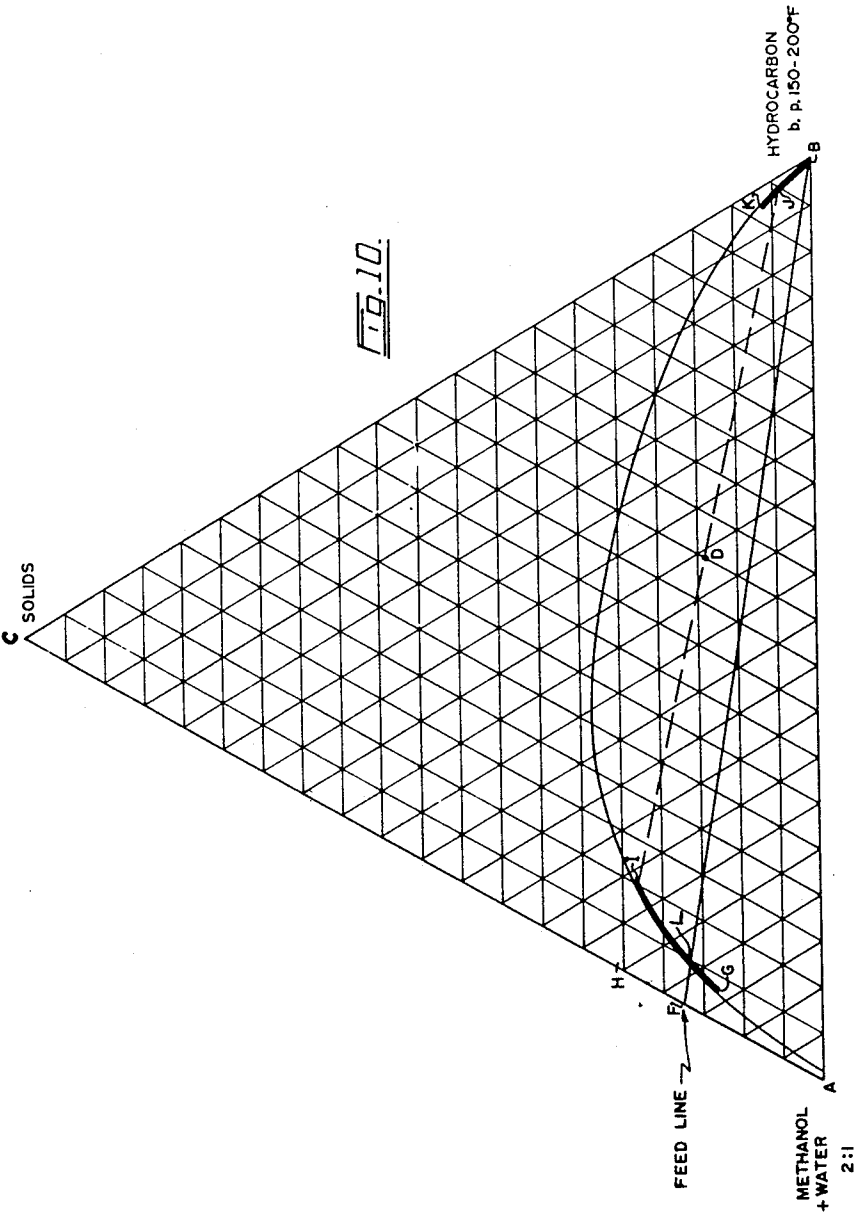
D. L. MITCHELL ET AL

3,803,114

PROCESS FOR PRODUCING UNSAPONIFIABLES-FREE TALL OIL PRODUCTS

Filed March 10, 1972

16 Sheets-Sheet 10



April 9, 1974

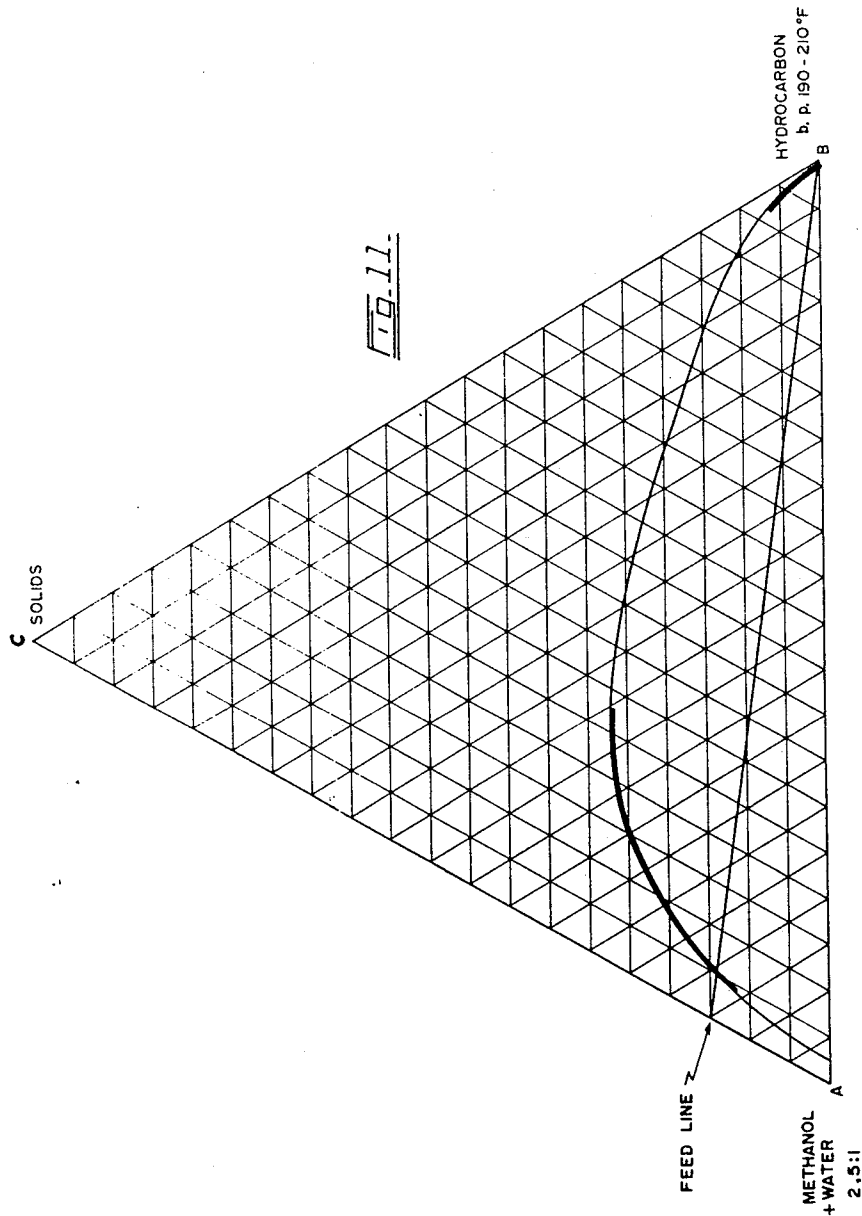
D. L. MITCHELL ET AL.

3,803,114

PROCESS FOR PRODUCING UNSAPONIFIABLES-FREE TALL OIL PRODUCTS

Filed March 10, 1972

16 Sheets-Sheet 11



April 9, 1974

D. L. MITCHELL ET AL

3,803,114

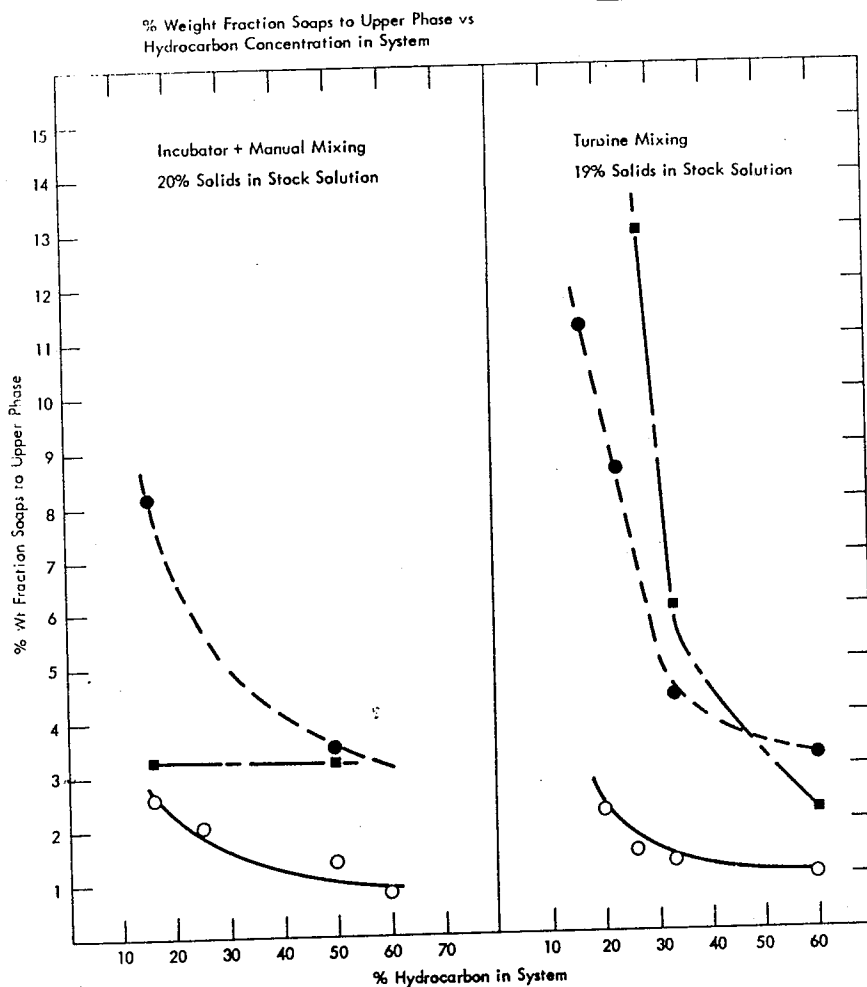
PROCESS FOR PRODUCING UNSAPONIFIABLES-FREE TALL OIL PRODUCTS

Filed March 10, 1972

16 Sheets-Sheet 12

Fig. 13.

Fig. 12.



April 9, 1974

D. L. MITCHELL ET AL

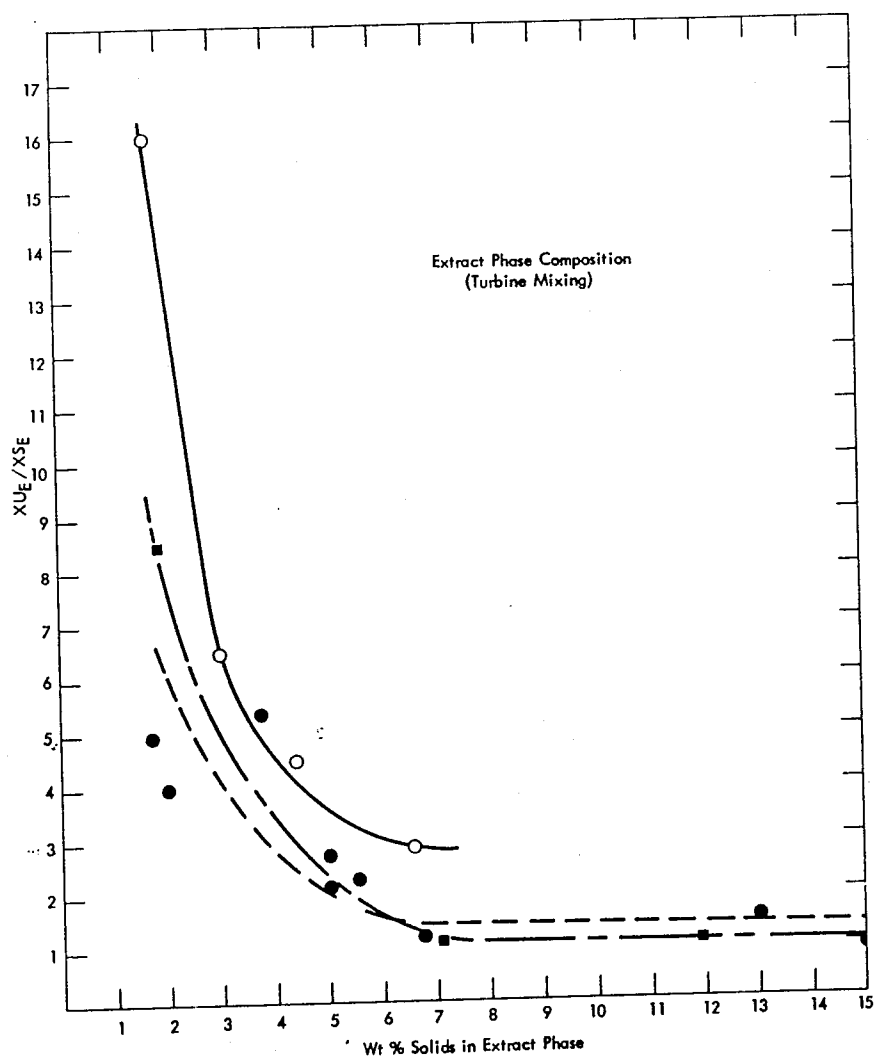
3,803,114

PROCESS FOR PRODUCING UNSAPONIFIABLES-FREE TALL OIL PRODUCTS

Filed March 10, 1972

16 Sheets-Sheet 13

Fig. 12-1.



April 9, 1974

D. L. MITCHELL ET AL

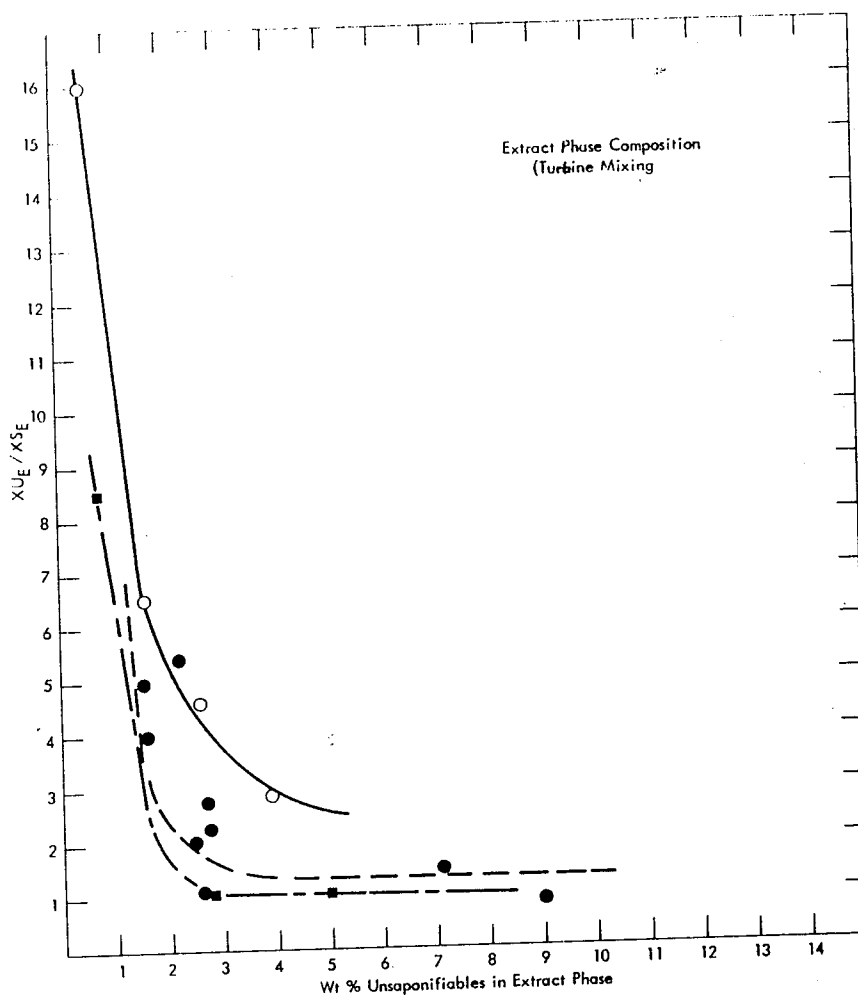
3,803,114

PROCESS FOR PRODUCING UNSAPONIFIABLES-FREE TALL OIL PRODUCTS

Filed March 10, 1972

16 Sheets-Sheet 14

Fig. 12-2.



April 9, 1974

D. L. MITCHELL ET AL

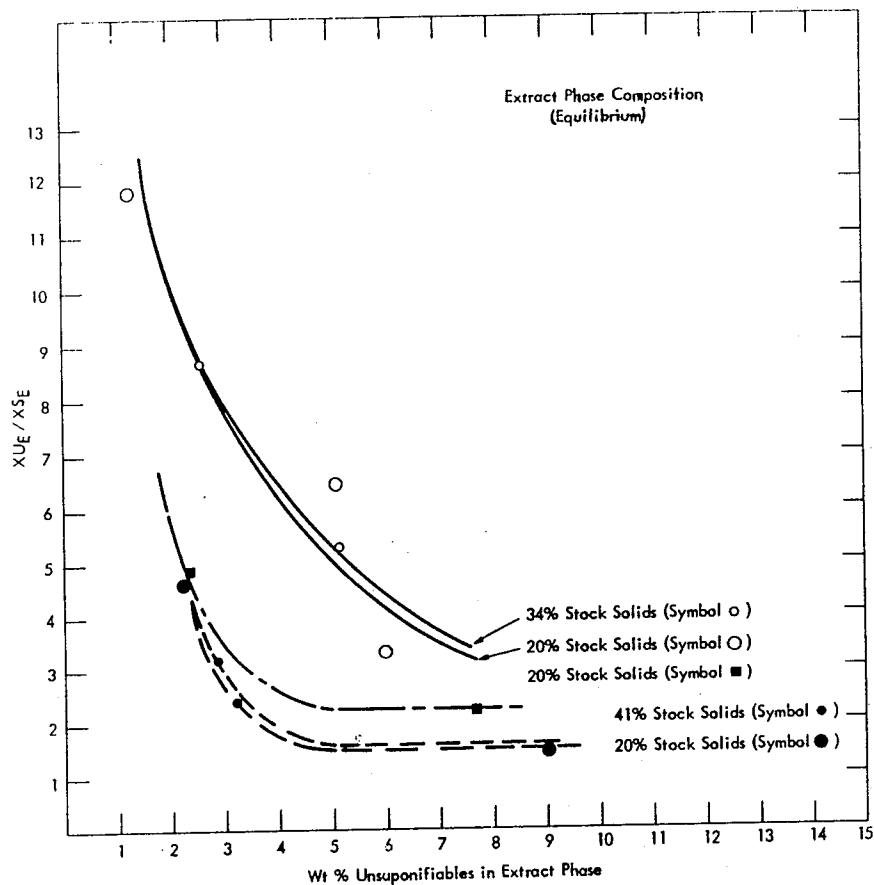
3,803,114

PROCESS FOR PRODUCING UNSAPONIFIABLES-FREE TALL OIL PRODUCTS

Filed March 10, 1972

16 Sheets-Sheet 16

Fig. 13-1



April 9, 1974

D. L. MITCHELL ET AL

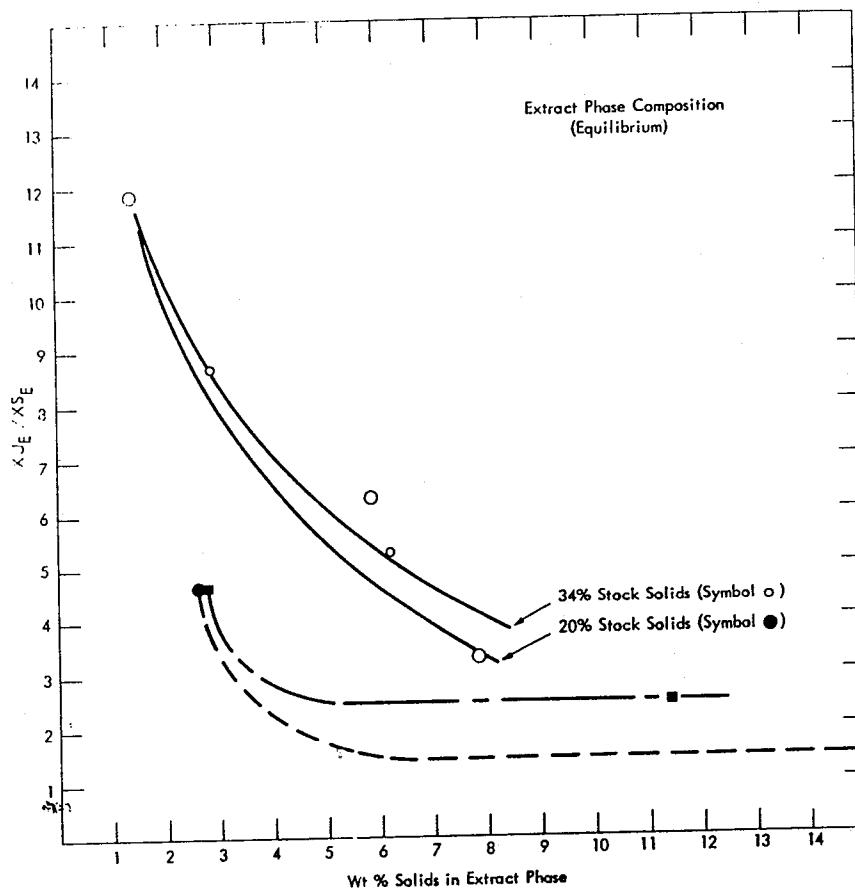
3,803,114

PROCESS FOR PRODUCING UNSAPONIFIABLES-FREE TALL OIL PRODUCTS

Filed March 10, 1972

16 Sheets-Sheet 16

Fig. 13-2



1

3,803,114

PROCESS FOR PRODUCING UNSAPONIFIABLES-FREE TALL OIL PRODUCTS

David Lawrence Mitchell and Frans Greebe, Edmonton, Alberta, and David Arthur Redford, Fort Saskatchewan, Alberta, Canada, assignors to St. Regis Paper Company, New York, N.Y.

Filed Mar. 10, 1972, Ser. No. 233,449

Int. Cl. C09f 1/04

U.S. Cl. 260-97.7

1 Claim

ABSTRACT OF THE DISCLOSURE

Crude soap skimmings, from the Kraft pulp process, are up-graded by removing contained unsaponifiabiles. This is done by admixing the skimmings with water and a demulsifying alcohol (e.g. methanol), clarifying the mixture, and containing the clarified solution with a hydrocarbon (e.g. heptane) whereby the unsaponifiabiles are extracted into the hydrocarbon phase. The composition of the extraction feed is controlled to ensure that substantially all the unsaponifiabiles are extracted while only a very small amount of the soaps report in the hydrocarbon phase. The raffinate is then distilled to recover the alcohol.

BACKGROUND OF THE INVENTION

This invention relates to a process for producing up-graded soap solution from Kraft pulp process soap skimmings. The enriched solution contains fatty and resin acid soaps, but has had the normally present unsaponifiabiles content substantially removed during processing. The product solution finds use as a high quality feed-stock from which crude and refined tall oil products can be made.

Soap skimmings are a by-product of the well known Kraft process. This process is used to produce wood pulp from woods which contain resinous constituents known as wood extractives. Woods especially abundant in these extractives are the various species of pine, balsam, cedar, larch and some species of spruce and hemlock.

The Kraft (or sulphate) process involves cooking wood chips. This is done at elevated temperature and pressure in dilute alkaline liquors which contain sodium hydroxide and sodium sulphide as the active ingredients. Cooking effects cellular breakdown and dissolution of the lignin, wood extractives and hemicelluloses. Additionally, it renders the cellulose in a dispersed, fibrous form which can be separated by filtration. The spent cooking liquor (known as "black liquor") is separated and concentrated to a solids content suitable for combustion in a recovery furnace (about 60-70% soluble solids). Concentration is carried out by passing the black liquor through a series of multiple-effect evaporators. After several stages (30% soluble solids content), a portion of the solids, known as crude sulphate soaps, becomes insoluble. At this point, the black liquor is transferred to a holding tank and these soaps are skimmed off and recovered. The skimmings consist of a mixture of solids material (50-70%) associated with an entrained liquid portion (30-50%).

The soap skimmings when diluted with water give a product which usually comprises:

as solids:

- suspended fibres
- insoluble sodium salts (organic and inorganic)
- some lignin

in solution:

- water
- some lignin
- fatty and resin acid sodium soaps unsaponifiabiles
- odor bodies (such as mercaptans and disulphides)
- color bodies (principally sodium soaps of oxidized resin acids and oxidized unsaponifiabiles)

2

Typical soap skimmings from Alberta, Canada and North American west coast mills would have the compositions given in Table I.

TABLE I
[Composition of soap skimmings]

Constituent	Percent by weight	
	Alberta	West coast
Sodium salts of fatty and resin acids.....	43	38
Unsaponifiabiles.....	10	15
Moisture and low molecular weight volatiles.....	35-40	37
Lignin, cellulose, inorganic salts.....	7-12	10

The soap skimmings are usually treated to produce crude tall oil; this product may be further refined to produce the distilled fractions of tall oil.

The first step in this treatment involves reacting the skimmings with sulphuric acid. Hydrogen ions substitute for the sodium ions to convert the soaps to fatty and resin acids. The products of acidulation separate into three layers in a batch reactor. The top layer is referred to as the crude tall oil layer. Its main constituents comprise fatty acids, resin acids, unsaponifiabiles and esters. Small amounts of suspended solids and water are also present in this layer. The second or intermediate layer is called the lignin layer. It contains the bulk of the lignin and insoluble non-soap solids which were originally present in the skimmings. The bottom layer is mainly made up of sodium sulphate and water.

The crude tall oil is drawn off and can be sold as such or can be further refined by fractional distillation. Typical compositions of "northern" (made from woods grown in Canada and the northern United States) and "southern" (made from woods grown in the southern United States) crude tall oils are shown in Table II.

TABLE II

[Analysis and characteristics of northern and southern tall oils]

	Percent by weight	
	Northern	Southern
Fatty acids.....	47-52	45-55
Resin acids.....	28-30	40-50
Unsaponifiabiles.....	19-21	5-8
Moisture.....	1-2	-----
Acid number.....	130-135	160-175

It will be noted that tall oils are characterized by their "acid number." This is simply a quantitative measure of the concentration of constituents present in the oil that possess acidic groups. More specifically, it is the number of milligrams of KOH required to neutralize one gram of the oil.

The crude tall oil is a dark brown, viscous, opaque liquid possessing an offensive odor. The dark color originates from traces of occluded black liquor and oxidized resin acids. Insoluble inorganic salts and short lengths of cellulose fibre product the opacity. (The Gardner Number serves as an industry measure of the color qualities of the material.) Kraft sulphurous products, hydrogen sulphide, organic sulphides and disulphides generate the unpleasant odor.

In this crude state, the applications of crude tall oil are limited to uses where color and odor are not very important. In addition to the limited applicability of the crude tall oils in general, northern crude tall oil suffers from an even greater disadvantage of applicability because of the proportionately higher unsaponifiabiles content; these constituents produce a plasticizing effect on certain formulations using crude tall oil.

For most applications, it is necessary to upgrade the crude tall oil. This is done by substantially eliminating color and odor bodies and also by separating the blend of acids into concentrated fractions of which fatty and

resin acids constitute the products of economic importance. Upgrading is normally done by distillation.

Distillation involves flashing the crude tall oil at 160°–260° C. and at a pressure of 1–10 mm. Hg. The volatile constituents are vaporized and leave behind a residue. The residue contains the occluded fibres, insoluble salts, suspended solids and lignin. In an idealized distillation, starting with a feed stock of low unsaponifiables content, the vapors would be fractionated into six product streams as follows:

- (1) Gases (water, sulphides, disulphides);
- (2) Heads (low molecular weight (C16) fatty acids and unsaponifiables);
- (3) A main fatty acid fraction (C18 chain acids);
- (4) A distilled tall oil fraction (C20 chain acids blended with some C20 ring acids);
- (5) A resin acid fraction (C20 ring acids); and
- (6) Pitch, containing esters, sterols and polymerization products.

It should be noted that the prior art distillation is carried out under acidic conditions.

Through these operations, the bulk of the undesirable insoluble suspended solids present in the soap skimmings have been removed. Additional insoluble suspended solids generated by the acidulation process have been further removed during acidulation or during the subsequent operation of flashing the crude tall oil prior to fractional distillation.

Returning again to Table II, it will be seen that the main difference, in terms of chemical composition, between the northern and southern crude tall oils is the amount of contained unsaponifiables. It is apparent that the extent of unsaponifiables content is governed by the species and geographic origin of the wood involved.

Unsaponifiables can be generally described as a class of organic compounds which do not contain a saponifiable group (such as carboxyl, thiolate or sulphonate). More specifically, FIG. 2 shows a breakdown of the unsaponifiables contained in a typical Alberta soap skimmings. These compounds can be divided into three general groups:

- (1) High molecular weight alcohols such as diterpene (C20) alcohols, linear (C20–C26) alcohols and sterols;
- (2) Diterpene aldehydes and ketones; and
- (3) Hhydrocarbons and triterpenes.

It will be noted that approximately $\frac{1}{2}$ of the unsaponifiables are made up of a complex combination of alcohols.

In comparison, tall oils originating from the southern United States differ in their unsaponifiables constituent composition both in kind and degree. Their major unsaponifiable constituents are the sterols and hydrocarbons; diterpene alcohols and diterpene aldehydes and ketones are not present as major constituents. The substantially decreased content of diterpene alcohols, aldehydes and ketones results in considerably different distillation characteristics and distillation products.

The presence of unsaponifiables is undesirable in both crude and refined tall oil products. This is particularly a problem when large amounts of unsaponifiables are present, as in the case of northern feeds. In the case of crude tall oil, unsaponifiables dilute the acid content resulting in products of low acid number. In the case of using northern crude tall oils for distillation feed-stock, various problems result in the distillation step and in the color quality and acid number of the distilled products. These characteristics may affect the marketability of northern crude tall oil destined for distillation feed-stock.

The tall oil industry has adapted itself to getting along with products having small amounts of unsaponifiables; however, it penalizes or refuses to use high unsaponifiables content products such as are obtained from northern woods.

The following examples will illustrate the difficulties in using northern crude tall oil either as a crude product or as a feed-stock for a distillation operation.

In limited operations, crude tall oil may be used as an ingredient in inexpensive, low quality paint, particularly where dark colored products are not considered a disadvantage. Such formulations are usually based on the acid number or acid content of the crude tall oil. It is common for paint manufacturers to require crude tall oil having an acid number greater than 160; a typical northern crude tall oil will only have an acid number of about 130.

The major proportion of available crude tall oil is utilized in subsequent refining processes of which fractional distillation is the most important and the most common. Northern crude tall oils are considered poor feed-stocks for such refining operations because of their contained unsaponifiables constituents. These tall oils have unsatisfactory distillation yields and the quality of the distillates is inferior to that produced by southern tall oils, particularly with respect to unsaponifiables content in distillants. These disadvantages come about in two ways. Firstly, the acids and hydroxyl containing unsaponifiables (alcohols) react with each other, particularly at elevated temperatures, to form esters. Most of these esters have sufficiently high molecular weights to be non-volatile and report in the pitch fraction during distillation and are subsequently lost. The acid content of the esters is also, of course, lost. Secondly, during distillation of northern tall oils the more volatile unsaponifiables compounds tend to be carried over with the acid fraction because the vapor pressures of the diterpene alcohols and aldehydes are very close to those of the fatty acids and resin acids. In this respect, the distillation characteristics differ from the southern tall oils. As a result, the volatile diterpene alcohols and aldehydes dilute or contaminate the separate acid streams, thus defeating, to some extent, the purpose of the distillation. Since ester formation is time dependent, the distiller could increase the distillation temperature and feed rate through the tower to reduce the esterification. However, in doing so, he will increase the carry-over of volatile unsaponifiables into the acid fractions. Consequently the distilled products will be substantially contaminated with non-acid constituents which may penalize the value of the products.

These problems facing the distiller are so serious that many northern crude tall oils cannot be fractionated on a paying basis because of the yields obtained and also because of the quality of the distillation products derived.

To sum up the foregoing, a northern pulp manufacturer produces a soap skimmings product which has an undesirably high unsaponifiables content. He suffers penalties if he sells the product in crude tall oil form. He finds that the fractionation procedures, which were originally developed for southern-type materials, are not usually applicable to his product.

One answer to all of these problems would be to remove the unsaponifiables from the soap skimmings.

Unsaponifiables have hydrophobic properties and are soluble in certain organic solvents. It had long been suspected that low molecular weight hydrocarbons, such as hexane and heptane, could be used to extract them from aqueous solutions. The unsaponifiables are preferentially soluble in the hydrocarbons and they, in turn, are substantially immiscible in the soap solution. However, there was a serious problem which prevented useful application of this knowledge. When the aqueous soap solution and the hydrocarbon were mixed together, they would form a very stable emulsion.

The problem of emulsification was solved by Christenson and Gloyer. Their solution was described in U.S. Pat. No. 2,530,809. Basically, they taught that certain alcohols would act as de-emulsifiers if provided in a water-soap skimmings-hydrocarbon system. They also taught operative ranges of composition which, if observed, would result in rapid phase separation. In other words, if water, soap skimmings, alcohol and hydrocarbon were shaken up together, the unsaponifiables would be extracted by

the hydrocarbon and, when the mixture was allowed to stand, the components would quickly separate into a lower phase, consisting mainly of soap-water-alcohol, and an upper phase consisting mainly of hydrocarbon and unsaponifiables. They further taught that the quantities of sodium soaps which did become dissolved in the upper phase could be removed by a subsequent operation of washing with water.

The process taught by Christenson and Gloyer was directed to the recovery of unsaponifiables as a source of sterols, useful in the drug industry. Although the patentees recognized that the removal of unsaponifiables would enhance acid yields from soap skimmings, they did not teach an industrially operative process for accomplishing this end.

The present invention is directed to providing such a process.

SUMMARY OF THE INVENTION

It is an object of this invention to provide a process for removing substantially all of the unsaponifiables and insoluble, non-soap solids from soap skimmings to produce a purified soap solution. The product solution should be a high quality feed-stock. Crude tall oil and distilled products made from it should be substantially free of unsaponifiables and should be characterized by high acid numbers and improved color characteristics.

It is another object to provide a process, the practice of which will result in improved yields of fatty and resin acids, in the form of distillation products, from soap skimmings.

It is another object to provide a soaps upgrading process, involving solvent extraction of unsaponifiables and alcohol recovery, which is carried out under alkaline conditions.

It is another object to provide a soaps upgrading process involving solvent extraction of unsaponifiables wherein washing of the extract fraction to recover dissolved soaps is not necessary.

It is another object to provide a soaps upgrading process, involving separation of suspended solids and sterols, wherein the solids and sterols are recovered in the form of a filter cake. This cake forms a preferable feed-stock for the production of phytosterols.

It is another object to provide a soaps upgrading process involving separation of undissolved solids wherein these solids are recovered as a hydrocarbon-wetted floc under two phase formation which minimizes emulsion formation and recovers an extractable portion in undegraded form.

It is another object to provide a soaps upgrading process, involving alcohol recovery by distillation, which is conducted in a manner to avoid foaming, fouling and plugging in the distillation column.

These and other objects of the invention will be apparent from consideration of the following specification and appended drawings.

In accordance with the invention, the following steps and limitations are employed:

Firstly, crude soap skimmings are admixed with water and a de-emulsifying alcohol to form a mixture comprising a soap solution, dissolved unsaponifiables and undissolved solids.

Secondly, the mixture is preferably treated to remove substantially all its undissolved solids. This may be done by mixing the mixture with hydrocarbon and allowing the product to settle to form an upper hydrocarbon phase and a lower soap solution phase. The undissolved solids report in the hydrocarbon phase as a hydrocarbon-wetted floc layer. This phase can be drawn off to leave a clarified soap solution.

Thirdly, the clarified soap solution is contacted with sufficient hydrocarbon to extract substantially all the unsaponifiables present therein.

Suitable alcohols and hydrocarbons are known from the prior art. We have found methanol, ethanol, n-propanol and isopropanol and mixtures thereof particularly suitable as the de-emulsifying alcohol. Methanol is preferred. Hexane, heptane and petroleum cuts containing one or both of them as major constituents are particularly suitable for use as the hydrocarbon solvent. Heptane is preferred. These hydrocarbons are solvents for the unsaponifiables, are stable in alkaline conditions and are substantially immiscible in the soap solution.

The composition of the soap solution fed into the extraction vessel, the extent of dilution therein with hydrocarbon and the composition of the distillation feed will preferably be controlled by the following limitations:

(a) Two phase separation of the soap solution and hydrocarbon must take place relatively quickly. This can be tested by placing a representative mixture in a laboratory separation funnel, shaking it manually for 10 minutes and allowing it to stand. If substantially complete separation occurs within 6 minutes the composition meets this requirement. U.S. Pat. No. 2,530,809 teaches systems in accordance with this requirement;

(b) The dissolved solids content in the extraction feed should be restricted to minimize retention of unsaponifiables in the raffinate phase. In other words, dissolved solids content should be less than a predetermined maximum amount. This maximum amount is that amount which will result in a raffinate having an exhaustively extracted acid number of 174, as arrived at by the following test:

Dilute a sample of the feed with hydrocarbon in the proportion which is to be used in the process; shake this mixture in a laboratory separation funnel to reach a single stage equilibration; draw off the hydrocarbon phase; repeat the procedure to take a total of six cross-current extractions. If the acid number of the raffinate phase is equal to or greater than about 174, then the dissolved solids content in the clarified soap solution is equal to or less than the preferred maximum permissible amount;

(c) The extraction feed composition and hydrocarbon dilution should be selected to ensure that the extract stream from the decanter and/or extraction vessel contains less than about 5.5% by weight dissolved solids;

(d) The ratio of dry, unsaponifiables-free solids to water in the feed to the distillation tower should be greater than about 3:7 so as to help prevent uncontrollable foaming therein.

Fourthly, the raffinate is distilled, preferably under alkaline conditions, to recover alcohol. The end product soap solution is substantially free of unsaponifiables and undissolved solids. It comprises a high quality feed-stock which may be acidulated to make superior crude tall oil.

Now, a number of the foregoing features require amplification:

Clarification of the soap solution prior to solvent extraction is important to the process. If the undissolved solids are not removed, plugging and fouling of the extraction tower, alcohol recovery tower and heat exchangers will occur. Additionally, clarification aids subsequent acidulation by removing a portion of the solids which would appear at the intermediate acidulation layer.

Exercising control of the dissolved solids in the extraction feed is a preferred feature. We have found that a high solids content results in large amounts of unsaponifiables being retained in the raffinate. By restricting solids content, a raffinate can be produced which, when acidulated, will have a desirable acid number (such as 174 or greater). The raffinate should have an acid number greater than about 174, otherwise the process is impractical.

Exercising control of the amount of solids dissolved in the extract phase is another preferred feature. This is done by carefully choosing the extraction feed composition. If the solids content in the extract phase is kept below about 5.5 percent by weight, dissolution of soaps in that phase is kept to a negligible amount. If the solids

content is allowed to exceed 5.5%, substantial dissolution of soaps in that phase will begin to take place. As a result, soap recoveries will decrease. Reclaiming of the lost soaps from the extract phase may then become an undesirable necessity.

Alkaline distillation of the clarified soap solution to recover alcohol is another preferred feature. We have found that foaming, which is the main stumbling block to distilling a soap solution, can be operatively controlled in a simple fashion. This is done by maintaining a minimum dry, unsaponifiables-free solids to water ratio in the feed to the distillation tower and by minimizing vapor velocities in the stripping section by pre-concentrating the distillation feed. These antifoaming measures are preferred features of the process.

Distillation is preferably carried out under alkaline conditions to avoid secondary recovery problems. If the soap solution is acidulated before alcohol recovery, dissolved lignins in the system become insoluble. These lignins cause serious fouling problems in the alcohol recovery tower and associated heat exchangers. The undissolved lignin would, therefore, have to be removed from the system before distillation. This lignin contains entrapped tall oil, alcohol and hydrocarbon. It would be necessary to salvage these by secondary recovery. In addition, noxious gases such as H_2S , CO_2 and mercaptans would be generated during acidulation. They may also appear in the distillation column. These gases are corrosive and may require use of special construction materials. Additionally, they have to be vented from the acidulation and distillation column. This results in a concomitant loss of alcohol and hydrocarbon which may have to be reclaimed by secondary recovery.

DESCRIPTION OF THE DRAWINGS

In the drawings:

FIG. 1 is a flow diagram of the process;

FIG. 2 is a schematic representation of the constituents which makeup the unsaponifiables in an Alberta soap skimmings;

FIG. 3 is a triangular coordinate phase diagram based on the data of Table 3A;

FIG. 4 is a triangular coordinate phase diagram based on the data of Table 4A;

FIG. 5 is a triangular coordinate phase diagram based on the data of Table 5A;

FIG. 6 is a triangular coordinate phase diagram based on the data of Table 6A;

FIG. 7 is a triangular coordinate phase diagram based on the data of Table 7A;

FIG. 8 is a triangular coordinate phase diagram based on the data of Table 8A;

FIG. 9 is a triangular coordinate phase diagram based on the data of Table 9A;

FIG. 10 is a triangular coordinate phase diagram based on the data of Table 10A;

FIG. 11 is a triangular coordinate phase diagram based on the data of Table 11A;

FIG. 12 is a plot showing the changes in amount of soaps which go to the upper phase during extractions with varying amounts of hydrocarbon. Three hydrocarbons were used: heptane (—x—x— curve), 150–200° F. refinery fraction (—●—●— curve), and 190–210° F. refinery fraction (—■—■— curve). High shear mixing was used;

FIG. 12-1 plots percent solids in the extract phase against the weight ratio of the unsaponifiables in the extract phase and the soap in the extract phase;

FIG. 12-2 is the same as FIG. 12-1 except that percent unsaponifiables in the extract phase is plotted. All the FIG. 12 curves are based on the data of Table 12A;

FIGS. 13, 13-1 and 13-2 are similar to FIGS. 12, 12-1 and 12-2 except that manual mixing was used. These figures are based on the data of Tables 13A, 13B and 13C.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The above mentioned limitations can be best understood and justified using triangular phase diagrams.

In our phase diagrams, we have plotted alcohol plus water, hydrocarbon and dry total solids. The semi-circular curve on each diagram divides the system into those compositions which would exist as a single phase (above the curve) from those compositions which would separate into two phases (beneath the curve). The curves have been developed by equilibrating a sample of a particular composition in a separatory funnel. The mixture was allowed to stand for 30 minutes and the extract and raffinate phases were subsequently analyzed. The compositions of the raffinate phases were plotted to provide the left hand side of the phase curve while the compositions of the extract phases were plotted to develop the right hand side. The line joining the raffinate, mixture and extract composition points is referred to as a "tie-line."

In FIG. 10, point D represents a composition of solids, hydrocarbon and aqueous alcohol phases in the mixture. This mixture separates into the two phases identified as points J and I on the phase diagram curve. A tie-line joins points I, D and J. The compositions of the two phases given by I and J represents the equilibrium composition of the two phase mixture. For example, if a system represented by point D contains 14% dry solids, 36% methanol-water and 50% by weight hydrocarbon, then the composition of the raffinate phase would be expressed as that given by point I on the phase diagram. This composition is solids 23%, methanol-water 67% and hydrocarbon 10%. The composition of the extract phase is given by point J on the phase diagram. This point has the following composition: solids 4%, methanol-water 1.5% and hydrocarbon 94.5%.

Not all compositions described under the phase diagram curve will give desirable systems for our process. As mentioned, systems which do not contain sufficient solids in the raffinate phase have a tendency to foam during subsequent alcohol recovery. Therefore a certain minimum solids content is desirable for operation of the alcohol recovery tower. Also, solids content in the system has a bearing on the degree to which the unsaponifiables are extracted during a multi-stage extraction operation. It has been found that systems containing a high solids content give extracted soaps which still contain some unsaponifiables. These soaps, upon acidulation, give undesirably low acid numbers. Turning now to the extract phase, we have also found that soap losses to that phase depend upon the percentage solids dissolved in it. Soap losses through solution into the extract phase are kept to a minimum when the solids content of the extract phase is kept below 5.5% by weight.

FIG. 10 has two portions of the curve darkened in with a thick, black line.

In accordance with the invention, in order to meet the requirements of the over-all process, any system (that is, composition of soaps, alcohol-water and hydrocarbon), when shaken in a separatory funnel to reach single stage equilibration, should have a tie-line whose ends lie in those portions of the curve described by the thick black lines. In other words, the composition of the raffinate phase, after single stage equilibrium, should be defined by any composition given by the thick black segment on the left hand portion of the diagram. Similarly, the composition of the extract phase, after single stage equilibrium, should be described by a composition given by the thick black line appearing at the right hand side of the diagram. All other tie lines that intersect the phase diagram at locations other than those given by the thick black lines will not give the preferred operating characteristics in the overall process.

How the thick black lines for a particular system are arrived at will be described hereinbelow.

The edge AC of the phase diagram of FIG. 10 represents a solution of crude soap solids dissolved in methanol and water. For example, point F represents a solution of 18% dry solids dissolved in methanol and water. If the solution at point F is diluted with hydrocarbon the line BF joining the 100% hydrocarbon apex to point F would describe all systems of varying degree of dilution. The line joining the 100% hydrocarbon apex to point F will be referred to hereafter as the feed line. It is desirable to use compositions which fall above the feed line in order to avoid foaming in the subsequent alcohol recovery step. This can best be described in the following manner. In order to avoid foaming in the alcohol recovery section, the distillation feed to the alcohol recovery tower should contain a dry dissolved solids to water ratio equal to or greater than about 3 to 7 to avoid uncontrollable foaming in the column. To put it another way, when all the alcohol and hydrocarbon in the raffinate has been removed, the unsaponifiables-free solids content of the solution should be greater than about 30%.

The extraction feed is made up of soaps and unsaponifiables but after exhaustive extraction the unsaponifiables are transferred into the extract phase. In an Alberta soap, the unsaponifiables constitute as much as 18% of the dry total solids. Therefore, in order to have an extracted soap possessing a dry, unsaponifiables-free, dissolved solids to water ratio of 3 to 7, it is necessary to have an extraction feed makeup containing sufficiently higher dissolved solids content to compensate for the percentage of the dry dissolved solids which are transferred as unsaponifiables during extraction. This would require an initial dry total solids content in the clarification feed to give a solids to water ratio of about 3.6-6.4. The preferred minimum dissolved solids content of any system is described by the feed line. Systems whose compositions either lie on or above this line will contain, after removal of their unsaponifiables constituents, dissolved solids to water ratio equal to or greater than 3 to 7. In single stage equilibrium such as would be obtained in a separatory funnel, such systems as described above will have a raffinate composition described by the left hand thick black line. The lower limit of the exhaustively extracted raffinate should contain dry dissolved solids to water in a ratio of 3 to 7. The upper limit of the exhaustively extracted raffinate is given in terms of acid number, of exhaustively extracted systems. As the dissolved solids content of the system is increased, the raffinate tends to retain unsaponifiables. Consequently, acidulation of the systems gives products of progressively lower acid number. There is an inverse relationship between the total dissolved solids content of the system and the acid number that can be obtained after six cross-current exhaustive extractions. As mentioned, it is desirable that the raffinate phase have an acid number equal to or greater than 174. Hence the upper limit limitations set in a single stage equilibrium would be given by point I on the left hand segment.

To summarize, the tie-line described by IDJ defines the system containing the highest solids content possible to give a soap solution composition I in equilibrium with extract of composition J in a single stage equilibrium reaction of the type carried out in a separatory funnel. If the solution of composition I is exhaustively extracted with further portions of hydrocarbon, the acid number of the derived tall oil will be 174. Therefore line IDJ defines the upper tie-line limit as set by an exhaustive extracted acid value of 174. All solids systems lying above line IDJ and toward apex C will of course have acid numbers after exhaustive extraction and acidulation that fall below a value of 174.

The point G is tied to a condition that occurs also after exhaustive extraction (that is, after six cross-current extractions). The dry solids to water ratio of point G should

be equal to or greater than 3 to 7. In order to obtain this minimum ratio after exhaustive extraction, an initial feed containing a solids content between compositions F and H should be used.

Turning now to the extract side of the diagram, the portion of line described by a solids content falling in the region of 0 to 5.5%, described by line BK, represents extracts which will contain suitable ratios of unsaponifiables to soaps. Selection of compositions which result in such extract solids contents will minimize the losses of soap to the extract phase.

Thus a box within the phase diagram can be constructed. It consists of the corners G, B, K, and I. The box G, B, K, I contains the compositions of dissolved solids, methanol-water and hydrocarbon systems which will conform to all the limitations described above. Thus for each system of hydrocarbon type, methanol to water ratio and soap type, a box of the type described can be constructed from the phase diagram.

We have prepared and included nine diagrams and supporting data tables which relate to selection of extraction feed composition. In each case, the soap skimmings used were obtained from a pulp mill in Hinton, Alberta, Canada. The diagrams (FIGS. 3 to 11 inclusive) and Tables 33A to 11A are based on experiments which involved three different methanol to water ratios, two different alcohols and three different hydrocarbons and, of course, variations in the proportions of the compositioned constituents, when equilibrated at 40° C.

Comparison of the figures and tables show that variation of the alcohol to water ratio has little effect on the results of extraction.

These same figures show that increases in extraction feed solids have the effect of increasing the solids in the extract phase. This leads to increases in the extract phase acid number, due to increased content of dissolved soaps. For example, in Table 3A, feed sample A has a solids content of 41.7%. Its extract and raffinate phase acid numbers are 17.9 and 152.5, respectively. Feed sample D, however, only has a solids content of 18.8%. Its extract and raffinate phase acid numbers are 5.5 and 162.9, respectively.

The said figures also illustrate that different hydrocarbons have different extraction selectivities. For example, comparison of the experiments labelled D in Tables 3A, 6A and 9A show that the two hydrocarbon blends tend to extract more soaps than n-heptane into the extract phase. The extract acid numbers vary between 5.5 and 22.6.

It will be appreciated that other soap sources will possibly require the construction of different phase diagrams and that the shape of the box as described therein may differ somewhat from these given herein. Also, the shape of the phase curve and the box described will be dependent on the temperature of the system. The major difference in the construction of different boxes will occur in describing the raffinate side heavy line. The length of this line is dependent upon the unsaponifiables content present in a particular soap and also upon the partition coefficients of the respective unsaponifiables present.

Turning now to the series 12 and 13 of the figures and tables, the effects of hydrocarbon selection, extent of hydrocarbon dilution and method of mixing are illustrated.

Dilution of the system with hydrocarbon had the effect of promoting selectivity of unsaponifiables extraction. This was particularly the case when at least a major portion of the solvent was n-heptane.

It will also be noted that soaps dissolution in the extract phase increased sharply when high energy input mixing of the composition took place before extraction. High energy mixing tended to promote emulsification. This had the consequence of trapping soaps in the extract phase. Again, n-heptane was a superior solvent as it was not as seriously affected by the type of mixing as were the other

hydrocarbons tested. Mixing should be carried out in a manner to minimize soaps retention in the extract phase. This could be done by contacting soap solution which is to be clarified with a liquid-contactor of the spray-tower type and using a gravity-operated column for extraction.

FIG. 12-1 plots percent solids in the extract phase against the weight ratio of the unsaponifiables in the extract phase and the soap in the extract phase. A high ratio is desirable since it means that most of the unsaponifiables and very few of the soaps are being extracted. It will be noted from the figure that there is a sharp increase in the tendency of the ratio to increase when the solids content in the extract phase is less than about 5.5%.

FIG. 13 plots the same type of data as FIG. 12-1. However in this case gentle mixing rather than high energy input mixing was used. A comparison shows that soap-water-alcohol-hydrocarbon systems which have low interfacial tension values, should be handled under conditions which do not introduce a high level of mechanical energy such as given by high shear mixing.

Let us turn now to a more detailed description of the process.

Preparation of feed

The de-emulsifying alcohols useful in the process are known from the teachings of Christenson and Gloyer. We have tested methyl, ethyl, propyl and isopropyl alcohols and blends thereof. We have found methyl alcohol to be superior to the others. Its use results in phase diagrams having larger areas giving two phase conditions. Additionally, use of methanol results in systems having longer tie-lines at moderate dissolved solids content. Therefore it is easier to get good final product acid numbers. Finally, methanol does not dissolve in the hydrocarbons to the same extent as do the other alcohols.

The hydrocarbon solvents are also known from the prior art. Good results may be obtained using refinery petroleum fractions containing blends of constituents boiling in the hexane-heptane region. Temperature cuts of such fractions can range from 150° to 200° F. and 190° to 210° F. A rough rule of thumb which may be used in selecting the solvent is that it should have a kauri-butanol value of about 32.

The moist soap skimmings usually are obtained from the pulp mill in the foam of a paste. This paste typically is made up of 55-65 percent by weight of dry total solids and the balance is water.

The moist soap is gently mixed with a pre-heated, three-component, two-phase stream made up of alcohol, water and hydrocarbon. Now, as mentioned, we have found that the system preferably should include methanol and heptane. A preferred feed composition for the clarification step using such components is as follows:

- (1) dry soap skimmings—20%
- (2) water—25%
- (3) methanol—55%
- (4) heptane—20% or more by weight of the mixture of 1+2+3.

The preferred temperature of operation of the extraction column is about 105° F. Depending on the temperature of the soap skimmings, the non-soap stream to the decanter may be pre-heated to give a decanter feed at about 105° F. We have found that solids separation in the decantation step is accelerated when the system is at elevated temperature.

Clarification

The blend is then fed into a decanter-type holding tank. In the tank, the mixture will separate into a lower soap phase and an upper hydrocarbon phase. At least a portion, and usually all, of the undissolved solids will appear in the upper phase as a flocculant, interfacial layer. Enough retention time should be allowed to enable substantially

all the undissolved solids to collect as stated. Usually about 40 minutes is ample.

The hydrocarbon and floc are taken from the tank as the overflow. The further treatment of this stream will be discussed hereinbelow.

The clarified soap solution is the feed which moves on into the solvent extraction column.

Solvent extraction

Solvent extraction will preferably be carried out counter-currently in a gravity-operated, perforated tray column. While this step can be carried out with either the light or heavy streams as the dispersed phase, we have found it best to have the soap solution as the dispersed phase.

The column should preferably operate as being equivalent to about six ideal extraction stages. We have checked the column performance in comparison to the results given by a simulated, laboratory countercurrent extraction of six ideal stages. The lab procedure followed is described in the textbook "Liquid Extraction," by R. E. Treybal, 2nd edition, at page 361 and references cited therein.

The mass flow rates through the tower will depend on the type of tower internals and will be limited by the flooding flow rates of the arrangement. We have successfully operated at 2 inch tower at a flow ratio of 1.5 hydrocarbon to 1 feed at rates up to 70% flooding and even higher.

Hydrocarbon recovery

The extract from the column will be treated for hydrocarbon recovery. This may be done by pumping it to elevated pressure, pre-heating the fraction, blending it with the overflow from the decanter, and then flashing the blend at atmospheric or sub-atmospheric pressure to liberate the hydrocarbon. The extract, which is free of suspended solids, will be heated to a high enough temperature so that, after combination with the overflow, it is hot enough to flash separate. Under most circumstances, a temperature of about 450° F. is suitable.

The vapor stream from the flash tank may advantageously be condensed by exchange of heat with the raffinate flowing from the extraction column to the alcohol recovery distillation tower. The raffinate is thus ready for partial vaporization, as will be discussed below. It is found that the amounts of heat available and required are usually close to balancing.

The bottoms product from the flash tank contains the unsaponifiables. They have not been degraded by heat. Therefore they are in excellent condition for further refining.

Alcohol recovery distillation

Turning now to the alcohol-rich raffinate from the extraction tower, it is distilled to recover the alcohol. We have successfully, continuously distilled the raffinate in an elongate glass column containing perforated trays equipped with downcomers. The column was provided with a thermal siphon-type reboiler and a phase separator at the feed point.

A portion of the feed, say about 50%, is vaporized in a pre-heater prior to entering the phase-separation section of the distillation tower. The vapors, chiefly comprised of alcohols, water and hydrocarbon, ascend into the rectifying section. The concentrated soap solution descends into the stripping section. This procedure will reduce the generation of gases in the stripping section and thereby help to minimize foaming there. Preferably, the raffinate will be pre-heated by the hydrocarbon vapors from the flashing step.

We have studied the foaming characteristics of the aqueous soap system using the ASTM Standard D-1173-53 (1965) test and also using lab batch distillations. These investigations indicated that substantial foaming

during distillation could be avoided if the dry, dissolved solids to water ratio in the distillation feed is equal to or greater than 3 to 7. This observation was confirmed by pilot plant operations.

The rectifying section of the tower should have about three or four theoretical stages. The stripping section should have about six theoretical stages.

Treatment of raffinate

The alcohol-free raffinate will be treated in accordance with the prior art. This will usually involve acidulation and, perhaps, fractional distillation to give refined products.

The invention will be better understood by reference to the following illustrative examples:

EXAMPLE NO. 1

This example involves producing crude tall oil using both the prior art and invention procedures. A comparison of the products is given.

A quantity of Hinton, Alberta, soaps paste was divided into two portions A and B. The soaps paste had the following compositions:

	Percent by weight
Sodium soaps of fatty and resin acids	43
Unsaponifiables	10
Moisture	35
Black liquor solids, fibre, inorganic salts	12

Portion A was admixed with pre-heated water and methanol to give a solution A' having the following make-up:

	Percent by weight
Dry soaps	20
Water plus black liquor solubles	25
Methanol	55

(Portion B was set aside to be directly acidulated for comparison purposes. This will be gone into below.)

300 pounds of solution A' were placed in a drum. The contents were stirred to give a thoroughly blended batch in which all of the soaps were dissolved.

The water used to make up solution A' had been pre-heated before blending to bring the temperature of the entire batch up to about 30° to 40° C. This was done as moderate heat improves the dissolution of the soaps and facilitates the separation of suspended solids in the subsequent decantation step.

150 pounds of pre-heated (30°-40° C.) heptane were mixed with solution A'. The heptane consisted almost entirely of n-heptane and had a boiling range of 203°-208° F. It had a kauri-butanol value of 32. The composition of the product mixture was:

	Percent by weight
Dry soaps	13
Water plus black liquor solubles	17
Methanol	37
Heptane	33

This mixture was allowed to settle and separate into two phases. The lower phase C comprised a clarified soap solution. The upper phase D comprised the heptane fraction; it contained the hydrocarbon-wetted insoluble solids in the form of a floc layer located at or about the interface of the two phases. Phase D also, of course, contained some unsaponifiables.

The soap phase C was drawn off.

The remaining heptane phase D was found to contain substantially all the undissolved solids originally in the mixture. It also contained about 3% by weight of the dissolved solids originally present. This 3% was made up of about 2.6% unsaponifiables and .4% soaps.

The clarified soap solution C had the following composition:

	Percent by weight
Dry soap	19.9
Water	21.9
Methanol	49.9
Heptane	8.3
Acid number:	153.

Soap solution C was fed into an extraction column for extraction with hydrocarbon. The column was a 2-inch diameter by 12-foot long glass column containing 28 perforated plates. Each plate was spaced 3 inches from its neighbor. It had 6 1/8 inch diameter perforations and a single downcomer of 3/8 inch diameter and 1 3/4 inch length. The column was jacketed and heated with hot water to keep the temperature within it at 105° F. Soap solution C was fed into the column at a point 2 feet below its top. Heptane, as previously described, was fed into the column at a point 30 inches above its bottom end. In this system, the solvent, heptane, was the continuous phase and the soap solution was the dispersed phase. A gravity loop in the line carrying raffinate from the tower provided control over the interface level, which was approximately 24 inches above the bottom of the column.

Soap solution C was fed into the column at 220 grams per minute. It was counter-currently extracted with pre-heated (40° C.) heptane which was fed in at 330 grams per minute. The column was operated at 70% of flooding.

Raffinate and extract fractions E and F were recovered, having the following compositions and acid numbers:

	Percent by weight	
Constituent	Raffinate E	Extract F
Dry solids	18.3	0.6
Water	22.4	0.6
Methanol	51.5	98.8
Heptane	8.0	
Acid number	178	>2

Extract F was fed into a single tube, all glass climbing film evaporator for recovery of solvent. The tube was 1 inch in diameter by 10 feet in length. It was jacketed and heated with steam at 30 p.s.i. The unit was operated at atmospheric pressure. The rate of feeding extract F was, of course, the rate at which it was produced from the extraction column. The product solution concentrate was recycled to the evaporator tube to obtain maximum heptane recovery.

The evaporator produced heptane condensate and an unsaponifiable product as a concentrate. The heptane condensate contained 99% heptane and about 1% methanol and water. The unsaponifiables product was not analyzed; however it had an acid number of about 2; this would indicate it was almost entirely made up of unsaponifiables.

The alcohol-containing raffinate E was then distilled in a column to recover alcohol. The column had a one inch diameter and was of the perforated tray, Oldershaw type. It had 30 trays in the stripping section and 30 trays in the rectifying section. The thermosyphon-type reboiler was designed to minimize possible foaming problems; its legs were attached to the column in a manner whereby the feed entered tangentially. The column was equipped with an overhead total condenser and a reflux divider of the oscillating funnel type. The feed section was provided with a preheater to vaporize about 50% of the feed. The liquid-vapor mixture entering the column was split in a phase-separator. The vapors ascended into the rectifying section while the concentrated soap solution descended into the stripping section.

Raffinate E was fed into the distillation column at rates varying from 2 to 6 cubic centimeters per minute. In accordance with this feed rate, the heat input to the feed pre-heater and the reboiler was adjusted to allow proper operation of the trays at a reboiler temperature of 98° C. to 100° C. The reflux ratio was adjusted to about 1 to 2 to 1 to 1.5 (product to reflux) to give a column top temperature of 62° C. to 62.5° C. This range of operating conditions gave products as follows:

Bottoms product G:	Percent by weight
Water	52-35
Methanol	0.0-0.4
Solids	48-65
Acid number: 177.	
Overhead product:	
Water	0.0-0.6
Methanol	83.4-87
Heptane	13-16

During distillation, excessive foaming did not cause any problems in the reboiler or in the column proper.

The recovered alcohol was recycled for mixture with portion A.

Table 14 provides data from a continuous run carried out as above for 17 hours after attaining distillation column equilibrium. This run demonstrated that products of consistent composition could be attained over long periods of time without uncontrollable foaming taking place.

Upon recovery, bottoms product G was acidulated. This involved stirring the soap solution G in a reactor with sufficient 10 normal sulphuric acid to bring the Ph to a value of about 4.0. During this period the contents of the reactor were maintained at 90° C. or higher. The contents were then allowed to settle. An extracted crude tall oil product H separated out as an oil layer. The lower aqueous phase was then drained off. Crude tall oil H was then washed with several changes of hot (90° C.) water to remove traces of lignin and inorganic salts. The oil was held at 90° C. or higher for several days to complete clarification.

Portion B, the aqueous crude soap solution mentioned at the beginning of this example, was also acidulated as above to produce a crude tall oil product I.

A comparison of the two crude tall oils follows:

	Crude tall oil (I)	Extracted crude tall oil (H)
Acid number	130-135	177-180
Saponification number	140-145	178.7-182.5
Resin acids, weight percent	28-30	36.3-42.0
Unsaponifiables, weight percent	19-21	2.2-3.3
Fatty acids, weight percent	47-52	52.5-60.5
Moisture, weight percent	1-2	1-2

EXAMPLE NO. 2

In this example, samples of prior art and extracted crude tall oil were distilled. The products of distillation are compared.

A batch of extracted crude tall oil was provided. It was obtained using the same procedure as described in Example No. 1 for product H. The batch had an acid number of 177 and an unsaponifiables content of 1.9% by weight. The batch was distilled using a Claisen distillation apparatus. No fractionation of volatiles was attempted. The following observations were noted:

(a) The heads fraction was virtually negligible with the first distillate appearing in the fatty acid region (160°-170° C. at 0.1 mm.);

(b) The fatty acids distilled as a pale yellow oil with Gardner values of 3-4;

(c) A pale resin fraction distilled over. It solidified upon cooling;

(d) Very little oily neutral product, following the resin acid fraction, appeared in the distillate;

(e) There was negligible decomposition or smoke produced during distillation;

(f) Some light boilers containing sulphur compounds collected in the cold trap.

Following are the data collected from the distillation experiment:

	Percent by weight		
	Run 1	Run 2	Run 3
Total distillation	86.6	94.0	89.7
Still residue	5.8	2.1	4.0
Losses and trap residue	7.6	3.9	5.7

A batch of crude tall oil, obtained using the same procedure as described in Example No. 1 for product I was provided. This batch was distilled as above. The following observations were noted:

(a) The distillate was collected over a boiling range of 115°-250° C. The first distillate appeared in the 115°-170° C. range. This product consisted primarily of a heads fraction (that is, a blend of lower molecular weight fatty acids (for example C16) and unsaponifiables);

(b) The boiling point and the viscosity of the distillate increased slowly, reaching a maximum around 200° C.;

(c) Decomposition occurred principally during the initial phases of the distillation, with the evolution of white smoke;

(d) Toward the end of the distillation, the viscosity of the product passed through a maximum value and a mobile, high boiling final product was obtained. This indicates decarboxylation was taking place.

Following are the data collected:

	Percent by weight	
	Run 4	Run 5
Total distillation	77.5	77.5
Still residue	19.6	17.0
Losses and trap residue	2.8	7.5

Following is a comparison of the products obtained in Runs 2 and 4:

	Distillate 2 (extracted)	Distillate 4 (not extracted)
Acid number	186.7	153.3
Unsaponifiables content, percent by weight	3.5	16.9
Gardner number	3-4	11

From the foregoing, the following observations can be made:

(1) Acid number values are greatly improved when the unsaponifiables are removed before distillation; and

(2) The practice of the invention produces a product having superior color qualities, as measured by Gardner number.

When the extracted distillate yield values are normalized to be equivalent to crude tall oil containing 19% unsaponifiables, a comparison yield figure of 76% for the extract method is calculated, while a distillate yield of 77.5% is obtained using the crude tall oil method. However, the latter distillate is heavily contaminated with volatile unsaponifiables. In other words, acid yields are improved by using the inventive process.

17 EXAMPLE NO. 3

In this example, extracted crude tall oil was solvent refined and fractionally distilled to produce end fractions having exceptionally good acid and Gardner numbers.

A batch of extracted crude tall oil (obtained using the same procedure as described in Example No. 1 for product H) was provided. The batch had an acid number of 182 and an unsaponifiables content of 1.4% by weight.

This batch was solvent refined by diluting it with a 20-fold excess of n-heptane to precipitate oxidized material, traces of lignin and moisture. The clarified solution was separated and the solvent recovered.

A 225-gram charge of the solvent-refined, extracted tall oil was then distilled in an all glass apparatus fitted with a 4 foot, electrically heated Vigreux column. The column was operated 10°–20° C. below the still-head temperature. Its reflux ratio was controlled by column and pot temperatures and was adjusted to be approximately 5 to 1.

A series of distillate fractions were collected. The first fraction consisted of a very small amount of a partly crystalline mixture of palmitic and 14-methylhexadecanoic acids. No heads fraction or preliminary decomposition was encountered.

The second fraction consisted of pale yellow fatty acids. This was followed by a liquid resin acid fraction and a resin acid fraction which solidified.

The following table shows the distillation conditions and results:

Fraction No.	Weight percent of charge	Bolling point, ° C.	Pressure, mm. Hg	Acid number	Gardner number
Charge	100			188	
Heads	0				
Fatty acids	28.0	164–170	0.2	198.4	1–2
Do	20.5	170–179	0.2	196.7	1–2
Do	9.8	175–185	0.2	167.1	1–2
Resin acids	16.1	190–200	0.2	172.4	
Do	13.0	>200	0.2	147.6	
Still residue	5.0				
Losses	8.0				

A center cut of the fatty and resin acids was redistilled to give the following results:

Fatty acids: Acid number—200; Gardner value—1.
Resin acids: Acid number—177.

EXAMPLE NO. 4

This example describes an alternative clarification step to the one described in Example No. 1. A comparison of products is given.

A soap paste, from Hinton, Alberta, whose composition was described in Example No. 1 was used for this example. The crude soap paste (60 g.) was shaken at room temperature, with methanol (120 g.), until the soluble soaps dissolved. The insoluble portion, J, was filtered off under positive pressure (100 p.s.i.) using a pressure filter fitted with a No. 50 filter paper. The filtrate K was diluted with sufficient water to give a solution L of methanol:water ratio of 2.0:1 as qualitatively determined by gas chromatography using a porapack column. The filter cake, J, consisted of a gel of solids and trapped soluble soaps. The cake was washed with a fresh portion of methanol (40 g.) and pressure applied until the cake did not expel any further washings. The same sequence of washings with methanol (40 g.) was applied a further two times to give an exhaustively washed filter cake J' and the pooled washings were used to dissolve the next batch of crude soap paste.

A second solution, M, was prepared from crude soap paste which had an almost identical solids content, and methanol-water ratio (2.0:1) to that described by solution L. Solution M (1 part by weight) was extracted in a separatory funnel with a petroleum hydrocarbon frac-

18

tion (B.P. 150°–200° F.) (0.8 part by weight). The suspended hydrocarbon-wetted insoluble solids were decanted with the extract phase. The raffinate was extracted, cross-currently, five times with a petroleum hydrocarbon fraction (B.P. 150°–200° F.) (0.8 part by weight, per extraction) to give raffinate N. Solution L (1 part by weight) was extracted in a separatory funnel six times, cross-currently with a petroleum hydrocarbon fraction (B.P. 150–200° F.) (0.8 part by weight, per extraction) to give raffinate O. Raffenates N and O were acidulated by the conventional method and the derived tall oils were separated from lignin particles by collecting the oils as an ether solution. After drying with anhydrous sodium sulphate, the tall oils were recovered by evaporating the ether. A comparison of the two extracted tall oils follows:

Solution designation	Percent total solids in feed	Feed acid no.	Methanol water ratio	Exhaustively extracted raffinate acid No.
Filtered feed—L	17.5	148.6	2.0:1	176.3
Feed to decanter—M	17.0	139.2	2.0:1	176.7

1 From raffinate O. 2 From raffinate N.

The exhaustively washed filter cake J' was dispersed in ethanol, and the suspended solids were ground using a mortar and pestle. This suspension was filtered under suction and the residue was washed thoroughly with added portions of ethanol. The filtrates were concentrated and their solids content was measured. The soluble portion extracted from filter cake J' constituted 2.3% dry solids, based on the dry total solids of the original soaps charged to the system. Another portion of this extract was acidulated to give a tall oil derivative of acid number 129.7. This value would represent a percentage soaps loss of the total system as equivalent to 2.1%.

EXAMPLE NO. 5

This example shows that isopropanol can be used in place of methanol with either hexane or heptane. It further shows that a mixture of methanol and isopropanol may be used.

Hinton, Alberta soap skimmings were mixed with varying amounts of water and alcohol to give stock solutions. (The letters "M" and "P" in the following Table 15 indicate methanol and isopropanol, respectively.) These solutions were exhaustively extracted with hydrocarbon.

The sequence of extractions followed involved six cross-current extractions employing one part of stock solution to eight parts of hydrocarbon, by weight. In some cases the hydrocarbon used was n-heptane, in other cases it was n-hexane.

The extracted soaps were acidulated and the tall oils collected by ether extraction. Acid number determination of these oils is reported as ether acid number.

TABLE 15

Hydrocarbon	Stock solution, percent			Ether acid No.
	Dry soap	Water	Alcohol	
Hexane	12	63	25 M	174.3
Do	12	63	25 P	179.2
Heptane	12	63	25 M	177.0
Do	12	63	25 P	181.7
Do	17	42	42 P	179.2
Do	17	33	50 P	179.9
Do	17	21	121 M	177.2
Do	8	30	62 M	178.2
Do	8	30	62 M	178.2
Do	8	30	62 P	179.9

1 Blends

TABLE 3A

Solids: Hinton, Alberta soaps skimmings
 Alcohol: methanol, alcohol/water, 1.5:1
 Hydrocarbon: n-heptane
 Temperature: 40° C.

	Composition of stock solution					Prepared mixture, grams		Analyses of phases					Acid No. after first equilib- rium	Acid No. after ex- haustive extraction	
	Percent w./w.			Ratio alcohol to water	Percent w./w.										
	Solids	MeOH	H ₂ O		Stock	Heptane	Phase	Weight, grams	Solids	H ₂ O	MeOH	Heptane			
A-----	41.7	35.0	23.3	1.5:1	150	150	{Upper-----	130	3.1	24.2	29.2	96.9	17.9	167.2	
B-----	41.7	35.0	23.3	1.5:1	300	100	{Lower-----	171	30.4	At point of separation			16.1		152.5
C-----	30.3	42.0	27.9	1.5:1	150	150	{Upper-----	142	2.6				97.4	25.7	172.0
							{Lower-----	150	25.1	30.0	38.3	6.5	156.8		
D-----	18.8	48.0	33.2	1.5:1	150	150	{Upper-----	148	1.5				98.4	5.5	176.6
							{Lower-----	148	15.9	35.2	44.4	4.6	162.9		
E-----	20	48.0	32.0	1.5:1	500	100	{Upper-----	81	5.3				94.1	20.9	173.6
							{Lower-----	517	17.2	31.7	45.1	6.0	146.9		

TABLE 4A

Solids: Hinton, Alberta soaps skimmings
 Alcohol: methanol, alcohol/water, 2:1
 Hydrocarbon: n-heptane
 Temperature: 40° C.

Analyses of phases													
Composition of stock solution				Prepared mixture, grams		Phase	Weight, grams	Percent w./w.				Acid No. after first equilibrium	Acid No. after exhaustive extraction
Percent w./w.			Percent w./w.										
Solids	MeOH	H ₂ O	Ratio alcohol to water	Stock	Heptane			Solids	H ₂ O	MeOH	Heptane		
A.....	34.6	42.9	22.5	1.9:1	100	100	Upper..... 91	2.9	8	96.4	18.6	170.8	
						Lower..... 106	27.3	22.3	37.4	13.1			
B.....	34.6	42.9	22.5	1.9:1	300	100	Upper..... 62	6.1	1.0	9.28	28.8	171.0	
						Lower..... 331	27.2	20.8	36.8	15.2			
C.....	26.8	50.0	23.2	2.1:1	100	100	Upper..... 96	2.3	4	95.5	19.7	173.9	
						Lower..... 99	21.8	24.1	45.9	8.2			
D.....	17.0	53.4	29.6	1.8:1	100	150	Upper..... 150	1.4	52.6	98.6	13.8	180.2	
						Lower..... 97	13.8	30.7	2.1	89.4			
E.....	20.0	53.4	26.6	2:1	500	100	Upper..... 91	7.9	6	2.9	43.4	175.0	
						Lower..... 504	16.9	26.7	50.2	6.2			
F.....	17.0	53.4	29.6	1.8:1	300	100	Upper..... 98	5.9	5	93.5	24.0	179.2	
						Lower..... 301	14.4	31.5	50.2	3.9			
G.....	40.0	40.0	20.0	2:1	150	150	Upper..... 127	3.9	98.1	96.1	43.7	170.9	
						Lower..... 168	29.2	16.7	33.2	20.9			

TABLE 5A

Solids: Hinton, Alberta soaps skimmings
 Alcohol: methanol, alcohol/water, 2.5:1
 Hydrocarbon: n-heptane
 Temperature: 40° C.

	Composition of stock solution					Prepared mixture, grams		Phase	Analyses of phases				Acid No. after first equilib- rium	Acid No. after ex- haustive extraction
	Percent w./w.			Ratio alcohol to water	Percent w./w.									
	Solids	MeOH	H ₂ O		Stock	Heptane	Weight, grams		Solids	H ₂ O	MeOH	Heptane		
A-----	41.4	41.8	16.8	2.5:1	150	150	{Upper----- {Lower-----	140 158	3.9 32.7	----- 14.1	----- 36.4	96.1 16.8	44.2 153.3	171.0
B-----	41.4	41.8	16.8	2.5:1	300	100			No separation					
C-----	30.7	49.5	19.8	2.5:1	150	150	{Upper----- {Lower-----	145 152	3.6 24.8	----- 19.6	----- 45.9	96.4 9.6	35.7 158.7	173.9
D-----	19.0	57.0	24.0	2.4:1	100	100	{Upper----- {Lower-----	109 95	2.0 15.6	----- 27.2	----- 53.1	97.5 4.1	19.5 166.0	
E-----	20.0	57.2	22.8	2.5:1	500	100	{Upper----- {Lower-----	95 499	10.0 17.0	1.1 22.9	3.3 54.5	85.6 5.7	48.2 150.3	176.6

TABLE 6A

Solids: Hinton, Alberta soaps skimmings
 Alcohol: methanol, alcohol/water, 1.5:1
 Hydrocarbon: Refinery fraction having boiling point 150-200° F.
 Temperature: 40° C.

Analyses of phases														
Composition of stock solution					Prepared mixture, grams		Phase	Weight, grams	Percent w./w.				Acid No. after first equilibrium	Acid No. after exhaustive extraction
Percent w./w.			Ratio alcohol to water	Stock	Hydro-carbon	Solids			H ₂ O	MeOH	Hydro-carbon			
Solids	MeOH	H ₂ O												
A.....	41.7	35.0	23.3	1.5:1	150	150	{Upper----- Lower-----	105 190	3.5 28.7	20.0 29.0	96.5 22.4	26.5 152.0	167.8	
B.....	41.7	35.0	23.3	1.5:1	300	100			No separation					
C.....	30.3	41.8	27.9	1.5:1	150	150	{Upper----- Lower-----	129 166	2.9 23.6	26.9 36.4	97.2 13.0	17.0 155.9	173.7	
D.....	18.8	48.0	33.2	1.5:1	150	150	{Upper----- Lower-----	141 152	2.3 15.7	3 34.0	97.7 7.1	10.2 164.7		179.0
E.....	18.8	48.0	33.2	1.5:1	205	50	{Upper----- Lower-----	31 262	8.1 16.7	1.5 34.3	88.9 43.1	23.8 149.8	177.4	

TABLE 7A

Solids: Hinton, Alberta soaps skimmings
 Alcohol: methanol, alcohol/water, 2:1
 Hydrocarbon: Refinery fraction having boiling point 150-200° F.
 Temperature: 40° C.

Temperature: 40° C.															
Composition of stock solution					Prepared mixture, grams		Analyses of phases							Acid No. after first equilibrium	Acid No. after exhaustive extraction
Percent w/w.			Ratio alcohol to water	Stock	Hydro-carbon	Phase	Weight, grams	Percent w/w.							
Solids	MeOH	H ₂ O						Solids	H ₂ O	MeOH	Hydro-carbon				
A.....	41.2	39.2	19.6	2:1	150	150	{Upper----- Lower-----	119 179	4.5 27.9	.3 18.6	1.1 33.0	93.8 20.4	52.5 152.2	173.2	
B.....	41.2	39.2	19.6	2:1	300	100	{Upper----- Lower-----	141 152	3.7 23.5	.2 23.5	.9 43.0	95.3 10.1	42.7 157.6		
C.....	31.2	45.8	22.9	2:1	150	150		152 147	2.8 16.2	No separation		97.2 5.8	32.0 162.9	178.6	
D.....	20.2	53.3	26.6	1:2	150	150	{Upper----- Lower-----	97 490	15.1 16.9	3.6 27.2	5.9 51.0	75.4 5.0	73.5 149.2		
E.....	20.2	53.3	26.6	2:1	500	100	{Upper----- Lower-----	490	16.9	27.2	51.0	5.0	149.2	178.1	

TABLE 8A

Solids: Hinton, Alberta soaps skimmings
 Alcohol: Methanol, alcohol/water, 2.5:1
 Hydrocarbon: Refinery fraction having boiling point 150-200° F.
 Temperature: 40° C.

Temperature: 40° C.														
Composition of stock solution					Prepared mixture, grams		Analyses of phases							
Percent w/w.				Ratio alcohol to water	Stock	Hydro-carbon	Phase	Weight, grams	Percent w/w.				Acid No. after first equilibrium	Acid No. after exhaustive extraction
Solids	MeOH	H ₂ O	Solids						H ₂ O	MeOH	Hydro-carbon			
A-----	41.4	41.8	16.8	2.5:1	150	150	{Upper-----	126	5.6	-----	3.0	91.4	63.8 } 152.9 }	174.2
							{Lower-----	171	23.0	14.8	35.3	21.9		
B-----	41.4	41.8	16.8	2.5:1	300	100	No separation					94.3	51.5	175.6
							{Upper-----	138	4.4	-----	1.33	11.4	158.7	
C-----	30.7	49.5	19.8	2.5:1	150	150	{Lower-----	160	23.3	19.8	45.5	96.4	39.3	177.6
							{Upper-----	144	3.0	-----	.6	4.0	165.4	
D-----	19.0	57.0	24.0	2.4:1	150	150	{Lower-----	148	15.1	26.5	54.3	80.3	58.1	177.2
							{Upper-----	30	28.8	2.1	4.7	152.4		
E-----	19.0	57.0	24.0	2.4:1	250	50	{Lower-----	262	15.6	25.6	53.7	5.0		

TABLE 9A

Solids: Hinton, Alberta soaps skimmings
 Alcohol: Methanol, alcohol/water, 1.5:1
 Hydrocarbon: Refinery fraction having boiling point 190-210° F.
 Temperature: 40° C.

Temperature: 40° C.															
Composition of stock solution					Prepared mixture, grams		Analyses of phases							Acid No. after first equilibrium	Acid No. after exhaustive extraction
Percent w./w.			Ratio alcohol to water	Stock	Hydro-carbon	Phase	Weight, grams	Percent w./w.				Hydro-carbon			
Solids	MeOH	H ₂ O						Solids	H ₂ O	MeOH					
A-----	40.0	36.0	24.0	1.5:1	150	150	{Upper----- Lower-----	102 186	3.7 23.3	----- 19.6	.1 28.6	96.2 23.4	31.7 150.4	169.1	
B-----	34.6	42.9	22.5	1.2:1	250	100	{Upper----- Lower-----	30 317	5.9 26.8	1.5 25.8	4.8 29.2	87.8 18.1	40.0 142.6		
C-----	30.0	42.0	28.0	1.5:1	150	150	{Upper----- Lower-----	132 160	3.0 23.7	----- 25.9	.6 39.1	96.4 11.3	15.2 154.8	173.2	
D-----	20.0	48.0	32.0	1.5:1	150	150	{Upper----- Lower-----	142 150	2.4 16.9	----- 31.3	.5 46.5	97.1 5.2	22.6 160.7		
E-----	20.0	48.0	32.0	1.5:1	400	100	{Upper----- Lower-----	72 426	7.1 17.0	.7 30.7	1.8 45.9	90.3 6.3	28.8 148.8	176.5	

TABLE 10A

Solids: Hinton, Alberta soaps skimmings
 Alcohol: methanol, alcohol/water, 2:1
 Hydrocarbon: Refinery fraction having boiling point 190-210° F.
 Temperature: 40° C.

Temperature: 40° C.														
Composition of stock solution					Prepared mixture, grams		Analyses of phases							
Percent w/w.				Ratio alcohol to water	Stock	Hydro-carbon	Phase	Weight, grams	Percent w/w.				Acid No. after first equilibrium	Acid No. after exhaustive extraction
Solids	MeOH	H ₂ O							Solids	H ₂ O	MeOH	Hydro-carbon		
A	40.0	40.0	20.0	2:1	150	150	{Upper----	119	4.0	.8	1.9	93.3	69.3	172.2
							{Lower----	178	27.4	20.4	27.5	24.8	150.5	
B	35.9	40.0	24.1	1.7:1	255	100	{Upper----	30	6.8	.3	.8	92.2	144.1	170.1
							{Lower----	323	27.2	23.3	30.0	19.5	44.7	
C	30.0	46.6	23.3	2:1	150	150	{Upper----	144	3.8	-----	1.4	94.8	156.5	174.2
							{Lower----	157	23.3	23.4	41.6	11.7	29.9	
D	20.0	53.3	26.6	2:1	150	150	{Upper----	148	2.8	-----	.8	98.4	163.6	176.9
							{Lower----	150	16.2	27.5	51.9	4.4	54.7	
E	17.0	53.4	29.6	1.8:1	400	78	{Upper----	50	11.0	2.0	3.6	83.4	148.3	176.1
							{Lower----	416	15.0	30.7	49.2	5.1		

TABLE 11A

Solids: Hinton, Alberta soaps skimmings
 Alcohol: methanol, alcohol/water, 2.5:1
 Hydrocarbon: Refinery fraction having boiling point 190-210° F.
 Temperature: 40° C.

Temperature: 40° C.														
	Composition of stock solution				Prepared mixture, grams		Phase	Analyses of phases					Acid No. after first equilibrium	Acid No. after exhaustive extraction
	Percent w./w.			Ratio alcohol to water	Stock	Hydrocarbon		Percent w./w.						
	Solids	MeOH	H ₂ O					Weight, grams	Solids	H ₂ O	MeOH	Hydrocarbon		
A.....	40.0	42.8	17.1	2.5:1	150	150	{Upper.... {Lower....	136 163	5.6 26.4	.6 13.5	2.6 32.4	91.2 27.7	73.8 153.0	173.6
B.....	40.0	42.8	17.1	2.5:1	300	100	{Upper.... {Lower....	152 145	4.3 22.4	.3 20.1	2.0 45.6	93.4 11.9	60.9 159.3	
C.....	30.0	50.0	20.0	2.5:1	150	150								155 143
D.....	20.0	57.2	22.9	2.5:1	150	150	{Upper.... {Lower....	83 512	11.5 15.6	1.9 26.2	4.0 52.2	82.5 6.0	67.3 150.0	175.6
E.....	20.0	57.2	22.9	2.5:1	500	100								

TABLE 12A

Solids: Hinton, Alberta soaps skimmings
 Alcohol: Methanol
 Temperature: 40° C.

Sample	Percent solids in system	Percent MeOH	Percent H ₂ O	MeOH: H ₂ O ratio	Percent hydrocarbon in system	Percent solids in upper phase	Acid No. upper phase	Percent wt. fraction soaps in upper phase ¹	Percent conc. soap in upper phase	Percent conc. unsaps in upper phase	Method of mixing
SP H-1 ¹ -----	12.5	35	19.5	1.8:1	33	3.0	29.6	1.3	0.4	2.6	Lab impeller, 1,350 r.p.m., 1 hr.
SP H-2 ¹ -----	14.1	39	21	1.8:1	26	4.4	35.0	1.5	0.8	3.6	Do.
SP H-3 ¹ -----	15.2	23	42	1.8:1	20	6.6	37.6	2.3	1.7	4.9	Do.
SP H-4 ¹ -----	7.9	-----	-----	1.8:1	60	1.7	11.6	1.0	0.1	1.6	Do.
SP I-1 ² -----	12.5	35	19.5	1.8:1	33	5.0	49.1	4.4	1.3	3.7	Do.
SP I-2 ² -----	12.5	35	19.5	1.8:1	33	5.0	56.0	4.6	1.6	3.4	Do.
SP I-3 ² -----	7.6	-----	-----	1.8:1	60	1.8	24.7	3.3	0.3	1.5	Do.
SP I-4 ² -----	12.5	35	19.5	1.8:1	33	7.1	65.7	7.0	3.3	3.8	Do.
SP I-5 ² -----	12.5	35	19.5	1.8:1	28	11.9	89.7	14.0	5.9	6.0	Do.
SP I-6 ² -----	7.7	-----	-----	1.8:1	60	1.9	23.4	2.2	0.2	1.7	Do.

¹ Hydrocarbon—Heptane.

² Hydrocarbon—Refinery fraction having boiling point 150-200° F.

³ Hydrocarbon—Refinery fraction having boiling point 190-210° F.

⁴ pH adjusted to 10.5.

⁵ Unsap-free basis.

TABLE 13A

Solids: Hinton, Alberta soaps skimmings
 Alcohol: Methanol
 Temperature: 40° C.

Sample	Percent solids in system	Percent MeOH	Percent H ₂ O	MeOH: H ₂ O ratio	Percent hydrocarbon in system	Percent solids in upper phase	Acid No. upper phase	Percent wt. fraction soaps in upper phase ¹	Percent conc. soap in upper phase	Percent conc. unsaps in upper phase	Method of mixing
1-----	12.8	40	22.2	1.8:1	25	5.9	24.0	2.0	.8	5.1	Manual shaking.
2-----	6.8	21.3	11.8	1.8:1	60	1.4	13.8	0.8	.1	1.3	Do.
3-----	17.3	21.9	11.3	1.9:1	50	2.9	18.6	1.0	.3	2.6	Do.
4-----	26.0	32.2	16.9	1.9:1	25	6.1	28.8	0.7	1.0	5.2	Do.
5-----	13.4	25	11.6	2.2:1	50	2.3	19.7	1.1	.3	2.0	Do.
6-----	16.7	44.4	22.2	2:1	16.7	7.9	43.4	2.1	1.9	6.0	Do.

¹ Unsap-free basis.

TABLE 13B

Solids: Hinton, Alberta soaps skimmings
 Alcohol: Methanol
 Temperature: 40° C.

Sample	Percent solids in system	Percent MeOH	Percent H ₂ O	MeOH: H ₂ O ratio	Percent hydrocarbon in system	Percent solids in upper phase	Acid No. upper phase	Percent wt. fraction soaps in upper phase ¹	Percent conc. soap in upper phase	Percent conc. unsaps in upper phase	Method of mixing
L-1-----	14.3	43	20	2.1:1	22	11.1	-----	-----	-----	-----	Incubator shaker, manual shaking
L-2-----	14.3	43	20	2.1:1	22	11.9	-----	-----	-----	-----	Do.
L-3-----	14.3	43	20	2.1:1	22	12.4	32.4	3.0	2.2	10.0	Do.
L-4-----	14.3	43	20	2.1:1	22	11.1	-----	-----	-----	-----	Do.
L-5-----	-----	-----	-----	-----	-----	9.6	-----	-----	-----	-----	Do.
L-6 ² -----	12.0	36	17	2.1:1	36	5.5	28.7	3.1	0.9	4.8	Do.
L-7 ² -----	8.8	30	12	2.1:1	52.2	2.7	26.2	3.2	0.4	2.3	Do.

¹ System L-3 with twice weight hydrocarbon added.

² System L-3 with three times weight hydrocarbon added.

³ Unsap-free basis.

TABLE 13C

Solids: Hinton, Alberta soaps skimmings
Alcohol: Methanol
Temperature: 40° C.

Sample	Percent solids in system	Percent MeOH	Percent H ₂ O	MeOH: H ₂ O ratio	Percent hydrocarbon in system	Percent solids in upper phase	Acid No. upper phase	Percent wt. fraction soaps in upper phase ¹	Percent conc. soap in upper phase	Percent conc. unsaps in upper phase	Method of mixing
1-----	20	20	10	2:1	50	4.0	69.3	3.8	1.5	2.5	Manual shaking.
2-----	25.8	28.8	17.3	1.7:1	39.3	6.8	44.7	3.8	1.0	2.9	Do.
3-----	15	23.3	11.7	2:1	50	2.8	29.9	2.8	0.5	2.3	Do.
4-----	10	26.6	13.3	2:1	50	11.0	54.7	3.0	3.4	7.7	Do.
5-----	14.2	45	24.8	1.8:1	16.3						

¹ Unsap-free basis.

TABLE 14

[Continuous distillation of an alcohol rich raffinate solution]

Time (hr. from start)	Temperature, ° C.				Feed (ml.) incremental difference	Bottoms product, percent			Distillate		
	Reboiler	Plate # 1	Plate # 30	Plate # 60		Solids	Water	Methanol	Incremental volume (ml.)	Percent methanol	Percent heptane
4-----	95.8	98	66	62	200	35.8	64.16	0.04	31	99.4	0.6
5-----	96.5	97	70	62	240	35.8	64.2	0	111	90.4	9.6
6-----	96.5	97	70	62	220	36.9	63.1	0	132	90.4	9.6
7-----	96.5	97	70	62	230	36.9	63.1	0	131	90.4	9.6
8-----	96.5	98	69.9	62	210	37.6	62.4	0	134	90.6	9.4
9-----	96.5	97	70	62	180	37.7	62.3	0	148	90.6	9.4
10-----	96	94	89.9	62	200	37.6	62.4	0	94	90.4	9.6
11-----	96.5	99	69.5	62	220	38.4	61.6	0	134	90.5	9.5
12-----	96	97	70.2	62	250	38.4	61.2	0	138	90.4	9.6
13-----	96.5	95	70	62	230	39.1	60.9	0	140	90.6	9.4
14-----	96.5	97	70	62	220	39.2	60.8	0	140	90.5	9.5
15-----	96.5	95	70	62	220	39.4	60.6	0	137	90.5	9.5
16-----	96.5	96	70	62	220	39.9	60.1	0	134	90.1	9.9
17-----	96.5	97	70	62	240	40.1	59.9	0	142	90.5	9.5

What is claimed is:

1. In a method for treating crude sulphate soap skimmings containing unsaponifiables comprising admixing the skimmings with water and de-emulsifying alcohol to produce an extraction feed containing undissolved solids, dissolved soaps and unsaponifiables, contacting the extraction feed with a hydrocarbon which is a solvent for the unsaponifiables and is substantially immiscible in water to produce a composition which separates into an extract phase containing unsaponifiables and a raffinate phase containing soaps, separating the extract phase from the raffinate phase, and recovering the unsaponifiables from the extract phase and the soaps from the raffinate phase, the improvement which comprises:

providing an essentially soap-free extract phase and a substantially unsaponifiable-free raffinate phase which is non-foaming on distillation by clarifying the extraction feed to remove undissolved solids; selecting the skimmings, water, alcohol and hydrocarbon mixture composition to provide: (a) a dissolved solids content such that the raffinate phase, when exhaustively extracted and acidulated, has an acid

number of at least 174, (b) an extract which contains less than about 5.5% by weight dissolved solids, and (c) a ratio of dry unsaponifiables-free dissolved solids to water in the raffinate phase which ratio is equal to or greater than about 3 to 7; distilling the alcohol from the raffinate phase under alkaline conditions, without washing, to recover alcohol contained therein; and recycling the recovered alcohol to the admixing step.

References Cited

UNITED STATES PATENTS

2,530,809 11/1950 Christendon et al. --- 260—97.6
2,530,810 11/1950 Christendon et al. --- 260—97.6

DONALD E. CZAJA, Primary Examiner

W. E. PARKER, Assistant Examiner

U.S. Cl. X.R.

260—97.6