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DEWAXING AID

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This invention relates to the preparation and incorporation in wax-bearing mineral oil of an improved type of wax crystal regulating material and to the dewaxing of wax-bearing oil in the presence of this regulating material.

The invention contemplates employing a modified type of wax crystal regulating material derived from fatty acids, fatty oils, metal soaps of fatty acids, and fatty acid esters.

In a pending application, Serial No. 226,241, there is described a dewaxing aid having wax crystal regulating properties obtained by reacting the above-mentioned materials with aluminum chloride at a temperature of around 175° to 350° F. The reaction product is advantageously neutralized with an alkaline agent, such as ammonia, at a temperature of around 140° to 200° F. Following this, the neutralized material is subjected to further heating at a temperature of around 200° F., prior to incorporation in the wax-bearing oil, as a dewaxing aid.

The dewaxing aid thus obtained is particularly effective in the presence of a relatively dry dewaxing solvent. In the presence of small amounts of water it is apparently less effective. For example, when dewaxing wax-bearing oil by filtration with a dewaxing solvent containing around 0.25 to 1.0% by weight of water, the resulting yield of dewaxed oil may be decreased by as much as 5 to 8%. There is a corresponding increase in the wax cake, while the filtration rate is substantially reduced.

Accordingly, the present invention concerns the further treatment of the dewaxing aid prior to incorporation in the wax-bearing oil so as to render it completely effective as a dewaxing aid in the presence of a dewaxing solvent containing small amounts of water. The invention thus contemplates subjecting the dewaxing aid to hydrolysis so as to decompose and remove the relatively unstable components and which apparently interfere with the wax crystal regulating properties of the material when in the presence of a wet dewaxing solvent.

The hydrolized material, after removal of the decomposed components, may be employed as such or, if desired, may be further treated by chilling in the presence of a small amount of dewaxing solvent liquid to a temperature of 0° F. and below in order to form a precipitate comprising the active ingredients in concentrated form. The concentrated material may then be incorporated in the wax-bearing oil to be dewaxed.

It is contemplated that this method of treatment, involving hydrolysis and separation of active material under dewaxing conditions, is applicable to any dewaxing aid which tends to hydrolize in the presence of water. It has particular application to dewaxing aids containing saponifiable material and is particularly useful in connection with fatty oils, such as palm oil, which have been previously treated with aluminum chloride and neutralized with ammonia, as previously described. More specifically, the hydrolysis and separation of active material is brought about by dissolving the aluminum chloride-treated and ammonia-neutralized fatty oil product in a dewaxing solvent such as methyl ethyl ketone, isobutyl ketone, metal butyl ketone, or a mixture of methyl ethyl ketone and benzol, etc. For example: 1 part by volume of the fatty oil product is dissolved in from 1 to 10 parts of the solvent. Water is then added to the mixture in an amount equivalent to about one-half the weight of the fatty oil product. The resulting mixture is agitated and subjected to settling for a long period of time, which may be as much as two or three days, during which hydrolysis takes place.

As a result, the mixture separates into water and solvent layers. The solvent layer is removed and may be filtered to remove traces of precipitated matter. The filtered layer is then chilled to about −15 to −20° F. and filtered at that temperature to remove a precipitate consisting of the active material. The precipitated active material constitutes the improved dewaxing aid which is found to retain substantially all its effectiveness in the presence of a wet dewaxing solvent and which does not give an objectionable increase in the saponification value of the dewaxed oil.

Examples of other fatty oils, besides palm oil, which may be used as the source material, include lanolin, tallow oil and olive oil. Fatty acid esters or fatty oils, such as glycol and glycerol stearate are also contemplate. The fatty acids from which the dewaxing aid may be derived are carboxylic acids, such as stearic, palmitic, oleic, linoleic, behenic and cerotic acids. Other acids are naphthenic acids and mixtures of naphthenic acids such as obtained in the refining of petroleum. Still other acids are abietic, ricinoleic, as well as oxidation products of paraffin wax.

Metallic soaps are also contemplated, such as the polyvalent metal soaps of the foregoing acids. The metals, for example, are aluminum, lead, magnesium, zinc, chromium, etc.

The following example describes the procedure followed in preparing a dewaxing aid from palm oil:

About 10 grams of palm oil are dissolved in about 100 grams of a light paraffin pale oil having a Saybolt Universal viscosity of around 100 to 300 seconds at 100° F. Instead of light pale oil other solvents, such as benzol, may be used. Aluminum chloride is slowly added to the solution during agitation, while the solution is maintained at a temperature of around 200 to

350° F. The aluminum chloride is added to the solution in the proportion of from about one-quarter to one part by weight of aluminum chloride to one part of palm oil. Hydrogen chloride is freely liberated during the first part of the reaction. When the addition of aluminum chloride is completed the reaction product is agitated and maintained at the same temperature for a short period of time, as, for example, about thirty minutes. Thereafter, the reaction product is cooled to a temperature of about 140 to 150° F. or even to room temperature, and added to an additional quantity of the pale oil so as to form a solution of about 5% concentration.

Ammonia gas is bubbled through the mixture at a temperature ranging from room temperature to 150° F. until the solution is saturated. Following this, the reaction may be continued by maintaining the mixture at a temperature of around 175 to 200° F. for a period of from one-half to one hour.

The neutralized solution is then dissolved in a mixture of methyl ethyl ketone and commercial benzol containing around 40% methyl ethyl ketone.

Water is then added to the extent of about one-half the weight of the fatty oil and the resulting mixture submitted to agitation so as to facilitate hydrolysis. Upon standing for two or three days there is a sharp separation into layers. Centrifuging may be employed in place of settling.

The water layer is removed, while the dry solvent layer is filtered to remove traces of precipitate, the latter apparently comprising hydrolized material. The filtered layer is then chilled to —15 to —20° F. to form a precipitate comprising the active ingredients, and which precipitate is removed by filtration.

Either the above-mentioned filtered layer or the ingredients precipitated at —15 to —20° F. may be used as the dewaxing aid.

The following examples show the results obtained when dewaxing a wax distillate:

		Grams of wax cake	Yield dewaxed oil	Neutralization No.	Filtration rate
			Per cent		
A	In the absence of a wax crystal regulator and using dry solvent	146	65	0.03	Fair.
B	In the presence of palm oil	75	78	0.15	Poor.
C	In the presence of palm oil treated with aluminum chloride at about 200° F. in the proportion of 10 grams of oil to 5 grams of aluminum chloride and subsequently neutralized with ammonia at around 200° F., using dry solvent	33	86	0.07	Rapid.
D	In the presence of the same modified palm oil product of "C" but using wet solvent	59 72	78 81	0.05 0.09	Very poor. Poor.
E	In the presence of the same modified palm oil product of "C" which has been subsequently hydrolized at 75° F. and using wet solvent	50 69	81 77	0.12 0.07	Good. Rapid.
F	In the presence of a precipitate obtained by filtering the palm oil product of "E" at a temperature of around —10° F., using a wet solvent	70.5	75	0.04	Good.
G	In the presence of the filtrate obtained in filtering at —18° F. the palm oil product of "E" and also using a wet solvent	60	81	0.15	Poor.

The foregoing experiments were all made when dewaxing a wax distillate lubricating oil stock which had previously been extracted with furfural and which was derived from Mid-Continent crude. The distillate had an A. P. I. gravity of 29.2, a Saybolt Universal viscosity at 210° F. of 70, a pour test of 115° F. and a neutralization number of around 0.03.

In experiments B to G, inclusive, the palm oil or modified palm oil product was employed in conjunction with a small amount of crude montan wax. The palm oil or modified palm oil product in each experiment amounted to 0.25% by weight of the wax distillate, while the montan wax amounted to 0.05%. The dewaxing solvent consisted of a mixture of 40% methyl ethyl ketone and 60% benzol and was mixed with the oil in the proportion of two parts of solvent to one part of oil. The montan wax was dissolved in the solvent oil mixture at a temperature of around 170° F. The solution was cooled to about 130° F. and the palm oil or modified palm oil product added. The solution was chilled to a temperature of around —10° F. and filtered to produce a dewaxed oil which, after removal of the solvent, had a pour test of around 0° F. to —5° F.

In the blank test, as indicated, a wax cake of 146 grams was obtained, while the yield of dewaxed oil amounted to 65%, the rate of filtration being described as fair.

It will be noted that in all cases when dewaxing in the presence of the wax crystal regulating material the volume of wax cake was substantially reduced and the yield of dewaxed oil substantially increased.

Comparing experiments A and B, it will be seen that when untreated palm oil is used as the dewaxing aid, the resulting dewaxed oil has a relatively high neutralization number, namely 0.15. However, when the palm oil has been treated with aluminum chloride, as in the case of experiment C, the neutralization number is reduced to 0.07; also a more rapid rate of filtration appears to be realized. In addition, there is an improvement in yield of dewaxed oil and also in the reduction of wax cake volume.

On the other hand, when the modified palm oil used in experiment C is employed in dewaxing oil in the presence of a wet solvent—that is, where the solvent contains around 0.5% of water by weight—there is an appreciable decrease in the yield of dewaxed oil with a corresponding increase in the volume of the wax cake. Furthermore, the filtration rates are relatively quite poor.

As shown upon reference to the results obtained in experiment E, however, where the treated palm oil has been also hydrolized, the filtration rate is very greatly improved.

While the yields of dewaxed oil and wax cake do not differ greatly from those realized in experiment D, nevertheless, they show a substantial improvement over those obtained when using the untreated palm oil, as in experiment B.

Experiments F and G demonstrate the difference in wax crystal regulating activity as between the filtrate and the precipitate obtained by subjecting the hydrolized palm oil product to chilling at a temperature below 0° F. and filtering.

As will be seen, the precipitate comprises material of relatively greater activity, since a good rate of filtration was realized when dewaxing in the presence of this precipitate. The neutralization number of the resulting dewaxed oil was 0.04. When dewaxing in the presence of the filtrate or liquid portion, a poor rate of filtration was realized; also the neutralization number of the resulting dewaxed oil was substantially increased.

In general, it appears that when dewaxing in the presence of the precipitated type of regulating material, as used in experiment F, the resulting dewaxed oil has a saponification number of less than 0.05, whereas in the case of dewaxing in the presence of the material used in experiment G, the saponification number is in excess of 0.05.

While the dewaxing of a wax distillate has been described in the foregoing examples, it is contemplated that the process is applicable to the dewaxing of other types of wax-bearing oils, including residual lubricating oil stocks.

Various solvents can be used for dewaxing, including the well-known and conventional dewaxing solvents and solvent mixtures. Satisfactory results are obtained by the use of a mixture of a wax anti-solvent and an oil solvent such as a mixture of acetone and benzol, methyl ethyl ketone and benzol, methyl ethyl ketone and isopropyl ether, acetone with benzol and toluol.

The hydrocarbon diluent type of solvent, such as propane, butane and gasoline, may be employed.

While aluminum chloride has been mentioned as the treating agent, it is contemplated that other catalytic agents may be employed, as, for example, ferric chloride. Also other neutralization agents may be employed, such as sodium hydroxide, potassium hydroxide, methyl amine, calcium oxide, etc.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. The method of preparing a modified form of wax crystal regulator suitable as a dewaxing aid from a compound selected from the group consisting of fatty oils, fatty acids and the soaps and esters thereof having wax crystal regulating properties which comprises dissolving the compound in a low viscosity mineral lubricating oil, slowly adding aluminum chloride to the said solution during agitation thereof and while maintaining the solution at a temperature of about 200° to 350° F., continuing the agitation at elevated temperature for a few minutes after the addition of the chloride has been completed, treating the reaction product with an alkaline neutralizing agent, dissolving the neutralized product in a dewaxing solvent liquid, incorporating water in the solution in an amount equal to about half of the dissolved product by weight, subjecting the solution to prolonged contact with the added water, thereafter subjecting the mixture to phase separation forming a water phase and a solvent phase comprising hydrolyzed material, removing the water phase, chilling the solvent phase to a temperature of about −15° to −20° F. and separating therefrom a precipitate comprising wax crystal regulating material.

2. The method of preparing a modified form of wax crystal regulator suitable as a dewaxing aid from a compound selected from the group consisting of fatty oils, fatty acids and the soaps and esters thereof having wax crystal regulating properties which comprises dissolving the compound in a low viscosity mineral lubricating oil, slowly adding to said solution aluminum chloride in the proportion of about one-quarter to one part by weight of aluminum chloride to one part of the compound, agitating the solution during such addition and maintaining it at a temperature of about 200° to 350° F. for a period not in excess of about 30 minutes after the addition is completed, treating the reaction product with an alkaline neutralizing agent while relatively hot, thereafter subjecting the treated mixture to heating at a temperature of about 175° to 200° F. for a short period of time, dissolving the heated product in a dewaxing solvent liquid, subjecting the solution to intimate contact with a substantial quantity of water for a prolonged period of time so as to effect decomposition of relatively unstable constituents, separating the mixture into a water phase and a solvent phase comprising the wax crystal regulating material and rejecting said water phase.

3. The method of preparing a modified form of wax crystal regulator suitable as a dewaxing aid from a compound selected from the group consisting of fatty oils, fatty acids and the soaps and esters thereof having wax crystal regulating properties which comprises dissolving the compound in a low viscosity mineral lubricating oil, slowly adding to said solution aluminum chloride in the proportion of about one-quarter to one part by weight of aluminum chloride to one part of the compound, agitating the solution during such addition and maintaining it at a temperature of about 200 to 350° F. for a period not in excess of 30 minutes after the addition is completed, treating the reaction product with ammonia at a temperature of about 140 to 150° F., and subjecting the treated product to heating at a temperature of about 175 to 200° F. for about 30 to 60 minutes, dissolving the heated product in a dewaxing solvent liquid, subjecting the solution to intimate contact with a substantial quantity of water for a prolonged period of time so as to effect decomposition of relatively unstable constituents, separating the mixture into a water phase and a solvent phase comprising the wax crystal regulating material and rejecting said water phase.

4. The method according to claim 1 in which the fatty oil compound comprises aluminum stearate.

5. The method according to claim 1 in which the fatty oil compound comprises stearic acid.

6. The method according to claim 2 in which the fatty oil compound comprises aluminum stearate.

7. The method according to claim 2 in which the fatty oil compound comprises stearic acid.

8. A wax crystal regulating material suitable as a dewaxing aid comprising the product obtained by reacting a compound selected from the group consisting of fatty oils, fatty acids and the soaps and esters thereof while dissolved in a low viscosity mineral lubricating oil with aluminum chloride in the proportion of about one-quarter to one part by weight of aluminum chloride per part of fatty oil compound at a temperature of about 200 to 350° F., continuing the reaction for a few minutes, treating the reaction product with ammonia at a temperature of about 140 to 150° F., subjecting the so treated reaction product to heating at a temperature of about 175 to 300° F. for around 30 to 60 minutes, dissolving the heated product in a solvent mixture composed of methylethyl ketone and commercial benzol containing 40% of the ketone, subjecting the solution to intimate contact with a substantial quantity of water for a prolonged period of time so as to effect decomposition of relatively unstable constituents, thereafter separating the mixture into a water phase and a solvent phase comprising the wax crystal regulating material, rejecting the water phase, chilling the solvent phase to a temperature of about −15 to −20° F. and separating therefrom a precipitate comprising the wax crystal regulating material.

9. A wax crystal regulating material suitable as a dewaxing aid comprising the product obtained by reacting a compound selected from the group consisting of fatty oils fatty acids and the soaps and esters thereof, while dissolved in a low viscosity mineral lubricating oil with aluminum chloride in the proportion of about one-quarter to one part by weight of aluminum chloride per part of said compound at a temperature of about 200 to 350° F., continuing the reaction for a few minutes, diluting the resulting reaction product with an additional quantity of said low viscosity oil to form a solution of about 5% concentration, treating the solution with ammonia at a temperature of about 140 to 150° F., subjecting the said ammonia treated solution to heating at a temperature of about 175 to 300° F. for about 30 to 60 minutes, dissolving the heated product in a solvent mixture composed of methylethyl ketone and commercial benzol containing 40% of the ketone, subjecting the solution to intimate contact with a substantial quantity of water for a prolonged period of time so as to effect decomposition of relatively unstable constituents, thereafter separating the mixture into a water phase and a solvent phase comprising the wax crystal regulating material, removing the water phase, chilling the solvent phase to a temperature of about −15 to −20° F. and separating therefrom a precipitate comprising the wax crystal regulating material.

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