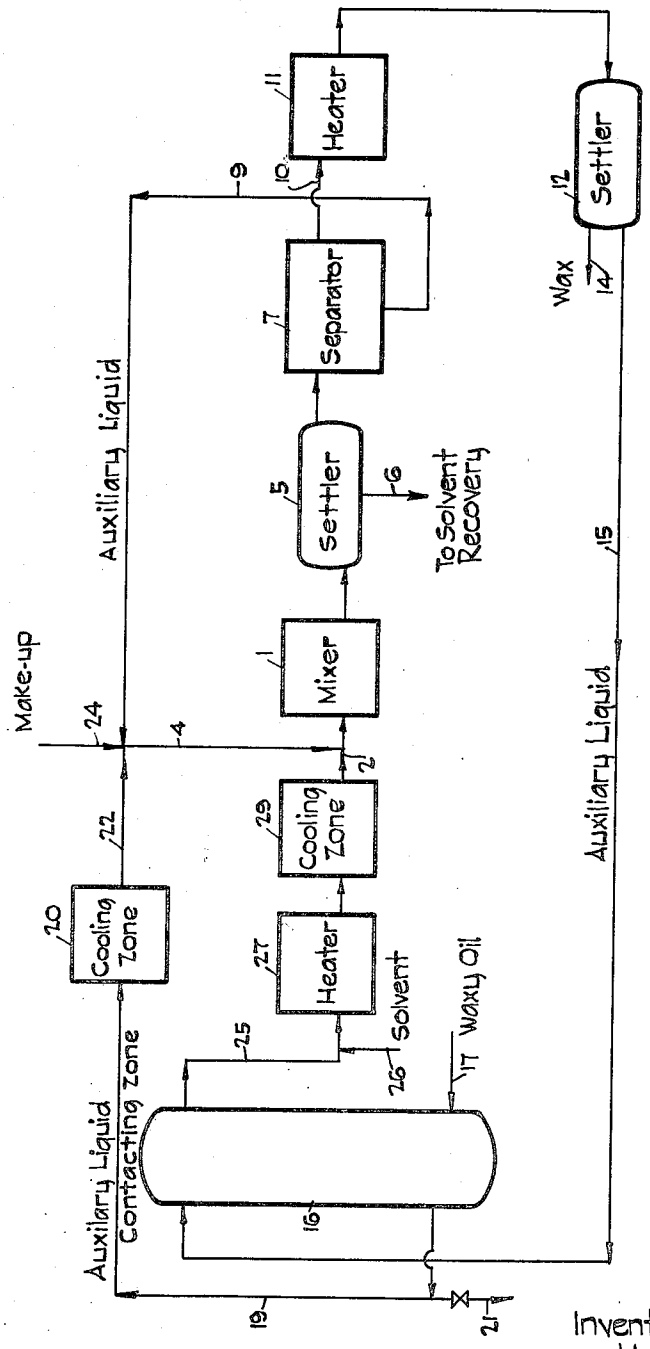
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DEWAXING MINERAL OILS

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DEWAXING MINERAL OILS

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This invention relates to a method of dewaxing waxy mineral oils or fractions thereof.

It has already been proposed to dewax wax-containing hydrocarbon oils; e. g., waxy mineral oils or fractions thereof, by contacting these wax-containing oils, preferably admixed with a suitable dewaxing solvent, at dewaxing temperatures, with an auxiliary liquid which is substantially immiscible with the waxy oil, preferably an aqueous liquid, containing a suitable surface-active agent and, if necessary, a demulsifying agent, under such circumstances that the wax passes into this auxiliary liquid. The oil phase is then separated from the resulting wax-containing auxiliary liquid, and the wax is then recovered from the auxiliary liquid phase. The separation of the wax from the auxiliary liquid can be accomplished, for example, by filtration, by centrifugation, or by heating the wax-containing auxiliary liquid phase, preferably after removal of a major portion of the auxiliary liquid therefrom, as by decanting, to obtain two immiscible liquids which can then be separated. In some cases, it may be desirable always to use fresh auxiliary liquid in the dewaxing step. Generally, however, it is preferred to recirculate the separated auxiliary liquid to the dewaxing step as the auxiliary liquid contains surface-active agent and demulsifying agent dissolved therein. Since certain undesirable substance, such as naphthenic acids, phenolates, etc., may gradually accumulate in the auxiliary phase, it is generally necessary to withdraw from the recirculating auxiliary liquid stream, either continuously or intermittently, a minor amount of auxiliary liquid in order to keep the concentration of impurities sufficiently low.

In those cases where a solvent is used in the dewaxing step, a substantial amount of solvent usually dissolves or is entrained in the auxiliary liquid phase. If the used auxiliary phase, or a portion thereof is withdrawn from circulation, the solvent dissolved or entrained therein is thus lost. When the wax-containing auxiliary liquid phase is heated to effect separation of the wax from the auxiliary liquid, the heated auxiliary liquid, before recirculation to the dewaxing step, must be cooled to dewaxing temperatures. This cooling requires a considerable amount of energy. It would, therefore, be advantageous to provide a method of dewaxing mineral oils by the above procedure wherein energy requirements and loss of solvent are kept to a minimum.

It is, therefore, a principal object of the present invention to provide an improved method of dewaxing mineral oils. Another object of the present invention is to provide an improved method of dewaxing mineral oil according to the above procedure wherein a saving of solvent and/or energy is achieved. Other objects and advantages will become apparent from the following detailed description made with reference to the accompanying drawing which is a schematic flow diagram which represents a preferred method of operation according to the present invention.

In accordance with the present invention, it has been found that in a method for dewaxing waxy oils wherein the waxy oil, preferably in admixture with a suitable dewaxing solvent, is contacted with a substantial proportion of an auxiliary liquid which is substantially immiscible therewith, and with a minor amount of a suitable surface-active agent at dewaxing temperatures and under such conditions that solid wax is preferentially wetted by the auxiliary liquid and thereby is transferred thereto, the oil phase is then separated from the resulting wax-containing

auxiliary liquid phase, and wax is recovered from the auxiliary liquid phase, the foregoing objects can be achieved by contacting at least a portion of the separated auxiliary liquid with untreated waxy oil.

Described in greater detail, the dewaxing method of the present invention comprises: (*a*) mixing the waxy oil with a substantial proportion of a dewaxing solvent which is a solvent for oil but is substantially a non-solvent for solid wax; (*b*) adjusting the temperature of the resulting mixture to obtain solid wax; (*c*) commingling the resulting oil-solvent phase containing solid wax dispersed therein with a substantial proportion of an auxiliary liquid which is substantially immiscible therewith and which has a dielectric constant higher than that of the oil-solvent phase, and with a minor amount of a surface-active agent (preferably an ionic surface-active agent); (*d*) correlating the dielectric constants of the two liquid phases so that the contact angle in the oil-solvent phase has value of at least about 90°, preferably at least about 110°, whereby the solid wax is preferentially wetted by the auxiliary liquid phase and thereby is transferred thereto; (*e*) separating the oil-solvent phase from the resulting wax-containing auxiliary liquid phase; (*f*) recovering the wax from the wax-containing auxiliary liquid phase; and (*g*) contacting, preferably in countercurrent flow, at least a portion of the separated auxiliary liquid with the untreated waxy oil charge stock.

The contact angle, generally represented by the symbol θ, is the angle which the interfacial tension of the two liquid phases, represented by γ, forms with the solid wax.

An organic solvent is generally employed in the above-described dewaxing operation. The organic solvent used should be a good dewaxing solvent, that is, it should be a good solvent for oil, but substantially a non-solvent for solid wax. Suitable dewaxing solvents include halogenated hydrocarbons such as ethylene dichloride, ethylene dibromide, chloroform, carbon tetrachloride, ethyl chloride, propyl chloride, ethyl bromide, propyl bromide, trichloroethane, tetrachloroethane, propylene chloride, trimethylene chloride, amyl bromide, tertiary amyl chloride, butyl chloride, butyl bromide, allyl bromide, beta,-beta'-dichlorodiethyl ether, chlorobenzene, bromobenzene, o-dichloro-benzene, tetrachloroethylene, tetrafluoroethylene, 2-chlorophenyl amine, 3-chlorophenylamine, and 1-amino-2-fluorobenzene, aliphatic and aromatic hydrocarbons such as petroleum ether, petroleum naphtha, gasoline, pentane, isopentane, hexane, heptane, octane, benzene, propylbenzene, cumene, amylbenzene, toluene, xylene, and cymene; ketones such as methyl isopropyl ketone, methyl isobutyl ketone, methyl ethyl ketone and mixtures thereof with hydrocarbons such as benzene and/or toluene; and other compounds such as nitrobenzene, furfural, aniline, toluidine, o-amino-ethylbenzene, m-aminoethylbenzene, N-methylaniline, N-ethylphenylamine, p-methoxy-aniline, 1 ethoxybutane, and methyl phenyl ether as well as various mixtures thereof, and with other solvents.

It is preferred that the dielectric constant of the oil-solvent phase be from about 2 to about 15, and preferably from about 3 to about 10.

The solvent is employed in the ratio of from about 3 to about 10 parts by weight of solvent to 1 part of oil.

The auxiliary liquid employed should have a higher dielectric constant than the oil phase and should be substantially immiscible therewith. In general, the auxiliary liquid should be strongly polar in character. Water, or an aqueous liquid is, therefore, preferred. As a rule, at least 50% of the auxiliary liquid consists of water. Lower alcohols, glycol or glycerol can be used alone as the auxiliary liquid, but combinations thereof with water are generally preferred. In order to lower the freezing point of water, salts, such as NaCl or $CaCl_2$, or alcohols, such as methyl or ethyl alcohol or ethylene glycol, can be added. The amount of auxiliary liquid employed should be sufficient to enable it to readily absorb the wax particle. The volume ratio of auxiliary liquid to oil phase should be at least 1:1, preferably in the range of from about 1:1 to about 3:1.

It is preferred that the auxiliary liquid phase have a pH value of greater than 7 since the contact angle increases as the pH of the auxiliary liquid phase increases.

Furthermore, a pH of greater than 7 promotes the formation of the more desirable oil-in-water emulsion (which is temporary) rather than a water-in-oil emulsion. The pH value of the auxiliary liquid phase can be adjusted, for example, by the addition of a minor amount of a basic substance such as an aqueous sodium hydroxide solution.

The surface-active agent must be selected so that, together with the correct adjustment of the dielectric constants of the two liquid phases, the contact angle of the solid wax in the oil phase is greater than 90°. The surface-active agent can be added to either the oil phase or the auxiliary liquid. It is preferred that the surface-active agent be soluble in the auxiliary phase since the auxiliary phase is generally recirculated. Either anionic or cationic surface-active agents can be used. Preferred surface-active agents are those which contain one or more alkyl radicals having 8 or more carbon atoms connected to a strongly polar group.

Anionic type surface-active agents are represented by the aliphatic and aromatic sulfates and sulfonates, particularly alkylated aromatic sulfonates, and salts of organic compounds of phosphorus. Specific examples include the alkali metal, particularly sodium salts of: dioctylbenzene sulfonic acid, the dioctyl ester of sulfosuccinic acid, and alkylated aryl polyether sulfate, a fatty acid ester of sulfoacetamide, a sulfonated fatty acid amide, a mixture of dibutylnaphthalene sulfonic acid and diisopropylnaphthalene sulfonic acid, dodecylbenzene sulfonic acid, mixtures of C_9-C_{13}-benzene sulfonic acids, heptadecyl-9-sulfate, tricosanyl-12-sulfate, di-3,5,5-trimethylhexyl phosphate and dioctyl phosphate.

Suitable cationic surface-active agents include the quaternary ammonium halides, such as stearyl dimethyl benzyl ammonium chloride.

Certain cationic agents, such as octadecylamine and dodecylamine are not sufficiently polar to dissolve in the auxiliary liquid. By adding an acid, e. g., HCl, whereby the corresponding amine hydrochloride is formed, satisfactory results are obtained. It is preferred to add the amine to the oil phase and the acid to the auxiliary liquid.

A similar situation arises with certain anionic agents, such as oleic acid, ricinoleic acid, sulfonated ricinoleic acid ester, sulfated fatty acid esters and various naphthenic acids. Positive results can be obtained with these agents by the addition of NaOH, preferably to the auxiliary liquid.

The surface-active agent is employed in the range of from about 0.01% to about 5%, preferably from about 0.02% to about 2%, based on the auxiliary liquid.

Owing to the presence of the surface-active agent, the various interfacial tensions have become so small that the formation of emulsions can be expected in many cases. The formation of emulsions is in itself not a disadvantage as it causes intimate contact between the water and oil phases. For the subsequent separation of the solid wax and the separation of the liquid phases from each other it is, however, necessary that no stable emulsions be formed. It has been found that the addition of a demulsifier will prevent the formation of persistent emulsions without harming the activity of the surface-active agent. The demulsifier used must not, of course, precipitate the surface-active agent.

When using an anionic surface-active agent, cationic demulsifiers are generally used. Suitable cationic demulsifiers are salts of polyvalent metals, preferably divalent metals, e. g., $MgSO_4$, $MgCl_2$, $CaCl_2$, $Ni(NO_3)_2$, $Zn(NO_3)_2$, $FeSO_4$,$CuSO_4$,$CdCl_2$ and $MnSO_4$. Certain monovalent metal salts, such as the lithium and ammonium salts can be used, for example, LiCl and NH_4Cl.

When using a cationic surface-active agent, an anionic demulsifier should be used. Preferred anionic demulsifiers are salts of monovalent cations and polyvalent anions, such as Na_2SO_3, K_2CrO_4, $Na_4P_2O_7$, Na_2SO_4, Na_2CO_3, K_2CO_3, K_2S, and $Na_2S_2O_3$.

Organic demulsifiers produce no results by themselves, but are active when used together with an inorganic salt such as sodium sulfate. Suitable organic demulsifiers include cyclohexylamine, phenol, diphenylamine, amyl alcohol, dodecyl alcohol, and cyclohexanol. Non-ionic surface-active agents are also active as demulsifiers when used with an inorganic salt such as sodium sulfate. Representative non-ionic surface-active agents include esters and ethers of polyhydroxy alcohols, particularly polyglycols, e. g., the monostearate and monoleate of polyethylene glycol, polyoxyethylene derivatives of alkyl phenols, and polyoxyethylene derivatives of sorbitol esters of fatty acids.

The demulsifier is employed in the range of about 0.0005% to about 1% by weight, based on the auxiliary liquid.

The method of dewaxing waxy oils by transfer of solid wax from an oil phase to an auxiliary liquid phase, and the principles on which this method is based are described in greater detail in the copending application of Mondria et al., Serial No. 262,438, filed December 19, 1951.

The separation of wax from the wax-containing auxiliary liquid phase can be accomplished by any suitable method, for example, by filtration, by centrifuging, or by heating whereby two immiscible liquid phases are formed which liquid phases can be easily separated. When the separation is effected by filtration or by centrifuging, the separated auxiliary liquid is at a suitably low temperature. A major proportion of the separated auxiliary liquid can therefore be recycled directly to the above-described dewaxing operation. A minor proportion of the separated auxiliary liquid which is to be withdrawn from circulation in order to maintain the concentration of impurities sufficiently low, is then contacted with the untreated waxy oil charge stock according to the present invention to recover any dewaxing solvent which is entrained or dissolved therein. Thus, dewaxing solvent which ordinarily would have been discarded is recovered. When the separation of wax from the wax-containing auxiliary liquid phase involves heating, the separated auxiliary liquid must be cooled to dewaxing temperatures before being recycled to the dewaxing step. In this case, the entire amount of separated auxiliary liquid is contacted with the untreated waxy oil charge stock whereby the auxiliary liquid is at least partially cooled to dewaxing temperatures. The untreated waxy oil is also heated, which is advantageous since, when a dewaxing solvent is employed, the mixture of waxy oil and solvent is generally heated until one liquid phase is obtained, and the mixture is then cooled to solidify the wax therein. The auxiliary liquid, cooled by contact with untreated waxy oil is then further cooled, if necessary, to dewaxing temperatures. A minor amount of auxiliary liquid can be bled off, either continuously or intermittently, after contact with the waxy oil to keep the concentration of undesirable impurities at a minimum. By the foregoing method, a considerable amount of heat energy is conserved.

According to a preferred method of separating wax from the wax-containing auxiliary liquid phase, a major proportion, for example from about 50% to about 80%, preferably from about 55% to about 75%, of the auxiliary liquid is first removed, for example, by crude filtration or by decanting. The auxiliary liquid thus separated is at a suitably low temperature and can be recycled directly to the above-described dewaxing operation. The mixture of solid wax and the remainder of the auxiliary liquid is then heated to obtain two immiscible liquid phases which are readily separated. The heated auxiliary liquid thus separated is then contacted with at least a portion of the untreated waxy oil charge stock whereby the auxiliary liquid is cooled and the waxy oil is heated, and whereby any solvent entrained or dissolved in the auxiliary liquid is transferred to the waxy oil. The auxiliary liquid can then be further cooled, if necessary, and returned to the dewaxing operation. After contact with the waxy oil, a minor amount of auxiliary liquid can be removed from circulation in order to maintain the concentration of undesirable impurities sufficiently low.

The auxiliary liquid is preferably contacted with the untreated waxy oil prior to mixing the waxy oil with dewaxing solvent. In some cases, however, for example, in the dewaxing of viscous oils, it may be desirable to add at least a portion of the dewaxing solvent before contact of the waxy oil with the auxiliary liquid. The auxiliary liquid is generally contacted with only a portion of the total amount of waxy oil to be dewaxed.

Prior to direct contact of auxiliary liquid and untreated waxy oil, the auxiliary liquid and the untreated waxy oil can be contacted in indirect heat exchange relationship.

The invention will be better understood from the following detailed description made with reference to the accompanying drawing which is a schematic flow diagram representing a preferred method of operation according to the present invention.

Now referring to the drawing, a mixture of waxy oil and dewaxing solvent (for example, ethylene dichloride), suitably cooled to the dewaxing temperature, is introduced into mixer **1** by means of line **2**. A suitable auxiliary liquid (preferably water) containing a surface-active agent and a demulsifier, which liquid has been cooled to the dewaxing temperature, is introduced into mixer **1** by means of line **4**. The resulting mixture is transferred to a settling zone **5** and is permitted to settle to obtain an oil-solvent phase and a solid wax-containing auxiliary liquid phase. The oil phase is removed from the settling zone **5** by means of line **6** and is passed to a solvent recovery unit, not shown. The wax-containing auxiliary liquid phase is passed to a separation zone **7** wherein a major portion of the auxiliary liquid is separated from the wax-containing auxiliary liquid phase, for example, by decanting or by crude filtration. The thus separated auxiliary liquid is recycled to mixer **1** by means of line **9**. The mixture of solid wax and the remainder of the auxiliary liquid is passed by means of line **10** to a heating zone **11** wherein the mixture is suitably heated to a temperature (about 80° C.) at which the wax is liquefied. The heated mixture is transferred to a settling zone **12**. Liquefied wax is removed from settling zone **12** by means of line **14**. The separated, heated auxiliary liquid is transferred via line **15** to a contacting zone **16** wherein it is countercurrently conducted with waxy oil introduced into contacting zone **16** by means of line **17**. Any solvent entrained or dissolved in the auxiliary is thereby transferred to the waxy oil. The auxiliary liquid, cooled by contact with the incoming waxy oil, is passed by means of line **19** to a cooling zone **20** wherein it is suitably cooled to dewaxing temperatures. Where dewaxing temperatures of about room temperature are employed, cooling can be effected in a cooling tower. If any wax passes into the auxiliary liquid in the contacting zone **16** (this generally does not occur), it is advisable to remove the wax prior to further cooling. A minor amount of auxiliary liquid is intermittently removed from line **19** by means of line **21** in order to maintain the concentration of undesirable impurities sufficiently low. The cooled auxiliary liquid from cooling zone **20** is returned to mixer **1** by means of line **22**. Make-up auxiliary liquid is supplied to mixer **1** by means of line **24**.

The waxy oil, heated by contact with the auxiliary liquid in contacting zone **16**, is removed therefrom by means of line **25**, and is mixed with a suitable dewaxing solvent introduced by means of line **26**. The resulting mixture is transferred to heating zone **27** wherein the mixture is suitably heated until one liquid phase is obtained. The heated mixture is then passed to cooling zone **29** wherein it is suitably cooled to dewaxing temperatures. The cooled mixture, containing solid wax dispersed therein is then transferred to mixer **1** for admixture with auxiliary liquid from line **4**.

The above-described dewaxing operation can be carried out in a number of stages at successively decreasing dewaxing temperatures, thereby obtaining a fractionation of the wax. Other modifications are also apparent from the foregoing description. For example, a portion of the oil phase can be separated from the solidified wax prior to contact with the auxiliary liquid.

It is to be understood that the waxy oil and the solvent can be chilled to dewaxing temperatures, either separately or in admixture, prior to contact with the auxiliary phase. Moreover, the auxiliary phase can be mixed with the oil phase prior to chilling.

I claim as my invention:

1. A method for dewaxing waxy oils which comprises: (1) mixing a waxy oil with a substantial proportion of an organic polar solvent which is a solvent for oil but which is substantially a non-solvent for solid wax and heating the mixture until a single liquid phase is formed; (2) cooling the mixture to a dewaxing temperature at which the wax solidifies, thereby forming a dispersion of solid wax particles in a liquid oil phase which is a solution of the oil and solvent; (3) intimately mixing the resulting dispersion of solid wax dispersed in the oil phase with a substantial proportion, at least equal in volume to the volume of the oil phase, of an aqueous liquid, at the dewaxing temperature, a minor amount of an ionic surface-active agent, and a minor amount of a demulsifying agent, whereby two liquid phases result, an oil phase containing dissolved minor amounts of the aqueous liquid, surface-active agent and demulsifying agent and an aqueous phase containing dissolved minor amounts of oil, solvent, surface-active agent and demulsifying agent, the dielectric constants of the two liquid phases being correlated so that the contact angle in the oil phase is at least 90°, whereby the solid wax is preferentially wetted by the aqueous phase and is transferred thereto to produce a dispersion of the solid wax in the aqueous phase as continuous phase, while the oil phase is substantially free from solid wax; (4) stratifying and separating the oil phase from the aqueous phase containing the dispersion of solid wax; (5) removing a major proportion of the liquid aqueous phase from the wax-containing aqueous phase at essentially the dewaxing temperature while maintaining the solid wax dispersed in a minor portion of the aqueous phase; (6) recycling the removed major proportion of aqueous phase, while maintaining the temperature thereof at essentially the dewaxing temperature, for contact with a further portion of oil phase containing solid wax dispersed therein in accordance with foregoing step (3); (7) heating the remaining minor portion of the aqueous phase containing the solid wax to a temperature at which the wax is liquefied and stratifying and separating the resulting liquefied wax and the minor portion of aqueous phase; (8) intimately contacting the thus heated and separated minor portion of aqueous phase with untreated waxy oil to be dewaxed in accordance with the foregoing steps to transfer at least a portion of the solvent therein and sensible heat thereof to the waxy oil; and (9) recycling the thus contacted minor portion of aqueous liquid for contact at the dewaxing temperature with a further portion of oil phase containing solid wax dispersed therein in accordance with foregoing step (3).

2. The method according to claim 1, wherein the dielectric constants of the two liquid phases are correlated so that the contact angle in the oil phase is at least 110°.

3. A method for dewaxing waxy oil which comprises: (1) mixing a waxy oil with a substantial proportion of an organic polar solvent which is a solvent for oil but which is substantially a non-solvent for solid wax; (2) adjusting the temperature of the resulting mixture to a dewaxing temperature at which the wax solidifies, thereby forming a dispersion of solid wax particles in a liquid oil phase which is a solution of the oil and solvent; (3) commingling the resulting dispersion of solid wax dispersed in the oil phase with a substantial proportion, at least equal in volume to the volume of the oil phase, of an aqueous liquid, at the dewaxing temperature, a minor amount of an ionic surface-active agent, and a minor amount of a demulsifying agent, whereby two liquid phases result, an oil phase containing dissolved minor amounts of the aqueous liquid, surface-active agent and demulsifying agent and an aqueous phase containing dissolved minor amounts of oil, solvent, surface-active agent and demulsifying agent, the dielectric constants of the two liquid phases being correlated so that the contact angle in the oil phase is at least 90°, whereby the solid wax is preferentially wetted by the aqueous phase and is transferred thereto to produce a dispersion of the solid wax in the aqueous phase as continuous phase, while the oil phase is substantially free from solid wax; (4) separating the oil phase from the aqueous phase containing the dispersion of solid wax; (5) separating wax from the aqueous phase; and (6) contacting at least a portion of the resulting separated aqueous phase with untreated waxy oil, to be dewaxed in accordance with the foregoing steps, to transfer a portion of the solvent therein to the waxy oil.

4. The method according to claim 3, wherein the separated aqueous phase is countercurrently contacted in step (6) thereof with the untreated waxy oil.

5. The method according to claim 3, wherein the organic polar solvent is ethylene dichloride.

6. The method according to claim 3, wherein the organic polar solvent is ethylene dichloride, the ethylene dichloride is employed in the ratio of from about 3 to about 10 parts by weight to 1 part of oil, and wherein the volume ratio of the aqueous liquid in step (3) to oil phase is from about 1:1 to about 3:1.

7. A method for dewaxing waxy oil which comprises: (1) mixing a waxy oil with a substantial proportion of an organic solvent which is a solvent for oil but which is substantially a non-solvent for solid wax; (2) adjusting the temperature of the resulting mixture to a dewaxing temperature at which the wax solidifies, thereby forming a dispersion of solid wax particles in a liquid oil phase

which is a solution of the oil and solvent; (3) commingling the resulting dispersion of solid wax dispersed in the oil phase with a substantial proportion, at least equal in volume to the volume of the oil phase, of an auxiliary liquid which is substantially immiscible therewith and which has a dielectric constant higher than that of the oil phase, the auxiliary liquid being at the dewaxing temperature, and with a minor amount of an ionic surface-active agent, whereby two liquid phases result, an oil phase containing dissolved minor amounts of the auxiliary liquid and surface-active agent and an auxiliary liquid phase containing dissolved minor amounts of oil, solvent and surface-active agent, the dielectric constants of the two liquid phases being correlated so that the contact angle in the oil phase is at least 90°, whereby the solid wax is preferentially wetted by the auxiliary liquid phase and is transferred thereto to produce a

dispersion of the solid wax in the auxiliary liquid phase as continuous phase, while the oil phase is substantially freed from solid wax; (4) separating the oil phase from the auxiliary liquid phase containing the dispersion of solid wax; (5) separating wax from the auxiliary liquid; and (6) contacting at least a portion of the resulting separated auxiliary liquid with untreated waxy oil, to be dewaxed in accordance with the foregoing steps, to transfer a portion of the solvent therein to the waxy oil.

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