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METHOD FOR DEWAXING OIL

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The present invention relates to the art of separating wax from wax-bearing oil, and more particularly the invention pertains to a method in which certain materials are added to the wax-bearing oil to condition the latter so that the wax may be more readily separated from the oil. The invention also relates to a process for the production of materials which when added to a wax-bearing oil condition the latter so that the wax may be more readily removed therefrom.

Many oils contain relatively large quantities of wax which impart a high pour point to the oil and thereby render these oils unsuitable for use as they are solid and will not flow at ordinary temperatures. In order to render these oils fluid at ordinary temperatures it is necessary to remove the wax present. This is usually accomplished by adding a suitable diluent to the wax-bearing oil, chilling the diluted oil to a temperature sufficiently low to precipitate the wax and then separating the precipitated wax from the diluted oil by settling, filtering or centrifuging.

We have discovered that wax may be more readily separated from oil by mixing the wax-bearing oil with certain materials which render the wax more readily separable from the oil. Hereinafter the materials which we employ to condition the wax present in wax-bearing oils in order that the wax may be more readily separated from the oil will be referred to as "wax modifiers" or "wax separation aids".

In carrying out our invention the wax-bearing oil is mixed with a small amount of the wax separation aid or wax modifier, produced according to our invention, after which the wax-bearing oil containing the small quantity of the wax modifier is chilled to precipitate the wax from the oil and the wax is then separated from the chilled mixture by settling, centrifuging or filtering. In many cases it may be desirable to dilute the wax-bearing oil with a suitable diluent prior to the chilling step in order to render the oil fluent at the dewaxing temperature. As diluents for the wax-bearing oil we may employ liquefied normally gaseous hydrocarbons such as ethane, ethylene, propane, propylene, butane or butylene, or mixtures thereof, light hydrocarbons such as pentane, hexane, heptane, octane, nonane, or hydrocarbon fractions such as naphtha, gasoline, kerosene or gas oil. We may also employ diluents such as acetone, acetone and benzol, ethyl alcohol, propyl alcohol, butyl alcohol, methyl ethyl ketone, diethyl ketone, methylpropyl ketone, ethylpropyl ketone, normally gas-

eous and normally liquid ethers, dichlorethylene or trichlorethylene or mixtures of these materials with the aforementioned hydrocarbons.

When the diluent employed is one which is normally gaseous at ordinary temperature (i. e. 60–80° F.) it may also be employed to produce the necessary degree of refrigeration to precipitate the wax from the oil by vaporizing a portion of the liquefied normally gaseous material from the diluted oil under reduced pressure.

Certain petroleum residues (cracked or uncracked) and particularly certain asphaltic residues contain bodies or substances which when added to a wax-bearing oil aid in the separation of the wax from the oil. Direct addition of the petroleum residue to the wax-bearing oil to aid in the separation of the wax therefrom is undesirable because these residues contain appreciable quantities of oil fractions which contaminate the final dewaxed product. Furthermore, these oily fractions have little or no effect upon the structure of the wax and therefore aid in no substantial manner in the separation of the wax from the wax-bearing oil. These oily fractions are merely diluents and reduce the potency of the wax separation aids present in the residuum. The residues oftentimes also contain undesirable color bodies such as asphalt, bituminous material and coke which discolor the final product.

Attempts have been made to recover the wax separation aids from petroleum residues by distillation. This method is unsatisfactory, however, because the wax separation aids in these residues boil over a wide range and they cannot be concentrated in any one particular distillate fraction. The light distillate fractions as well as the heavy distillate fractions contain appreciable quantities of the wax separation aids which are diluted with the distillate oils.

We have discovered a method whereby the wax separation aids may be recovered from petroleum residues in such form as to be substantially free from both the undesirable oily fractions and color bodies present in the residuum.

In accordance with the preferred method of the present invention petroleum residues are extracted with a solvent which will dissolve the undesirable oily fractions present but which does not dissolve any appreciable quantity of the wax separation aids present in the residue. The solvent solution of oily fractions is then decanted away from the insoluble residue containing the major quantity of the wax separation aids and the residue from which the oily fractions have been removed is then distilled and the wax sep-

aration aids are recovered as a distillate fraction.

As solvents for the oily fractions present in the residue we may employ liquefied normally gaseous hydrocarbons such as ethane, propane, butane or mixtures thereof or unsaturated liquefied normally gaseous hydrocarbons such as ethylene, propylene or butylene, or we may use gasoline, naphtha, alcohol and benzol, alcohol and ether, ether and acetone or benzol and acetone. The preferred solvents are the liquefied normally gaseous paraffinic hydrocarbons and light petroleum naphtha. By light petroleum naphtha we mean a hydrocarbon fraction boiling between 100° F. and 400° F.

As a specific example of the preferred method of recovering the wax separation aids a cracked asphaltic residue is distilled with fire and steam until a still residue is obtained having a melting point between 200° F. and 400° F. (A. S. T. M.—Ball and Ring melting point method). The residue is then removed from the still and mixed with 3 to 5 parts of petroleum naphtha to one part of the still residue and at a temperature of about 100–125° F. This mixture is allowed to settle into two phases. The upper phase comprises a naphtha solution of the oily fractions and the lower phase comprises the remaining undissolved residue containing the major portion of the wax separation aids and such impurities as asphalt bituminous material, coke or color bodies. The upper phase consisting of the naphtha and dissolved oily fractions is decanted away from the insoluble residue and this residue is then distilled, preferably with steam at a temperature sufficiently high to cause the wax separation aids to be vaporized and separated from the undesirable constituents present in the residue. These vapors are then condensed and this condensate which is substantially free from undesirable oily fractions and asphaltic bodies is then employed as a wax separation aid in the separation of wax from oil. The temperature employed during the distillation will range from 400° F. to 650° F.

It will be understood that we may also employ petroleum residues other than those which contain asphalt, and that we may also employ uncracked petroleum residues as well as cracked residues for the production of our wax separation aids by the method described above. In addition to employing petroleum residues as the source of our wax separation aids we may also employ oxidized petroleum fractions, oxidized petrolatum and paraffin wax, heavy extracts produced from petroleum by means of selective solvents such as nitrobenzene, aniline, cresol, phenol and sulphur dioxide, resinous materials produced during the conversion of hydrocarbon fractions by a cracking operation, coal tar pitch, gas tar and lignite. These materials contain appreciable quantities of wax separation aids and may be treated by the above method for their recovery.

In some instances it may be desirable to substitute liquefied normally gaseous hydrocarbons for the naphtha in the preceding example as the extractant for the oily fractions present in the crude stock undergoing treatment. For example the petroleum residuum may be first extracted with a liquefied normally gaseous hydrocarbon such as liquid propane in the proportion of one part of the residuum to 3 to 5 parts of liquid propane at a temperature of about 60° F. to 75° F. and under sufficient pressure to maintain the propane in the liquid state. The propane solution of oily fractions may then be separated from the portion of the petroleum residue which

is undissolved by the liquid propane and the latter may then be distilled with fire and steam to separate the wax separation aids present as distillates from the undesirable constituents present in the propane insoluble residue. Liquid propane is capable of dissolving the oil fractions present in the petroleum residue but possesses a lower solvent power for the wax separation aids present in the residue than petroleum naphtha.

In some instances it is desirable to further repress the solvent power of the oil extractant by performing the extraction of the crude stock containing the wax separation aid at a reduced temperature. For example when naphtha or liquefied propane is employed as the solvent for the oily fractions present in the petroleum residues, it may be desirable to perform the extraction at temperatures within the range of 0° F. to –25° F. At this lowered temperature the naphtha or liquid propane will still dissolve the oily fractions present in the residue but will dissolve less of the wax separation aids as they are less soluble in these solvents at the lowered temperature. As a further modification the petroleum residues may be intimately mixed with naphtha at a temperature of about 100° F. and then the temperature of the mixture may be lowered to about 0° F. to –25° F. and after phase separation between the solvent and dissolved fractions and the fractions insoluble in the solvent these phases may be separated. The undissolved portion of the residue is then distilled in the manner described above in order to separate the wax separation aids as distillates from the undesirable portions of solvent insoluble residue.

The wax separation aids produced by the foregoing method are effective as aids for separation of wax from oil. For example if 0.1 to 1.0% of the distillate produced according to the preceding example is mixed with a wax-bearing oil the wax present in the wax-bearing oil may be more readily separated from the oil by such methods as centrifuging, cold settling or filtration.

The following is an example of dewaxing a wax-bearing oil with the above described wax separation aids: A waxy distillate of S. A. E. 30 grade having a pour point of 90° F. was mixed with 0.5% of the wax separation aid produced by naphtha extraction and distillation of a cracked asphaltic residue having a melting point of 325° F. This mixture was then diluted with liquid propane in the proportion of one part of the waxy distillate to 5 parts of liquid propane at a temperature of about 100° F. The diluted waxy oil containing the wax separation aid was then cooled at the rate of about 1° to 3° F. per minute until a temperature of about –35° F. was attained. The chilled mass was then filtered and the propane was then removed from the filtrate by distillation and the dewaxed filtrate had a pour point of –5° F. (A. S. T. M.—D—97—30).

It is therefore an object of the present invention to produce wax separation aids from petroleum residues and other materials which contain wax separation aids, undesirable oily fractions and/or undesirable asphaltic or bituminous materials by first extracting the crude stock with a solvent for the oily fractions present in the crude stock, separating the solvent and dissolved oily fractions from that portion of the crude stock which is insoluble in the solvent and then fractionally distilling that portion of the crude stock which is insoluble in the solvent and recovering the wax separation aids as a distillate.

It is another object of this invention to mix a wax-bearing oil with a small quantity of the above wax separation aids, chill the mixture of wax-bearing oil containing the said wax separation aid to a temperature sufficiently low to precipitate wax and then remove the precipitated wax from the chilled mixture by cold settling, centrifuging or filtering.

It is another object of this invention to extract petroleum residues containing wax separation aids, undesirable oily fractions and asphalt-like materials with a solvent for the oily fractions, remove the solvent and dissolved oily fractions from the residue which is insoluble in the solvent, distill said solvent insoluble residue into a distillate and bottom fraction, mix a small quantity of said distillate with a wax-bearing oil, chill the mixture of wax-bearing oil and distillate to a temperature sufficiently low to precipitate the wax and remove the precipitated wax from the chilled mixture by cold settling, filtration or centrifuging.

It is a further object of this invention to mix a wax-bearing oil with the above described wax separation aid, commingle the wax-bearing oil containing the wax separation aid with a diluent, chill the diluted oil to a temperature sufficiently low to precipitate the wax and remove the precipitated wax from the chilled and diluted oil by centrifuging, filtering or cold settling. Furthermore, when liquefied normally gaseous hydrocarbons are employed as diluents for the wax-bearing oil containing the wax separation aid, it is an object of the present invention to produce the chilling of the oil by vaporizing a portion of the liquefied normally gaseous hydrocarbon under reduced pressure from the solution.

Another method of recovering the wax separation aids present in such materials as petroleum residues, cracked waxes, oxidized paraffin, oxidized petrolatum, extracts obtained by extracting heavy oils with selective solvents (such as cresol, nitrobenzene, aniline or sulphur dioxide) oxidized petroleum fractions, coal tar residuum, gas tar residues and lignite is as follows:

The foregoing materials may be contacted or mixed with an adsorbent clay such as fuller's earth, diatomaceous earth, Florida clay or Death Valley clay and these clays or earths will adsorb the wax separation aids present. The clay upon which the wax separation aids are adsorbed may be recovered from admixture with the above materials by settling, filtering or centrifuging and then added to a wax-bearing oil to condition the oil for the separation of the wax therefrom. While these clays or earths are capable of adsorbing the wax separation aids present in the foregoing materials at ordinary temperature, in many instances it is found to be desirable to contact the crude stock containing the wax separation aids with the clay or earth at a temperature of 150° F. to 350° F. and then recover the clay from the mixture by settling, filtering or centrifuging.

When the crude stock is solid or viscous it is desirable to add a thinning agent such as naphtha, gasoline, kerosene or benzol and then contact the thinned material with the clay or earth. In case the contact temperature of the stock and clay is above the boiling point of the thinning agent it is necessary to place the thinned stock containing the clay or earth in a vapor tight pressure vessel to insure against loss of the thinning agent. After the contact period the clay having the wax separation aids adsorbed thereon

may be separated from the diluted crude stock by filtering, centrifuging or settling.

As a specific example of this modification a cracked asphaltic residue having a melting point of 300° F. (Ball and Ring) was mixed with petroleum naphtha in the proportion of 50 parts of the cracked residue to 100 parts of the naphtha. To the mixture of cracked residue and petroleum naphtha there was added 20 parts of Death Valley clay. This mixture was heated and agitated for a period of about one hour in a closed vessel and at a temperature of about 325° F. After the contact period the hot mixture was filtered and the clay thus obtained was found to be very effective as a wax separation aid in the separation of wax from oil. We have also found that clays or earths which are recovered as "spent clay" during the color treatment of gasoline or lubricating oil are also suitable as wax separation aids.

If a small amount of the spent clay is added to a wax-bearing oil it aids materially in the separation of the wax from the oil. An example of a spent clay obtained from the treatment of lubricating oil stock is as follows: A lubricating oil distillate produced from Santa Fe Springs crude oil having a Saybolt universal viscosity of 600 seconds at 100° F. was contacted with Death Valley clay in the proportion of 100 ml. of the lubricating oil distillates to 10 grams of the Death Valley clay at a temperature of about 325° F. for a period of about 5 minutes. After the contact period the hot mixture of clay and oil was then filtered and the clay recovered in the filter was found to be effective as a wax separation aid for the separation of wax from oil.

The clays or earths which are recovered after contact with the various crude stocks containing the wax separation aids are usually relatively free from oil fractions and therefore the addition of these clays or earths to a wax-bearing oil to aid in the separation of wax therefrom does not result in the contamination of the waxy oil with undesirable oil fractions. Furthermore, these clays or earths do not materially impart to the wax-bearing oil any appreciable discoloration. If desired, the oil content of these clays or earths upon which the wax separation aids are adsorbed, may be lowered by washing the clays or earths with light solvents such as naphtha, gasoline, liquefied normally gaseous hydrocarbons or benzol, which will dissolve the oil fractions present but will not dissolve the wax separation aids to any appreciable extent.

By contacting the clays or earths upon which the wax separation aids are adsorbed with these solvents at ordinary temperature i. e. 60° F. to 75° F. or at a lowered temperature i. e. 0° F. to -30° F. the oily fractions are dissolved in the solvent and may be separated from the clay or earth by simple decantation of the solvent and dissolved fractions from the clay or earth or by filtration.

The following is an example of employing these clays or earths upon which the wax separation aids are adsorbed in the separation of wax from a wax-bearing oil. A wax-bearing oil having a pour point of about 90° F. (A. S. T. M. D-97-30) was mixed with about 2.0% of a clay which had been contacted with a Santa Fe Springs asphaltic residuum in the manner described above. To this mixture was added liquid propane in the proportion of one part of the waxy oil to five parts of liquid propane. The diluted oil was then chilled at the rate of about 1° F. to 3° F.

per minute until a final temperature of about -35° F. was obtained and the chilled mixture was then passed through a filter. The propane was removed by distillation and the dewaxed oil was found to have a pour point of $+10^{\circ}$ F.

In addition to the use of the above described materials as wax separation aids, we have found that the resinous materials recovered from crank case oils or from filters employed in connection with internal combustion engines to purify the lubricating oil employed in the crank case, have a beneficial effect in improving the dewaxing characteristics of wax-containing oils. These resinous materials may be recovered from crank case oils which have been employed in the internal combustion engine for a thousand miles or more by mixing the used oil with a suitable diluent, preferably liquid propane, in a closed vessel in a volumetric ratio of say 4 to 8 volumes of propane to one of the oil. The propane precipitates the resinous materials from the oil. If desired, precipitation may be supplemented or aided by lowering the temperature of the mixture to approximately 40° F. to -40° F. by vaporizing a portion of the propane under reduced pressure. After allowing the precipitated material to settle, the supernatant solution is decanted. The precipitated resins may be washed with fresh propane to remove any oil entrained therein after which they are distilled to vaporize entrained propane. A small amount of these materials, say 1%, is sufficient to aid in the separation of wax from oils by methods described hereinabove. It is believed that these materials have been rendered valuable as wax separation aids because of the oxidation conditions existing in crank cases for long periods of time while maintained at elevated temperatures. If desired, the precipitated resins may be further oxidized with air, oxygen, ozone or hydrogen peroxide at an elevated temperature prior to their use as wax separation aids.

The wax separation aids may be recovered from filters employed in connection with internal combustion engines by circulating a suitable solvent, such as benzol, at an elevated temperature through the filter. The solution of solvent containing the materials removed from the filter may then be distilled to separate the solvent after which the resinous materials may be dissolved in a small quantity of heavy oil. This solution may then be mixed with propane to precipitate the resinous materials in accordance with the procedure described above for recovering the resinous materials from used crank case oils.

We have also found that asphalt precipitated from asphalt containing oils by means of propane, are valuable wax separation aids. These precipitated asphalts may also be further oxidized and/or treated in accordance with methods described above either before or after oxidation.

It is to be understood that the above examples are merely illustrative and are not to be construed as limiting the invention which we claim.

We claim:

1. A method for conditioning a wax-bearing oil preparatory to the separation of wax therefrom which comprises mixing said oil with a clay or earth containing wax separation aids which have been separated by means of said clay from an oil containing the same.
2. A method as in claim 1 in which the wax separation aid is separated by means of said clay or earth from a cracked petroleum fraction.
3. A method according to claim 1 in which the material containing the wax separation aid is contacted with clay at an elevated temperature.
4. A method of conditioning a wax-bearing oil preparatory to the separation of wax therefrom which comprises mixing said oil with a substantially non-volatile oxidized asphaltic residue.
5. A method for conditioning a wax-bearing oil preparatory to the separation of wax therefrom which comprises mixing said oil with an asphaltic fraction recovered from a used crank case oil.
6. A method for conditioning a wax-bearing oil preparatory to the separation of wax therefrom which comprises mixing said oil with an oxidized asphaltic fraction recovered from asphalt containing oils by means of a solvent.
7. A method of conditioning a wax-bearing oil preparatory to the separation of wax therefrom comprising mixing said oil with a wax separation aid recovered from a petroleum residue by extracting said petroleum residue with naphtha to remove the oily fractions present in said residue, distilling naphtha extracted residue and recovering said wax separation aid as a distillate.
8. A method of conditioning a wax-bearing oil preparatory to the separation of wax therefrom comprising mixing said oil with a wax separation aid recovered from a cracked petroleum residue by extracting said cracked petroleum residue with naphtha to remove the oily fractions present in said residue, distilling naphtha extracted residue and recovering said wax separation aid as a distillate.
9. A method of conditioning a wax-bearing oil preparatory to the separation of wax therefrom comprising mixing said oil with a wax separation aid recovered from a cracked asphaltic petroleum residue by extracting said cracked asphaltic petroleum residue with naphtha to remove the oily fractions present in said residue, distilling naphtha extracted residue and recovering said wax separation aid as a distillate.
10. A method for conditioning a wax-bearing oil preparatory to the separation of wax therefrom comprising mixing said oil with a wax separation aid recovered from a petroleum residue having a melting point between 200° F. and 400° F. by extracting said residue with naphtha to remove the oily fractions present in said residue and said oil free residue is subjected to distillation to recover the wax separation aid as a distillate.

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