

June 7, 1966

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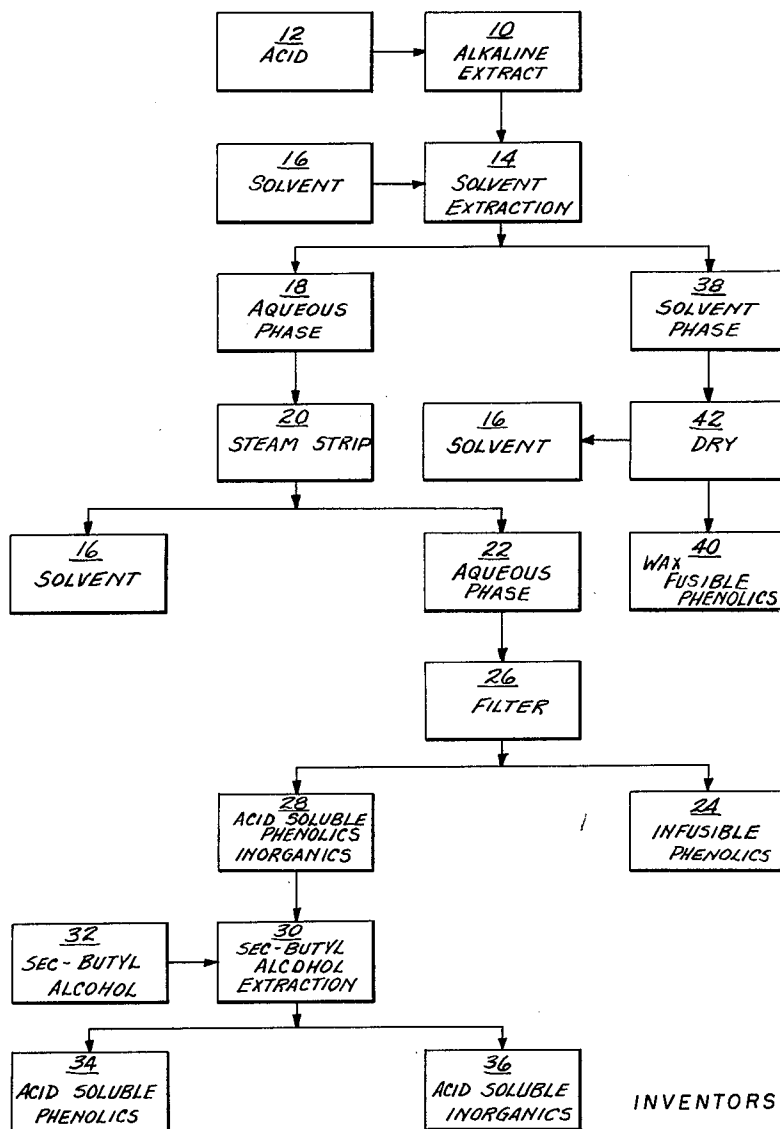
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FRACTIONATION OF ALKALINE EXTRACTS OF TREE BARKS

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9 Sheets-Sheet 1

Fig. 1.



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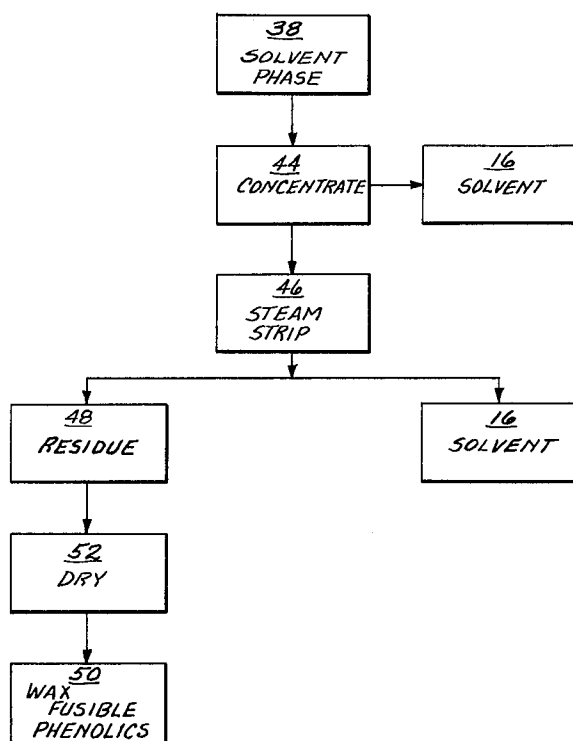
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FRACTIONATION OF ALKALINE EXTRACTS OF TREE BARKS

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Fig. 2.



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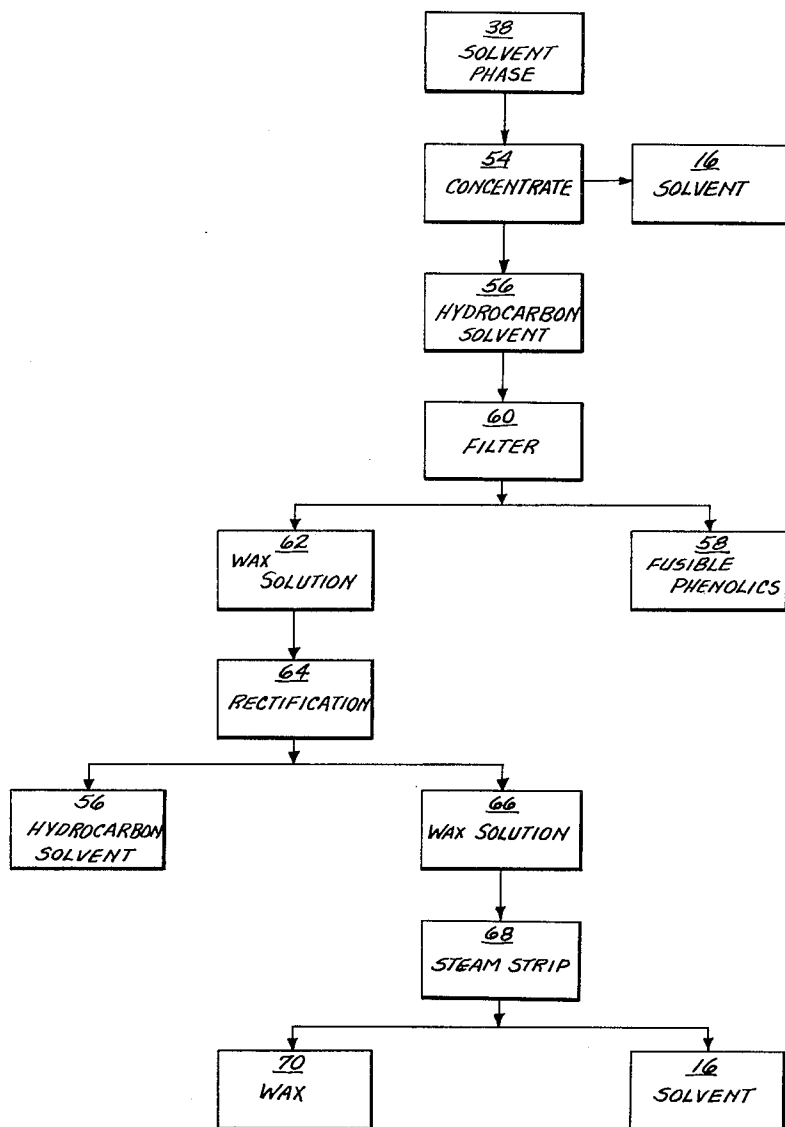
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FRACTIONATION OF ALKALINE EXTRACTS OF TREE BARKS

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Fig. 3.



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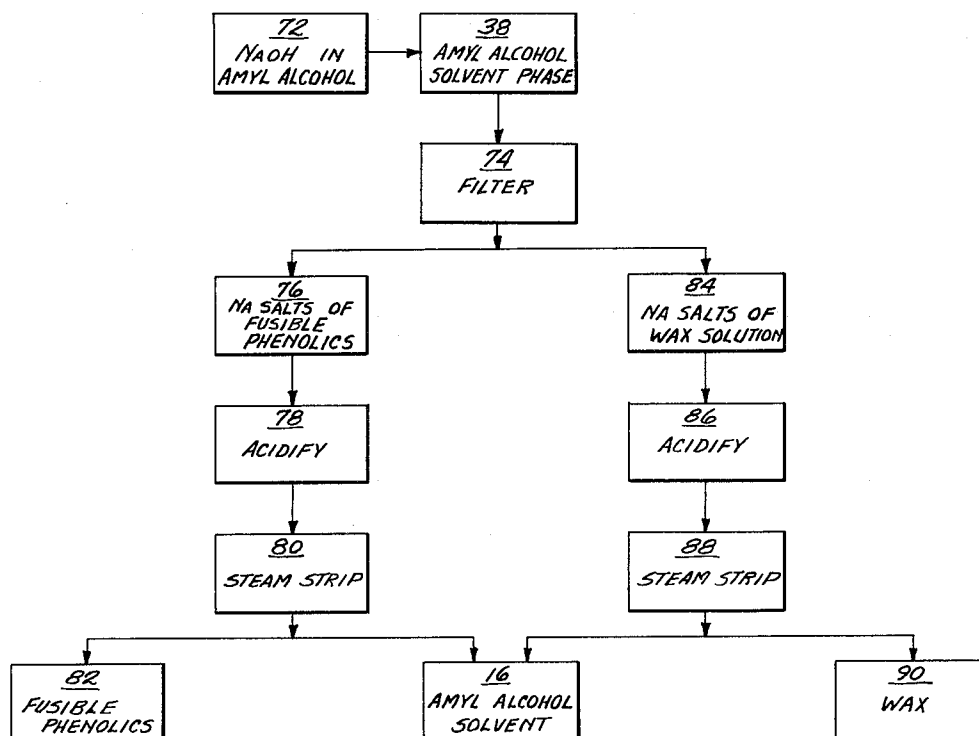
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Fig. 4.



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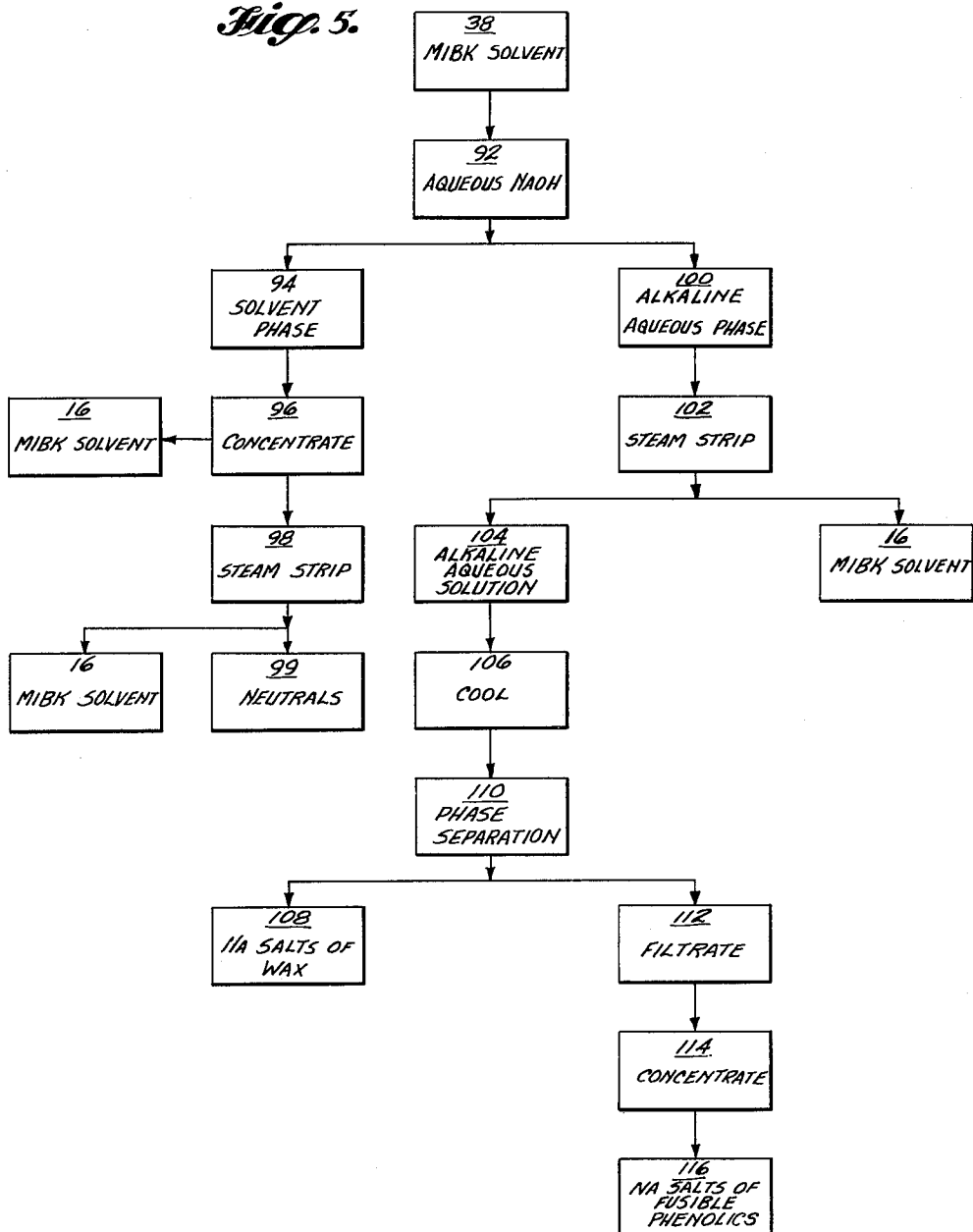
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FRACTIONATION OF ALKALINE EXTRACTS OF TREE BARKS

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Fig. 5.



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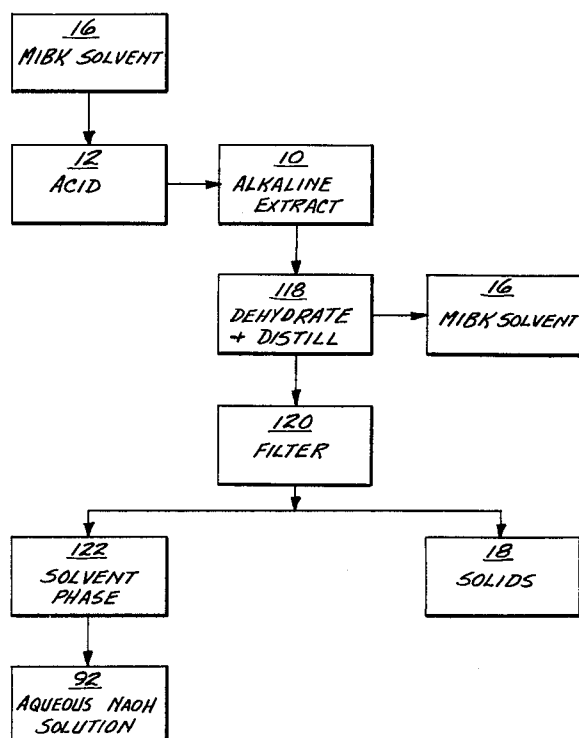
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Fig. 6.



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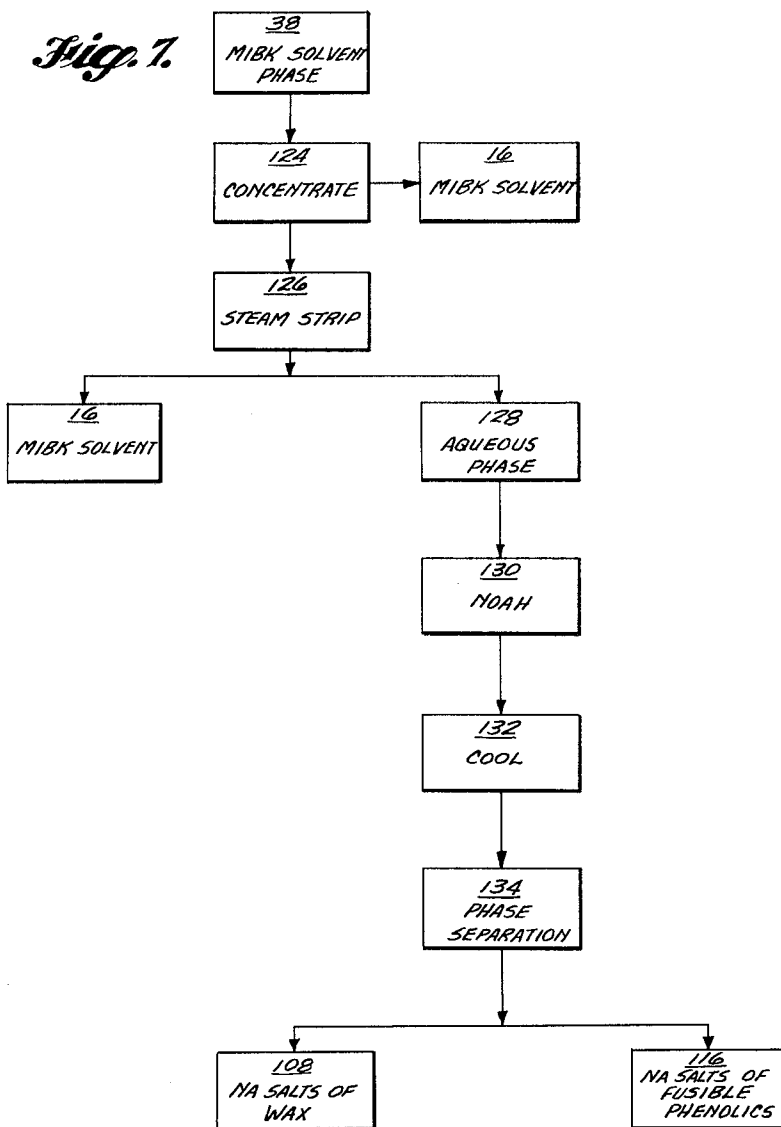
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FRACTIONATION OF ALKALINE EXTRACTS OF TREE BARKS

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9 Sheets-Sheet 7



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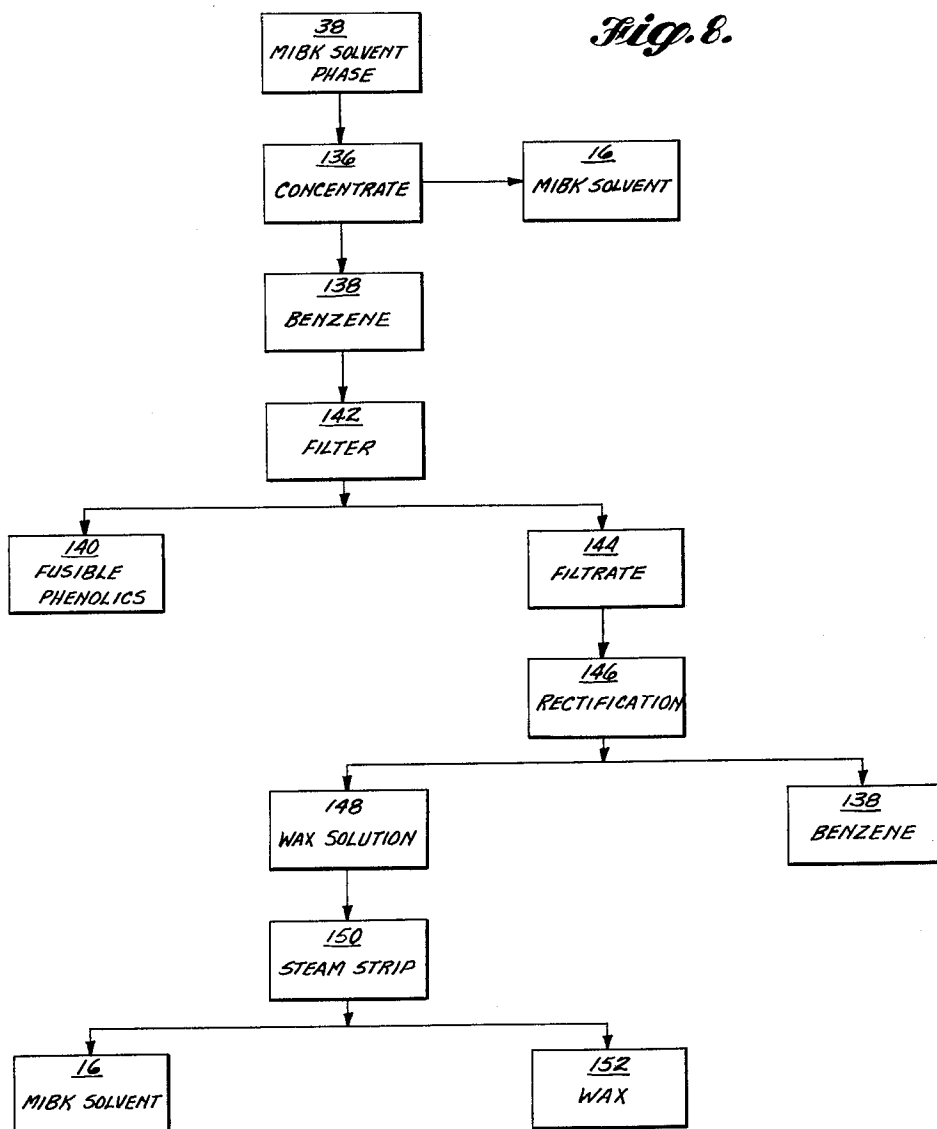
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FRACTIONATION OF ALKALINE EXTRACTS OF TREE BARKS

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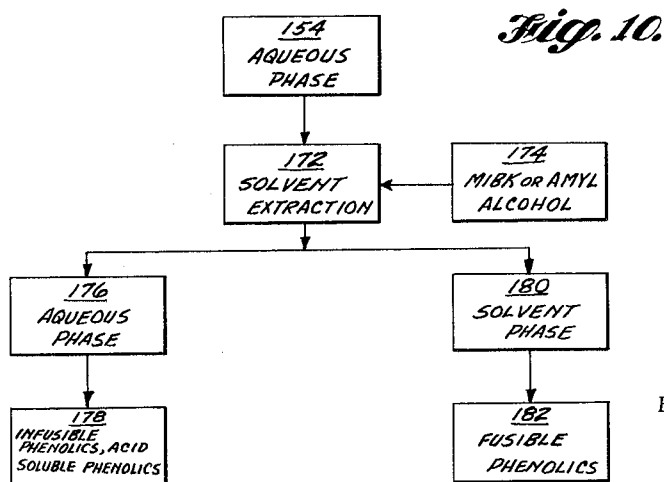
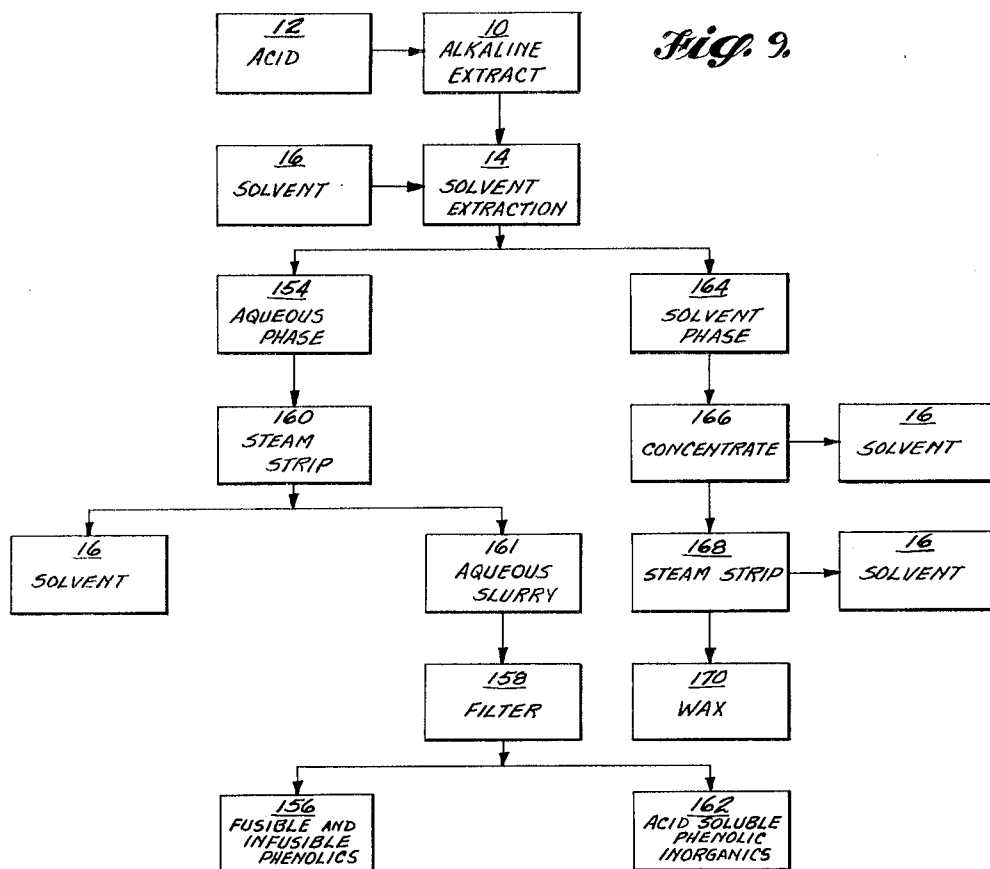
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FRACTIONATION OF ALKALINE EXTRACTS OF TREE BARKS

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FRACTIONATION OF ALKALINE EXTRACTS
OF TREE BARKS

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4 Claims. (Cl. 260-412.5)

This invention relates to the separation of chemical products contained in the barks of trees, and more particularly to the recovery of those constituents contained in alkaline extracts of tree barks.

The alkaline extract of the barks of trees contains a complex mixture of organic chemicals classified into four general types. The wax fraction is comprised primarily of fatty acids, hydroxy fatty acids and neutrals such as long chain alcohols and phytosterols. The fusible phenolic fraction contains low molecular weight polyphenolic acids and fatty acid esters of phenolic or polyphenolic acids, and is characterized by being substantially completely fusible below the temperature of 160° C. The infusible phenolic fraction includes the higher molecular weight polypenic acids and is characterized by a decomposition temperature of about 275° to 300° C. The acids soluble phenolic fraction contains tannin and tannin-like materials and a small amount of carbohydrate.

The wax components may be utilized in the manufacture of floor waxes, fabric coating and moisture proofing agents, rubber antioxidants, pigment vehicles for transfer paper, and in the form of the lithium salt of the wax as a lube oil detergent. The fusible phenolics are materials which melt and may be used as additives or diluents which take part in a reaction, and may be used specifically as additives or diluents in laminating resins for paper and in binders for lignocellulosic materials. The infusible phenolics char and burn but do not melt and may be used as additives in oil well drilling fluids, in cement slurries as thinners in place of water, and may also be used as cement grinding aids. The acid soluble phenolics fraction may be added to tannin liquids, may be used as an additive in oil well drilling fluids, and may also be used as a precipitating agent for proteins in the effluents of food processing plants. The neutral mixture which is approximately 75% long chain alcohols and esters may be converted to detergents and surface active agents. If desired, the alcohols may first be separated from the mixture by urea.

Because of the commercial importance of these constituents, various attempts have been made heretofore to separate them. For example, fractional acidification has achieved a rather crude separation of wax plus fusible phenolics, infusible phenolics and acid soluble phenolics. In another procedure, direct solvent extraction of the bark resulted in recovery of wax, flavanoids and tannins, while in still another procedure alcoholic sodium hydroxide was employed to extract the bark.

The prior procedures, such as those exemplified above, have been deficient in certain respects. They have not achieved the degree of fractionation desired for upgrading the products to commercially satisfactory standard. They have not achieved effective separation of all four constituents described hereinbefore. The processes involved in some of the prior methods require bulky and expensive equipment, involve solvent recovery operations which are expensive, and require control procedures which render them economically unfeasible.

Accordingly, it is the principal object of the present invention to provide a process by which the constituents contained in the alkaline extracts of tree barks may be

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recovered efficiently and economically, in an upgraded condition suitable for diverse commercial applications.

Another important object of this invention is to provide a process of the class described which is adaptable to large scale commercial operation, providing high production capacity with relatively simple and inexpensive equipment and with a minimum of process complication.

The foregoing and other objects and advantages of this invention will appear from the following detailed description, taken in connection with the accompanying drawings in which:

FIGURE 1 is a flow diagram illustrating a process embodying the features of the present invention;

FIGURES 2-8, inclusive, are fragmentary flow diagrams illustrating various modified procedures for treatment of the solvent phase; and

FIGURE 9 is a flow diagram illustrating a further modified process embodying the features of the present invention.

FIGURE 10 is a flow diagram illustrating a variation of the modified process of FIGURE 9.

In general, the process of the present invention involves the acidification of the alkaline bark extract to the extent that three of the four constituents are rendered insoluble, followed by solvent extraction of the acidified slurry with a water immiscible solvent, such as ketones, alcohols, aromatic hydrocarbons, chlorinated aliphatic hydrocarbons, aliphatic hydrocarbons, and mixtures of an aliphatic hydrocarbon with a water immiscible polar solvent. The constituents of the bark extract thus are separated initially in the immiscible aqueous and solvent phases, the constituents contained in each phase being dependent upon the type of solvent employed in the extraction. Further separation of the constituents then may be achieved by appropriate further processing of one or both phases.

In a typical procedure, the alkaline bark extract is prepared by reducing the bark to a particle size such that a major portion passes an 8 mesh screen but is retained on an 80 mesh screen (U.S. Sieve Series). The bark then is fed to an extraction cell wherein it is subjected to the action of an aqueous alkaline solution for a time predetermined to dissolve the alkaline soluble content of the bark.

The alkaline solution may be prepared from a basic acting compound of an alkaline metal or ammonia, preferably caustic soda, sodium carbonate or caustic potash, in an amount ranging from 5 to 25% of the dry weight of the bark, preferably 10 to 16% in the case of caustic soda. The ratio of bark to aqueous media also is controlled to produce an alkaline extract having an organic solids concentration of from 5 to 25%.

The extracting is conducted at a temperature between ambient temperature and the boiling point of the cell contents at atmospheric pressure, or at a higher temperature if superatmospheric pressures are employed. Reaction time may vary from 10 to 180 minutes, preferably from 30 to 90 minutes.

Upon completion of reaction, the aqueous alkaline slurry is passed through a separator where the bark residue solids are separated from the extract. The bark fines carried with the extract then are removed, preferably by centrifuging, and the fines-free liquid alkaline extract then is ready for subsequent treatment in accordance with the present invention.

Referring now to FIGURE 1 of the drawings, the alkaline extract 10 is acidified from the source 12 with a strong organic or mineral acid, to convert the soluble alkaline salts of the wax, fusible phenolics and infusible phenolics to the insoluble free acid form. This requires acidification to a pH of not more than about 4.0 preferably about 3.0. The acidification step may be carried out with hydrochloric, phosphoric, sulfurous, oxalic, or

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acetic acid, but preferably sulfuric acid is used. Although acid strength is not critical, it should be high enough to avoid excessive dilution and low enough, preferably not more than about 50%, to prevent localized overheating. Provision must be made for venting and accommodating foam formation. Foaming may be minimized by preliminary additional heating of the extract which normally reaches the acidification stage at a temperature of from 70 to 80° C.

Acidification also must be accompanied with vigorous agitation to prevent the formation of the gell-like lumps of precipitated wax and phenolics. As acidification proceeds, an increase in viscosity occurs. Maximum viscosity is reached at about pH 5.0 and thereafter decreases to a minimum as the pH approaches 3.0. This intermediate condition of high viscosity and lumping make vigorous agitation essential in order to insure adequate mixing and pH control.

The ultimate pH of the solution also is determined in part by the solids content of the extract. For example, at the higher solids content level of 15 to 25%, a pH of about 2.5 may be necessary to minimize the formation of emulsion during subsequent solvent extraction.

The acidified extract now is subjected to solvent extraction at 14. Although various types of extraction are suitable for this purpose, a multiple stage countercurrent batch extraction is employed in the embodiment illustrated in FIGURE 1. The solvent 16 is a ketone, such as methyl isobutyl ketone or one of the isomers or combinations of isomers of amyl alcohol. Thus, the solvent may be n-amyl, iso-amyl, sec-amyl, t-amyl, or various mixtures thereof. The amount of solvent is not critical but practical considerations dictate a preferred range of between 25 to 100% of the weight of the acidified extract, and a preferred temperature range of extraction between 25° C. and 80° C. In general, greater proportions of solvent are required as the extraction temperature is decreased, in order to minimize the problem of emulsion formation.

Extraction time depends in part upon the amount of solvent and the extraction temperature, and it appears to depend upon the degree to which the solvent wets the solids and the rate at which the solids are dissolved. It has been determined that a contact time of ten minutes at 70°–80° C. for each countercurrent stage in a three stage extraction provided complete extraction of wax and fusible acid phenolics using an amount of n-amyl alcohol or methyl isobutyl ketone equivalent to 25% of the weight of the acidified extract.

The aqueous phase 18 from the solvent extraction contains the infusible phenolics and the acid soluble phenolics and inorganics. Steam stripping 20 of the aqueous phase effectively removes any dissolved solvent 16. Although the precipitated infusible phenolics interfere somewhat with the steam stripping, their removal by filtration prior to stripping is not preferred because they tend to absorb a substantial quantity of solvent which thus would be lost.

The aqueous phase 22 following steam stripping contains the precipitated infusible phenolics and the acid soluble phenolics and inorganics. The infusible phenolics 24 are recovered by filtration 26, washed and dried. The acid soluble phenolics and inorganics 28 contained in the filtrate may be concentrated, for example, to 50–80% solids, for commercial utilization. Alternatively, the filtrate may be extracted at 30 with hot secondary butyl alcohol 32 to recover the soluble phenolics 34 as an additional commercial product. The inorganic content 36 may be recovered from the aqueous phase.

The solvent phase 38 of the solvent extraction 14 contains the wax and fusible phenolics fractions. These may be recovered as a mixture 40 simply by drying, as indicated at 42 in FIGURE 1. However, these fractions also tend to absorb about 25% by weight of the solvent, and therefore it is preferred that the combined fractions

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be recovered in accordance with the procedure illustrated in FIGURE 2.

In FIGURE 2, the solvent phase 38 is concentrated at 44 to about 50% solids and then steam stripped at 46 to remove the solvent 16. The residue 48 resulting therefrom contains the wax and fusible phenolics fractions, and these are recovered at 50 by drying at 52. Since the fusible phenolics appear to be quite heat sensitive, the drying preferably is effected in vacuum at a temperature not exceeding about 50° C.

Referring now to FIGURE 3 of the drawings, there is illustrated a process by which the solvent phase 38 of extraction is processed for separation and recovery of the wax and fusible phenolics fractions. The solvent phase preferably is concentrated at 54 to about 35–50% solids and mixed at 56 with from 5 to 10 times its weight, preferably about 7 times, of a hydrocarbon solvent such as an aliphatic hydrocarbon such as hexane, or heptane, or a chlorinated hydrocarbon such as trichlorethylene, or an aromatic hydrocarbon such as benzene or toluene. Because of subsequent solvent recovery, it is preferred that the solvent phase be concentrated as much as possible in order to reduce to a minimum the quantity requirement of hydrocarbon solvent.

The fusible phenolics fraction is insoluble in the hydrocarbon solvent and thus is recovered at 58 by filtration 60. The wax fraction is soluble in the filtrate mixture 62 of extract solvent and hydrocarbon solvent. The hydrocarbon solvent is recovered by rectification 64, leaving the wax in solution in the extract solvent at 66. This solution is steam stripped at 68 to recover the solvent 16, and the light colored quality wax 70 is dried.

FIGURE 4 illustrates a modified procedure for separating and recovering the wax and fusible phenolics fraction when amyl alcohol is used as the extracting solvent. To the amyl alcohol solvent phase 38 is added sodium hydroxide 72 dissolved in a small amount of amyl alcohol. The sodium salts of the fatty acids and neutral wax constituents remain in solution, whereas the sodium salts of the fusible phenolics are precipitated. Accordingly, the slurry is filtered at 74 to recover the salts of fusible phenolics at 76. If desired, this fraction may be acidified at 78 and steam stripped at 80 to separate the solvent 16 from the free acid form of the fusible phenolics 82.

The filtrate 84 containing the sodium salts of the fatty acids (wax) also may be acidified at 86 and steam stripped at 88 to separate the solvent 16 from the free acid form of the wax 90.

In FIGURE 5 of the drawings, the solvent extraction 14 of the acidified alkaline extract 10 of FIGURE 1 employs the water immiscible methyl isobutyl ketone. The aqueous phase 18 of said extraction carries the infusible phenolics and acid soluble phenolics and inorganics, as in the embodiment illustrated in FIGURE 1. The solvent phase 38 is treated with aqueous sodium hydroxide solution 92 to form an aqueous phase containing the soluble sodium salts of the wax and fusible phenolics fractions and a solvent phase containing neutrals. The solvent phase 94 then is concentrated at 96 and steam stripped at 98 to recover the methyl isobutyl ketone solvent 16. The residue 99 remaining comprises the neutrals such as long chain alcohols and phytosterols, and this fraction may be recovered for commercial use.

The alkaline aqueous phase 100 is steam stripped at 102 to remove its solvent content 16. The aqueous solution 104 containing the sodium salts of the wax and fusible phenolics fractions then at 106 is cooled to a temperature of about 15° C., whereupon the sodium salts of the wax precipitate and may be recovered at 108 by phase separation at 110. The filtrate 112 is concentrated at 114 to recover the sodium salts of fusible phenolics 116. The sodium salts of the wax and fusible phenolics fractions may be converted to the acid forms, in the manner described in connection with FIGURE 4.

In FIGURE 6 the methyl isobutyl ketone solvent 16 is mixed with acid solution 12 and this mixture then is added to the alkaline extract 10 to convert the soluble sodium salts to the insoluble acid forms. The slurry then is dehydrated at 118 with a substantial proportion of the solvent being recovered by distillation. The resulting solvent slurry is filtered at 120 and the solids washed with solvent. The solids at 18 contain the infusible phenolics fraction and the acid soluble phenolics and inorganics, and these are mixed with water and recovered in the manner previously explained in connection with FIGURE 1.

The solvent phase and wash is combined at 122 and this mixture is treated with aqueous sodium hydroxide solution 92 for the recovery of neutrals, wax and fusible phenolics, in the manner explained in connection with FIGURE 5.

In FIGURE 7 the processing of the solvent phase 28 differs from that in FIGURE 5, as follows: The solvent phase is concentrated at 124 and then steam stripped at 126 to recover the methyl isobutyl ketone solvent 16. Sodium hydroxide 130 is added to the aqueous phase 128 to form the soluble sodium salts of the wax and fusible phenolics fractions. The solution is cooled at 132 and separated at 134 in the manner explained in connection with FIGURE 5, to separate the sodium salts of the wax 108 and salts of fusible phenolics 116.

In FIGURE 8, the methyl isobutyl ketone solvent phase 38 is concentrated at 136 and mixed with four to five times its weight of benzene 138, in the manner similar to the embodiment illustrated in FIGURE 3. The insoluble fusible phenolics fraction 140 is recovered by filtration at 142. The filtrate 144 is rectified at 146 to recover the benzene solvent 138, and the ketone-wax solution 148 is concentrated and steam stripped at 150 to separate the remaining solvent 16 from the wax fraction 152.

Where it is desirable to first recover the wax, the modified process illustrated in FIGURE 9 may be used wherein the alkaline bark extract 10 is acidified 12 and then subjected to a countercurrent solvent extraction 14 with a hydrocarbon solvent 16, such as an aromatic hydrocarbon, or a chlorinated hydrocarbon, or an aliphatic hydrocarbon, or a mixture of an aliphatic hydrocarbon with up to 25% of a water immiscible polar solvent. Suitable examples of such hydrocarbons are benzene, toluene, xylene, cumene, ethylene dichloride, dichlorobutane, trichlorethylene, dichloropentane, hexane, heptane, octane, kerosene, and mixtures, such as hexane and amyl alcohol. The aqueous phase 154 is steam stripped at 160 to recover the solvent 16. The aqueous slurry 161 contains the precipitate 156 of insoluble fusible phenolics and infusible phenolics, and these are recovered as a mixture by filtration at 158. The filtrate 162 carries the acid soluble phenolics and inorganics which may be recovered in combination, or separated, in the manner described in connection with FIGURE 1.

The solvent phase 164 of the solvent extraction 14 preferably is concentrated at 166 by vacuum evaporating and then steam stripped at 168 to recover the solvent 16 from the wax fraction 170.

Another modification for processing the aqueous phase 154 of FIGURE 9 is illustrated in FIGURE 10 wherein the aqueous phase 154 is mixed with a solvent 172 such as methyl isobutyl ketone or amyl alcohol 174 to provide an aqueous phase 176 containing the infusible phenolics and acid soluble phenolics 178 and a second solvent phase 180 containing the fusible phenolics 182. Each of these phases may be further processed to recover these products by procedures indicated in the previous flow diagrams.

From the foregoing it will be apparent that the present invention affords a variety of procedures by which to

effect the separation of the four basic constituents contained in the alkaline extract of tree barks. These constituents may be separated one from each other, or in various mixture combinations, as desired for subsequent commercial utilization. The procedural steps and production equipment are uncomplicated, thus accommodating large scale production at minimum cost. Raw materials recovery is achieved efficiently and economically, thus contributing further to economic production.

It will be apparent to those skilled in the art that various modifications may be made in the process steps and conditions described hereinbefore without departing from the spirit of this invention and the scope of the appended claims.

Having now described our invention, we claim:

1. A process for fractionating an aqueous alkaline extract of tree bark containing wax, acid soluble phenolics, fusible phenolics and infusible phenolics, comprising

(a) agitating and acidifying the extract to a pH of not more than 4.0 to form an aqueous slurry of insolubilized wax, fusible phenolics and infusible phenolics, and the acid soluble phenolics remaining in solution,

(b) extracting the acidified aqueous slurry with a water-immiscible organic solvent selected from the class consisting of alcohols, ketones, aromatic hydrocarbons, chlorinated aliphatic hydrocarbons, aliphatic hydrocarbons, or mixtures of an aliphatic hydrocarbon with up to 25% of a water-immiscible polar solvent, to form a solvent phase containing at least the wax component and an immiscible aqueous phase containing the remainder of said components,

(c) separating the immiscible aqueous and solvent phases, and

(d) separating from the respective aqueous and solvent phases the components carried therein.

2. The process of claim 1 wherein the aqueous phase contains the infusible phenolics and acid soluble phenolics, and the solvent phase contains the wax and fusible phenolics, and further comprising mixing the solvent phase with from five to ten times its weight of a hydrocarbon solvent in which the fusible phenolics are insoluble and the wax is soluble, separating the insoluble fusible phenolics from the solvent mixture, and separating the wax from the solvent mixture.

3. The process of claim 1 wherein the extracting solvent is amyl alcohol and further comprising adding to the solvent phase an amount of alkali sufficient to form a soluble alkali salt of the wax and an insoluble alkali salt of the fusible phenolics, and separating said alkali salts.

4. The process of claim 1 wherein the aqueous phase contains the fusible and infusible and soluble phenolics, and the solvent phase contains the wax, and further comprising mixing the aqueous phase with a second solvent selected from the class consisting of at least one of the isomers of amyl alcohol and methyl isobutyl ketone to form a second solvent phase containing the fusible phenolics and an aqueous phase containing the acid soluble phenolics, separating the second solvent phase from the aqueous phase, and separating from the respective aqueous and second solvent phase the fractions carried therein and separating the fusible phenolics from the second solvent phase and the infusible and acid soluble phenolics from the aqueous phase.

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