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DEWAXING WAX-BEARING MINERAL OIL

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6 Claims. (Cl. 196—18)

This invention relates to the separation of wax from mineral oil.

The invention contemplates a process of dewaxing wax-bearing mineral oil containing either a naturally-occurring or an added wax crystal modifying substance wherein the oil is mixed with a dewaxing solvent liquid and the mixture of oil and solvent then heated to an elevated temperature substantially above the minimum temperature at which the wax-bearing oil appears to be in complete solution in the solvent. Thereafter, the heated mixture is chilled to precipitate the wax constituents which are subsequently removed.

The invention has reference to dewaxing with a solvent composed of mixed aliphatic ketones, and particularly a mixture composed of a high molecular weight member of the series of aliphatic ketones, and a relatively low molecular weight member of the same series, such as disclosed in my copending application, Serial No. 20,193, filed May 7, 1935, for Dewaxing hydrocarbon oil.

The invention is particularly adapted to dewaxing relatively viscous oils having a Saybolt Universal viscosity above 80 seconds at 210° F. as, for example, an oil of around 90 or 100 seconds at 210° F. containing naturally-occurring asphaltic and resinous constituents which apparently modify the crystal form of the wax, as will be more fully explained below. The invention involves dewaxing oil of this character under conditions such that these naturally-occurring constituents apparently assist crystallization of the wax in a more readily separable and filterable form.

The invention is also applicable to dewaxing less viscous oils to which wax crystal modifying material has been added. Relatively low viscosity oils, and especially low viscosity distillate oils, are deficient in the naturally-occurring modifying material above referred to and, therefore, it is advantageous to add a modifying material to these oils, and dewax them by the process of my invention. The addition of this material to the more viscous oils may also result in further improvement when dewaxed by my process. Such added materials may comprise Montan wax, aluminum stearate and the synthetic modifying material obtained by condensation of chlorinated paraffin wax and naphthalene. These materials may be added in small amounts, i. e., around 0.20 to 1.0% by weight of the wax-bearing oil.

In my co-pending application, Serial No. 41,393 filed Sept. 20, 1935, for Dewaxing mineral oil, I have broadly disclosed an improved process of dewaxing oil of the above type in which the oil is mixed with a dewaxing solvent and the resulting mixture heated to a temperature of around 15° to 50° F. above the minimum temperature at which the wax and oil appear to be completely dissolved in the solvent, and thereafter chilling the heated mixture in order to precipitate the wax in a form which is very readily filterable from the cold mixture.

The present invention relates to a modification of the process described in my above mentioned application, Serial No. 20,193, in which wax-bearing oil is mixed with a solvent consisting of mixed ketones and the resulting mixture is subjected to heating to a temperature of from 15° to 50° F. above the minimum temperature at which the wax-bearing oil appears to be completely soluble in the ketone solvent liquid mixture. Following this the heated mixture is chilled to precipitate the wax and the precipitated wax removed by filtration.

As described in my co-pending application, Serial No. 41,393, I have found that the wax precipitated from the cold mixture of wax-bearing oil and solvent which has been previously subjected to heating to elevated temperature prior to chilling is much more readily separated from the cold mixture, and as a consequence, the wax may be filtered from the chilled mixture at rates ten or twelve times greater than where the mixture is not subjected to the preliminary heating step of my invention.

The resulting filter cake of wax is less voluminous and, in addition, an increased yield of dewaxed oil is obtained.

As therein explained, it is thought, in the case of viscous oils, that certain of the naturally-occurring asphaltic and resinous hydrocarbon constituents constitute wax crystal modifying substances. Where the mixture of oil and solvent is not heated to a sufficiently elevated temperature, these constituents are present in the mixture as a colloidal solution. In this form, they possibly form films on the small plate-type paraffin crystals formed during preliminary precipitation of the wax from the solution, and these films inhibit the normal transformation of the plate-type wax crystals into the more easily filterable type of crystal.

By heating to temperatures of 15° to 50° F. above the minimum temperature of apparent complete solution of the wax-bearing oil in the solvent, these colloidal or low solubility substances are apparently completely dissolved in the solvent. It is believed that upon chilling the heated solution, they precipitate therefrom substantially coextensively with the wax in the form of nuclear particles which actually assist crystallization of the wax in a more readily separable and filterable form. In the case of relatively less viscous oils to which wax crystal modifying substances have been added, it is believed that, as in the case of the naturally-occurring wax crystal modifying material, these added substances are probably also precipitated from the previously heated solution in a form in which they act as nuclear particles serving to modify wax crystallization.

The minimum temperature at which the wax-bearing oil appears, on visual inspection, to be completely soluble in the dewaxing solvent, or in homogeneous admixture therewith, depends upon the nature of the oil as well as upon the solvent. In the case of a selective dewaxing solvent of the character of a mixture of about 30% acetone and 70% benzol, for example, the minimum temperature of apparent complete solution of wax-bearing oil in the solvent may range from around 90° to 125° F., the minimum temperature for relatively viscous oils being in the upper portion of this temperature range.

I have found that a solvent composed of a mixture of an aliphatic ketone having around seven to ten carbon atoms and a relatively lower member of the series having up to six carbon atoms is very responsive to the application of the procedure of my invention. When a mixture of such solvent and wax-bearing oil of the type referred to above is heated to temperatures in the range of about 140° to 175° F., then chilled to precipitate the wax, the precipitated wax constituents may be filtered from the cold mixture at rates as high as 40 gallons of wax free oil per square foot of filtering surface per hour, such rates being even greater than in the case of using a solvent consisting of a mixture of methyl ethyl ketone and benzol by the same procedure.

Relatively high molecular weight ketones having from seven up to about ten carbon atoms have a comparatively high solvent power for mineral oil at temperatures of the order of 0° F. and below. The solubility of mineral oil is greater in these higher members than in the relatively lower members of the series having fewer carbon atoms. The lower members of the series, such as acetone, methyl ethyl ketone and also methyl isobutyl ketone, have desirable anti-solvent properties for wax at these low temperatures. Accordingly, it has been found that the high molecular weight ketones, due to their high solubility for oil, provide, when mixed with a lower member of the series, a selective solvent mixture which is well adapted to the dewaxing of mineral oil.

These relatively high molecular weight ketones comprise dipropyl ketone, propyl isobutyl ketone, methyl normal hexyl ketone, ethyl normal amyl ketone and ethyl isoamyl ketone. Still higher members of the series, such as ethyl hexyl and propyl hexyl ketones, even though they are solids at temperatures of below about 25° F., may nevertheless be used in combination with a relatively lower member of the series to provide a dewaxing solvent since the solid point of a selective solvent mixture of such a high molecular weight ketone with acetone or methyl ethyl ketone is depressed below normal dewaxing temperatures.

The lower members of the series of aliphatic ketones which are suitable as wax anti-solvent liquids comprise acetone, methyl ethyl ketone and methyl isobutyl ketone.

Methyl isobutyl ketone which contains six carbon atoms combines the properties of wax anti-solvent action and good oil solvent action to a considerable extent. However, I have found that when this compound is mixed with a higher member of the series of aliphatic ketones, such as dipropyl ketone, and which has a relatively higher solubility for oil, an improved dewaxing solvent liquid mixture is obtained. Such a mixture may be used for dewaxing at relatively lower temperatures than methyl isobutyl ketone alone, and when used at temperatures relatively below 0° F., this mixture continues to exert a solvent action upon substantially all of the liquid oil constituents.

In order to further describe the invention, reference will now be made to a specific example in which a solvent refined wax-bearing distillate was dewaxed with a mixture of methyl ethyl ketone and dipropyl ketone.

The wax-bearing distillate was derived from a Mid-Continent crude and solvent extracted with furfural to remove the relatively low viscosity index constituents. The resulting solvent refined or raffinate oil had the following tests:

Gravity, °A. P. I	26.9
Viscosity Saybolt Universal @ 160° F	282
Viscosity Saybolt Universal @ 210° F	112
Carbon residue %	.32
Paraffin %	11.5
Pour test °F	120

One part of the above oil was mixed with four parts of a solvent mixture consisting of 45% methyl ethyl ketone and 55% dipropyl ketone. This mixture was then heated to a temperature of 175° F. and thereafter chilled to a temperature of 0° F. The chilling was effected in a vertical brine jacketed vessel and precooled nitrogen gas was caused to bubble through the solution in the vessel at the rate of about five cubic feet of gas per hour per square foot of horizontal cross sectional area of the chilling vessel.

The resulting chilled mixture while maintained at a temperature of 0° F. was filtered in a vacuum filter to separate the precipitated wax as a filter cake.

The filter cake was not subjected to washing subsequent to filtration and the resulting slack wax, after removal of the solvent, was found to comprise about 41% of paraffin, having a melting point of 145–146° F.

The filtrate, after removal of the solvent, had a pour test of 0° F. and comprised 74% of the wax-bearing oil charged to the filter.

The filtration rate obtained during this run was calculated on the basis of the time required to filter 0.2 gallon of wax-free oil per square foot of filtering area and, as thus calculated, amounted to 43 gallons of oil per square foot of filtering surface per hour as compared with a rate of about one to two gallons per square foot of filtering surface per hour when the same mixture of wax-bearing distillate oil and solvent was dewaxed without heating the mixture to a temperature above 130° F.

While the treatment of a viscous distillate lubricating oil stock has been specifically described above, it is contemplated that the invention is applicable to residual stocks as well as distillate stocks. Also, while the invention is particularly adapted to the treatment of relatively viscous stocks, it may also be applied to the treatment of less viscous stocks containing small amounts of added wax crystal modifying substances.

I have found that satisfactory results are obtained when the solvent is mixed with the oil in the proportion of about three or four parts of solvent and one part of oil. However, it is contemplated that the proportion of solvent may vary from one to about six parts of solvent to one part of oil.

It is also desirable from the standpoint of realizing the maximum benefit from the preliminary heating step of my invention to avoid subjecting the mixture of wax-bearing oil and solvent to excessive agitation during chilling. Mechanical stirring, and particularly excessive mechanical stirring, deforms the crystal structure of the wax, rendering it more difficult to filter. I have found that it is desirable to apply relatively low stirring rates not in excess of about five revolutions per minute and preferably to employ gaseous agitation. I have found that the filter rate may be increased two to four times by substituting gas for the agitating medium in the prodcedure of my invention.

When gas is employed as the agitating medium it is preferable to precool the gas to a temperature substantially that of the dewaxing temperature. Furthermore, it is advantageous to saturate the chilled gas with the dewaxing solvent prior to introduction to the chilling vessel so as to avoid the removal of any solvent from the chilling mixture by the gas.

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.

I claim:

1. In the dewaxing of wax-bearing mineral oil, the method which comprises mixing the oil containing wax crystal modifying material with a solvent liquid comprising a mixture of dipropyl ketone and methyl ethyl ketone, heating the mixture to a temperature in the range of 140 to 175° F., chilling the heated mixture to a temperature of the order of 0° F. to precipitate the wax constituents, and separating the thus precipitated wax constituents from the cold mixture.

2. In the dewaxing of wax-bearing mineral oil containing wax crystal modifying material, the method which comprises mixing the oil with a solvent comprising a mixture of about equal parts of dipropyl ketone and methyl ethyl ketone, the oil and solvent being in the ratio of about one part of oil to from two to six parts of solvent mixture, heating the mixture to a temperature of around 175° F., chilling the mixture to a temperature of 0° F. to precipitate the wax constituents, subjecting the mixture during said chilling to relatively mild agitation, and separating the thus precipitated wax constituents from the cold mixture.

3. The method of dewaxing a wax-bearing mineral oil having a Saybolt Universal Viscosity above 80 seconds at 210° F. and containing asphaltic and resinous material which comprises mixing about one part of the oil with about four parts of a solvent consisting of a mixture of high and low molecular weight aliphatic ketones such that at temperatures of around 90° to 125° F., the solvent mixture just completely dissolves the oil and wax, and at temperatures of 0° F. and below the mixture has substantially complete solvent action on the liquid constituents of the oil and substantially no solvent action upon the solid waxy constituents of the oil, heating the mixture to a temperature in the range of 140 to 175° F., chilling the heated mixture to a temperature of the order of 0° F. to precipitate the wax constituents, and separating the thus precipitated wax constituents from the cold mixture.

4. In the dewaxing of wax-bearing mineral oil, the method which comprises mixing the oil containing wax crystal modifying material with a solvent comprising an aliphatic ketone having around 7 to 10 carbon atoms mixed with an aliphatic ketone having up to 6 carbon atoms such that the wax and oil appear to be completely dissolved in the solvent at a temperature of less than 130° F., heating the solution of wax-bearing oil in the solvent to a temperature substantially above 130° F. such that upon chilling to about 0° F. and filtering to remove the wax the filtering rate is materially greater than that realized when heating to a temperature not above 130° F., chilling the thus heated solution to precipitate the wax and removing the wax so precipitated.

5. In the dewaxing of wax-bearing mineral oil, the method which comprises mixing the oil containing wax crystal modifying material with a solvent comprising an aliphatic ketone having around 7 to 10 carbon atoms mixed with an aliphatic ketone having up to 6 carbon atoms such that the wax and oil appear to be completely dissolved in the solvent at a temperature of around 125° F., heating the solution of wax-bearing oil in the solvent to a temperature of 15 to 50° F. above the aforesaid solution temperature such that upon chilling to about 0° F. and filtering to remove the wax the filtering rate is materially greater than that realized when the mixture is heated to a temperature of about 125° F., chilling the thus heated solution to precipitate the wax and removing the wax so precipitated.

6. In the dewaxing of wax-bearing mineral oil, the method which comprises mixing the oil containing wax crystal modifying material with a solvent comprising an aliphatic ketone having around 7 to 10 carbon atoms mixed with an aliphatic ketone having up to 6 carbon atoms such that the wax and oil appear to be completely dissolved in the solvent at a temperature of around 125° F., heating the solution of wax-bearing oil in the solvent to a temperature of around 175° F. such that upon chilling to about 0° F. and filtering to remove the wax the filtering rate is materially greater than that realized when heating to a temperature of about 125° F., chilling the thus heated solution to precipitate the wax and removing the wax so precipitated.

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