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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 polar 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. Separation of the wax from the auxiliary liquid is generally accomplished by removing as much of the auxiliary liquid as possible by filtration. The resulting wax phase is still contaminated with a considerable amount of the auxiliary liquid. For example, when filtering the wax from the wax-containing auxiliary liquid phase, a sponge-like cake of wax is obtained, the water content of which may be several times that of the wax. The wax is usually removed from the remaining auxiliary liquid by heating the mixture to a temperature (about 70° C.) at which the wax liquefies. Two immiscible liquid phases, which can be readily separated, as by decanting, are formed. This heating operation, however, requires a considerable amount of energy, since a highly polar liquid, and particularly water, possesses a high specific heat. Furthermore, before recirculation of the separated auxiliary liquid to the above-described dewaxing operation, it must be cooled to the dewaxing temperature.

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 oils according to the above-outlined procedure wherein a saving of energy is achieved in the separation of the wax from the wax-containing auxiliary liquid phase. Other objects and advantages will become apparent from the following detailed description.

In accordance with the present invention, it has been found that in a method of dewaxing waxy oils wherein the waxy oil, preferably in admixture with a suitable dewaxing solvent, is contacted with a substantial proportion of a substantially polar 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, and the oil phase is then separated from the resulting wax-containing auxiliary liquid phase, the foregoing objects can be achieved by contacting the wax-containing auxiliary liquid phase with an organic liquid which is substantially less polar than the auxiliary liquid and substantially immiscible therewith under such conditions that the contact angle of the solid wax in the organic liquid phase is less than 90°, whereby

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the solid wax is transferred to the organic liquid phase.

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 a substantially polar 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 of the solid wax in the oil-solvent phase has a 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) commingling the wax-containing auxiliary liquid phase with a substantial proportion of an organic liquid which is substantially less polar than the auxiliary liquid, preferably a substantially non-polar organic liquid, and which is substantially immiscible with the auxiliary liquid, under such conditions that the contact angle of the solid wax in the organic liquid is less than 90° whereby the solid wax is transferred to the organic liquid; (g) separating the resulting wax-containing organic liquid phase from the polar auxiliary liquid; and (h) recovering wax from the wax-containing organic liquid. The separated polar auxiliary liquid can be recirculated for contact with further portions of solid wax-containing oil-solvent phase.

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-chlorophenylamine, 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-aminoethylbenzene, 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 CaCl₂, 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 dibutyl-naphthalene sulfonic acid and diisopropyl-naphthalene sulfonic acid, dodecylbenzene sulfonic acid, mixtures of C₈-C₁₃-benzene sulfonic acids, heptadecyl-9-sulfate, tricosanyl-12-sulfate, di-3,5,5-trimethyl-hexyl phosphate and dicotyl 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., MgSO₄, MgCl₂, CaCl₂, Ni(NO₃)₂, Zn(NO₃)₂, FeSO₄, CuSO₄, CdCl₂ and MnSO₄. Certain monovalent metal salts, such as the lithium and ammonium salts can be used, for example, LiCl and NH₄Cl.

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 Na₂SO₃, K₂CrO₄, Na₄P₂O₇, Na₂SO₄, Na₂CO₃, K₂CO₃, K₂S, and Na₂S₂O₃.

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 monooleate 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 organic liquid employed in the separation of the solid wax from the auxiliary liquid in accordance with the principles of the present invention should be substantially less polar than the auxiliary liquid and substantially immiscible therewith. Substantially non-polar organic liquids, such as hydrocarbons, are preferred. It is also preferable to use a relatively low boiling organic liquid, that is, one boiling below about 125° C., and preferably below about 100° C., so that the wax can readily be separated therefrom by distillation. The most suitable organic liquids are hydrocarbons having less than about 10 carbon atoms per molecule, preferably less than about 8 carbon atoms per molecule, and particularly the lower alkanes, such as propane, butane, pentane, hexane, and heptane, and the relatively low boiling aromatics, such as benzene and toluene. The lower molecular weight aliphatic ketones, such as methyl ethyl ketone and methyl isobutyl ketone, can also be employed. It is preferred to saturate the organic liquid with wax prior to admixture thereof with the solid wax-containing auxiliary liquid to substantially prevent dissolution of the solid wax in the organic liquid.

In order that the solid wax be transferred from the polar auxiliary liquid to the substantially less polar organic liquid, it is necessary that the contact angle of the solid wax in the organic liquid be less than 90°. This condition can be satisfied by suitably selecting the organic liquid, by adjusting the pH value and/or the temperature of the auxiliary phase, by changing the nature and/or the quantity of the auxiliary phase and/or by changing the quantity and/or the nature of the surface-active substance present in the auxiliary phase. The most attractive method of operation, particularly in a continuous operation, is to meet the above condition by suitably selecting the organic liquid so that the wax is immediately transferred from the polar auxiliary liquid to the less polar organic liquid. By selecting a non-polar organic liquid

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such as the hydrocarbons described, the wax is immediately transferred from the polar auxiliary liquid to the non-polar organic liquid without any changes or adjustments in the nature of the mixture.

In practice, the solid wax-containing auxiliary liquid phase obtained from the above-described dewaxing operation is suitably mixed with a substantial proportion, for example, from about 100% to about 500% by weight, based on the waxy oil charge stock, of the less polar organic liquid. If desired, a portion of the auxiliary liquid can be removed, as by decanting or by filtration, from the wax-containing auxiliary liquid phase prior to the admixture with the less polar organic liquid. The organic liquid employed is preferably at the same temperature as the solid wax-containing auxiliary liquid phase. Two liquid phases are formed, the wax having merged into the organic liquid phase. The polar auxiliary liquid is readily separated from the wax-containing organic liquid, as by decantation. The separated polar auxiliary liquid phase is generally recycled for contact with further portions of solid wax-containing oil-solvent phase as described above. Since the auxiliary phase has not been heated, no cooling is required prior to recycling. The wax is readily recoverable from the organic liquid by distillation, if desired, after removal of a portion of the organic liquid, as by decantation or filtration. The separated organic liquid can be recycled, after cooling to the desired temperature, for contact with further portions of solid wax-containing auxiliary liquid phase.

By the practice of the present invention, it is possible to avoid filtration entirely, while at the same time, conserving a considerable amount of energy heretofore consumed in heating the wax-containing auxiliary liquid phase to a temperature at which the wax liquefies and, after separation of the wax from the auxiliary liquid, in cooling the separated auxiliary liquid to dewaxing temperatures for recirculation to the dewaxing step. Furthermore, there is loss of surface-active agent. Substantially all of the surface-active agent adsorbed on the paraffin wax crystals remains in or reenters into the auxiliary liquid. Thus, substantially all of the surface-active agent employed in the dewaxing operation can be recycled directly to the dewaxing step together with the separated auxiliary liquid.

The following examples serve to illustrate the process of the present invention:

Example I

A distillate from an Indonesian crude oil was diluted at a temperature of about 70° C. with about 300% by weight, based on the waxy distillate, of ethylene dichloride, and the mixture was subsequently slowly cooled (in about 45 minutes), with stirring, to a temperature of about 20° C. The resulting slurry was mixed with about 400% by weight, based on the waxy distillate, of water containing about 0.027% by weight of sodium dodecyl benzene sulfonate (propylene tetramer) and about 0.8% by weight of NaOH. The mixture was permitted to settle, and two sharply divided phases were obtained, an oil-ethylene dichloride phase and a solid wax-containing aqueous phase. After separation of the oil-ethylene dichloride phase, the solid wax-containing aqueous phase was stirred for about ½ minute with about 300% by weight, based on the waxy distillate, of pentane maintained at 20° C. and saturated with solid paraffin wax as the less polar organic liquid. The mixture was permitted to settle, and two phases were formed, an aqueous phase and a solid wax-containing pentane phase. A major portion of the pentane was removed by decanting, and the remainder was removed by distillation. The separated pentane can be recycled for admixture with further portions of solid wax-containing aqueous phase.

Similar results can be obtained with the use of a reduced amount of pentane, for example with about 150% by weight, based on the waxy distillate.

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Example II

A solid wax-containing aqueous phase obtained in the same manner as described in Example I, was stirred for ½ minute with about 300% by weight, based on the waxy distillate, of methyl ethyl ketone maintained at 20° C. and saturated with wax. The mixture was permitted to settle and two sharply divided phases were formed. The wax had merged quantitatively into the ketone phase. After separation of the aqueous phase, the wax was separated from the methyl ethyl ketone by decantation followed by distillation.

Example III

A slurry of solid wax in a mixture of oil and ethylene dichloride obtained in the same manner as described in Example I, was mixed with stirring for about ½ minute with about 400% by weight based on the waxy distillate, of water containing about 0.1% by weight of sodium dodecyl benzene sulfonate (propylene tetramer) as surface-active agent, about 0.16% by weight of NaOH, and about 0.01% by weight of MgSO₄ as demulsifier. The mixture was permitted to settle, and two phases were obtained. The wax had been transferred to the aqueous phase. After separation of the oil-ethylene dichloride phase therefrom, the solid wax-containing aqueous phase was stirred for about ½ minute with about 300% by weight, based on the waxy distillate, of n-heptane maintained at about 20° C. and saturated with solid wax. The mixture was permitted to settle, and two sharply divided phases were formed, an aqueous phase and a solid wax-containing n-heptane phase. After separation of the aqueous phase, the wax was separated from the n-heptane by decantation, followed by distillation.

I claim as my invention:

1. In a method of dewaxing a waxy mineral oil, the combination of steps comprising: (1) mixing the waxy mineral oil with a substantial proportion of a dewaxing solvent which is a solvent for the mineral oil but which is substantially a non-solvent for solid wax, and adjusting the temperature of the mixture to obtain a single liquid phase of the solvent, oil and wax; (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 the 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 a substantially polar auxiliary liquid which is substantially immiscible therewith and which has a dielectric constant higher than that of the oil phase, the auxiliary liquid being essentially at the dewaxing temperature, and with a minor amount of a surface-active agent, whereby two liquid phases result, an oil phase consisting essentially of mineral oil and solvent and an auxiliary liquid phase containing dissolved said surface-active agent, and correlating the dielectric constants of the two liquid phases 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) stratifying and separating the oil phase from the auxiliary liquid phase containing the dispersion of solid wax; (5) commingling the wax-containing auxiliary liquid phase with an organic liquid, which is substantially less polar than said auxiliary liquid and is substantially immiscible therewith, under conditions such that the contact angle of the solid wax in the organic liquid phase is less than 90°, whereby the wax is transferred to said organic liquid phase; and (6) stratifying and separating the organic liquid phase containing the wax dispersed therein from the auxiliary liquid phase.

2. The method according to claim 1, wherein the organic liquid is a substantially non-polar organic liquid.

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3. The method according to claim 1, wherein the organic liquid is a substantially non-polar organic liquid having a boiling point below about 125° C.

4. The method according to claim 1, wherein the auxiliary liquid is a substantially aqueous liquid, and wherein the organic liquid is a substantially non-polar organic liquid having a boiling point below about 125° C.

5. The method according to claim 1, wherein the auxiliary liquid is a substantially aqueous liquid, wherein the surface-active agent is an ionic surface-active agent, and wherein the organic liquid is a substantially non-polar organic liquid having a boiling point below about 125° C.

6. The method according to claim 1, wherein the auxiliary liquid is a substantially aqueous liquid, wherein the surface-active agent is an ionic surface-active agent, and wherein the organic liquid is a hydrocarbon having a boiling point below about 125° C.

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7. The method according to claim 6, wherein the hydrocarbon is essentially pentane.

8. The method according to claim 1, wherein the dewaxing solvent is ethylene dichloride, wherein the auxiliary liquid is a substantially aqueous liquid, wherein the surface-active agent is a water-soluble ionic surface-active agent, and wherein the organic liquid is a hydrocarbon having a boiling point below about 125° C.

9. The method according to claim 8, wherein the surface-active agent is sodium dodecyl benzene sulfonate and wherein the organic liquid is essentially pentane.

References Cited in the file of this patent

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