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METHOD OF TREATING MINERAL OILS

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This invention pertains to the treatment of mineral oils, petroleum residues, lubricating oil distillates, coal tar and coal tar oils, and other hydrocarbon mixtures, and is more particularly concerned with a method of separating mineral oils into fractions of different physical and/or chemical properties by means of extractants which are at least partially miscible with water or with certain polar substances which reduce the solvent power of the extractants for hydrocarbons.

It is known to refine hydrocarbon oils by contacting them with water-soluble selective solvents, such as sulfur dioxide, alcohols, phenols, furfural, ether, acetone, etc. It is, moreover, known to control the solvent power of certain solvents by diluting them with certain quantities of water. In such processes it is important that the solvent be sufficiently selective to effect the desired degree of separation between the different components of oil.

In accordance with my invention I regulate the solvent power of certain selective solvents, such as alcohols, by controlling or varying their content of a polar substance such as water or some other compound, such as methyl or ethyl alcohol or acetone, etc., having the property of reducing the solvent power of the solvent, in the manner hereinafter more fully described, thereby rendering these solvents suitable for dewaxing and for deasphaltizing, as well as for extracting mineral oils to concentrate desirable components into one or more fractions, such as lubricating oil fractions, in a so-called "cold fractionating" process, without the necessity of first diluting the oil with a light fraction.

The success of such a process depends largely upon the sharpness of the separation which is attainable, and this, again, is influenced by the facility with which the solvent power of the solvent can be controlled and varied under operating conditions. I have found that those secondary and tertiary alcohols which are liquid at the temperature of treatment and in the presence of oil, and which are at least partially miscible with the highly polar substances which I employ to regulate their solvent power are eminently suitable as solvents in the process of my invention. I have, moreover, found tertiary butyl and tertiary amyl alcohols to be the most suitable, and they constitute the preferred solvents of my invention. A few specific examples of other alcohols which are valuable are tertiary hexyl alcohol, secondary butyl and secondary amyl alcohols. The alcohols need not be highly refined, and ordinary commercial products containing mixtures of alcohols and/or water and/or other impurities can be readily used.

In the preferred form of this invention the alcohol is added to the oil in such quantities and under such conditions of temperature and pressure to substantially saturate the oil without causing it to separate into two phases at the temperature of treatment. A suitable mixing device may be employed to effect the proper contacting of the oil and the alcohol. A highly polar substance, preferably water, is then added to the solution in carefully controlled quantities to separate some of the oil components as a separate liquid or semi-liquid phase, which may be separated from the complementary phase by any means, such as centrifuging or decantation. When this treatment is applied to oils containing asphaltic or resinous materials, these impurities will be found in the separated phase, the desirable oily components remaining dissolved in the alcohol. The alcohol and the polar substance can be recovered from each of the phases, by known means, as, for example, by distillation, or washing.

According to another embodiment of my invention I initially dilute the alcohol with all or a portion of the requisite amount of the polar substance, and add the diluted alcohol to the oil. In this method it is more difficult to get the oil into solution, and it is, therefore, often necessary to cause intimate contact between the alcohol and the oil by an agitator or some other mixing device. The requisite amount of the polar substance (if not already present) is then added, and the mixture is allowed to separate, as described above.

After separating the asphaltic material from the oil-alcohol solution according to either of the above methods a further quantity of a suitable polar substance is added to the oil phase, thereby further decreasing the solvent power of the alcohol, and causing the formation of two phases, which may be separated in any desired manner, as by gravity or centrifuging, without changing their composition. The parted phases may be separately treated to remove the solvents and polar substances from the oil and/or the oil impurities by any desired method. In this manner additional quantities of asphalt will be removed from the oil, the asphalt being obtained by removing the solvents from the precipitate. The addition of further quantities of the polar compounds may, moreover, be repeated. If de-

sired, the successive extractions may be at different temperatures.

When working with an oil of low asphaltic content, or an oil which has been deasphaltized in the first step of the process or by other known means, this treatment is effective to separate it into fractions of differing chemical and physical properties, as, for example, molecular size, boiling range, temperature viscosity curves, carbon residues, etc. When seeking to produce a separation of this type the repeated addition of the polar substance is especially applicable.

It is, further, also possible to subject the precipitated phase to further treatment to recover further quantities of oil. Thus, after separating the oil-alcohol solution from the precipitate, according to either of the methods described, a further quantity of the same or of another alcohol is added to this residue, thereby causing further separation into two phases. In this manner additional quantities of oil can be recovered from the residue. The solvent power of the additional alcohol must be carefully controlled to prevent the dissolving of substantial amounts of the asphalt, and at the same time cause the dissolving of the desired quantity of oil. This control can be effected by adding the highly polar substances having the property of reducing the solvent power of the main solvent, as described above.

Water will normally be employed as the polar substance referred to in the above examples because of its availability at low cost. It is, however, also possible to use certain oxygenated aliphatic substances which have a low solvent power for hydrocarbons, and especially for asphalt, such as lower aliphatic alcohols and ketones, as, for example, methyl or ethyl alcohol, or acetone, methyl ethyl ketone, methyl propyl ketone, etc. Moreover, many of the higher alcohols are substantially immiscible in water, but are yet at least partially miscible with a solubility reducing substance other than water. The substitution of these substances makes it possible to use such water-insoluble alcohols. Moreover, many of the polar substances are water-miscible and render the water-immiscible alcohol at least partly water-miscible. In this event the polar substance may consist of an aqueous solution of such a polar substance.

The amounts of the polar substance, as well as operating conditions of the process, such as temperature, alcohols used, etc., depend on the nature of the oil being treated and on the desired properties of the fractions, and can be conveniently determined by experiments on a small scale.

By suitably chilling the oil-alcohol mixture, either before or after, but preferably after the addition of water, I am enabled to effect the simultaneous dewaxing of the oil. Alternatively, I may dewax my oil in one of the successive stages following the deasphalting stage.

When wax and asphalt are separated in one step, I may also employ the process of my invention to separate these two constituents, since the wax is relatively more soluble in the alcohols.

The process of this invention may be further illustrated by the following examples which are not, however, intended to limit the scope of this patent to any specific features contained in the examples.

Example I

Three parts by volume of tertiary butyl alcohol containing 5% of water by volume were thoroughly mixed with one part of mixed petroleum residues having a sulfur content of 1.22%, a black color and viscosity index less than zero. Upon standing, the mixture separated into two well defined phases, the upper phase being light green in color, and containing the larger part of the alcohol, while the lower phase was black in color. The lower phase was heated to separate the alcohol and water, and yielded a soft asphaltic material having a sulfur content of 1.80% by weight. A green oil having a sulfur content of 0.89%, viscosities 262 and 47 seconds S. U. at 100° F. and 210° F., respectively (corresponding to a viscosity index of about 67) and amounting to 63.3% by weight of the residue used was obtained from the upper phase by distilling off the alcohol and water at atmospheric pressure.

Example II

Ten parts by volume of a Ventura residue were dissolved in 30 parts of tertiary amyl alcohol. The mixture remained homogeneous upon prolonged standing.

Three parts of water were then added to the solution while agitating. A precipitate was formed, which was permitted to settle, whereupon the liquid was decanted. The precipitate was heated and yielded a very hard asphaltic material upon cooling after the removal of the alcohol and water.

Four parts of water were then added to the decanted solution of oil, alcohol, and water. Some of the water was thrown out of solution, but most of it entered the main body of the solution, causing it to separate into a green upper layer and an asphaltic precipitate. This precipitate was heated to expel the alcohol and water, and yielded a medium hard asphalt. The yield of refined oil obtained by distilling off the alcohol from the upper phase was 62.8% of the original residue used. The refined oil had a green color and was in all respects similar to that obtained in Example I.

Example III

Nine parts by volume of a Ventura residue were thoroughly mixed with 10 parts of aqueous 95% tertiary butyl alcohol, and the mixture allowed to separate into two phases. The upper layer was decanted and after the water and alcohol had been evaporated from it, yielded 21.2% by weight on the Ventura residue used of an oil having an appearance similar to that of the preceding examples.

Five parts by volume of 95% tertiary butyl alcohol were thoroughly mixed with the lower layer of the preceding treatment, and produced a new separation into phases. After settling, the upper phase was decanted and the alcohol and water separated from it by distillation. An additional 11% by weight on the original Ventura residue of refined oil was recovered in this manner.

It is not always necessary to recover the solvents from the separated mineral oil portions, and all or a part of these alcohols may be left in the oil. For example, such solvents as tertiary butyl alcohol may be left in mineral oil stock to be cracked and recovered from the resulting pressure distillate as the corresponding olefine.

I claim as my invention:

1. A process for separating hydrocarbon oils into different fractions comprising the steps of mixing a liquid hydrocarbon oil with a tertiary

aliphatic alcohol at a temperature to produce a homogeneous solution of the hydrocarbon oil in the alcohol, adding a lower aliphatic ketone to the resulting solution in a quantity sufficient to cause the formation of two liquid phases, and separating said phases substantially at the said temperature.

2. A process for separating hydrocarbon oils into different fractions comprising the steps of mixing a liquid hydrocarbon oil, a tertiary aliphatic alcohol containing from 4 to 5 carbon atoms, and a lower aliphatic ketone at a temperature which would produce a homogeneous solution of the hydrocarbon oil in the pure alcohol, the quantity of the ketone being sufficient to cause the formation of two liquid phases, and separating said phases.

3. A process for separating hydrocarbon oils into different fractions comprising the steps of mixing a liquid hydrocarbon oil with a tertiary aliphatic alcohol at a temperature to produce a homogeneous solution of the hydrocarbon oil in the alcohol, adding methyl ethyl ketone to the resulting solution in a quantity sufficient to cause the formation of two liquid phases, and separating said phases substantially at the same temperature.

4. A process for separating hydrocarbon oils into different fractions comprising the steps of mixing a liquid hydrocarbon oil, a tertiary aliphatic alcohol containing from 4 to 5 carbon atoms, and methyl ethyl ketone at a temperature which would produce a homogeneous solution of the hydrocarbon oil in the pure alcohol, the quantity of the ketone being sufficient to cause the formation of two liquid phases, and separating said phases.

5. A process for separating hydrocarbon oils into different fractions comprising the steps of contacting said oil with a tertiary aliphatic alcohol and a lower aliphatic ketone, under conditions causing the formation of two liquid phases containing alcohol, ketone, and different portions of the oil, and separating the said phases from one another.

6. A process for separating hydrocarbon oils into different fractions comprising the steps of contacting said oil with a tertiary aliphatic alcohol and a methyl ethyl ketone, under conditions causing the formation of two liquid phases containing alcohol, ketone, and different portions of the oil, and separating the said phases from one another.

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