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HYDROCARBON OIL TREATMENT

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The present invention relates to the art of mineral oil refining, and has particular reference to the separation of crude petroleum or petroleum products into fractions of different chemical composition while of approximately the same distillation range.

In accordance with my invention, crude petroleum or petroleum products, particularly oils of substantial viscosity, are separated into various fractions by extraction with a solvent, and more particularly with selective solvents such as the nitrogen-containing derivatives of thiophene, for example, nitro-thiophene, amino-thiophene and thiophene nitrile.

It is recognized in the art that mineral oils, such as petroleum, comprise essentially a mixture of hydrocarbons of various groups or homologous series of compounds, such for example, as paraffins of the general formula C_nH_{2n+2}, olefins of the general formula C_nH_{2n}, hydroaromatics and polymethylenes of the same empirical formula, and various other series of compounds of chain and/or ring structures in which the hydrogen to carbon ratio is less than in the foregoing series. A large number of individual compounds of each series and of differing boiling points are present in petroleum.

The various types of crude petroleum, which are generally classified into three groups, namely, paraffinic base, naphthenic or asphaltic base, and mixed base, contain the various series of hydrocarbons mentioned heretofore in different proportions. For example, in the paraffinic base crude oils, such as those obtained from the oil fields of Pennsylvania, there is a relatively high proportion of hydro-carbons having a chain structure and a high hydrogen to carbon ratio, whereas in the naphthenic or asphaltic base crude oils, there is a relatively large proportion of hydrocarbons having ring structures and a low hydrogen to carbon ratio. Mixed base crude oils such as are obtained from the Mid-Continent oil fields, contain hydrocarbons in proportions intermediate between these two extremes.

The paraffin base oils and their distillates are said to be more paraffinic than the mixed base oils and their distillates and these in turn are more paraffinic than the naphthene base oils and their distillates. Conversely the naphthene base oils are more naphthenic than the mixed base oils and these in turn more naphthenic than the paraffin base oils. The usual criteria of the degree of paraffinicity or naphthenicity of an oil are the viscosity-gravity constant and the viscosity index. The viscosity-gravity constant is a constant relating viscosity and specific gravity and is described in an article entitled "The viscosity-gravity constant of petroleum lubricating oils" by J. B. Hill and H. B. Coates which will be found in vol. 20, page 641 et seq., of Industrial and Engineering Chemistry. Viscous oils resulting from the distillation of Pennsylvania type crudes have viscosity-gravity constants ranging from about .805 to about .828, and in most instances are below .820. Those resulting from the distillation of Mid-Continent crudes have viscosity-gravity constants ranging from about .835 to about .855, whereas those from naphthenic crudes are generally higher than .860. The viscosity index is a coefficient based on the change of viscosity with temperature, and is described by Dean and Davis in vol. 36, page 618 of Chemical and Metallurgical Engineering. The more paraffinic oils are characterized by low viscosity-gravity constants and high viscosity indices, whereas the more naphthenic oils are characterized by higher viscosity-gravity constants and low viscosity indices.

My invention is based upon the discovery that oils containing both the paraffinic series of hydrocarbons and the various naphthenic series may be fractionally extracted with a selective solvent such as a nitrogen-containing derivative of thiophene. The various series of hydrocarbons possess a differential solubility in such solvent, the naphthenic hydrocarbons being much more soluble therein than the paraffinic hydrocarbons. By means of extraction with such solvent, it is possible to effect a partial separation of the naphthenic hydrocarbons from the paraffinic, and to obtain from an oil containing both classes of hydrocarbons, an oil which is much more paraffinic than the original oil and one which is much more naphthenic. By my invention, for example, it is possible to produce an oil of the quality normally obtained from Appalachian crudes, from crudes of the mixed base type from the Mid-Continent area or from those of the naphthenic base type and, conversely, to obtain oils from mixed base crudes or paraffinic base crudes such as are normally obtained from the naphthenic oils of the Gulf Coast area. In general, from oils from any source there may be obtained by my process, oils which are respectively more paraffinic and more naphthenic than the oils normally obtained from such source by distillation.

In accordance with my invention, I first mix the oil to be treated with a suitable proportion of a nitrogen-containing derivative of thiophene at a temperature such that complete solution is effected and a homogeneous liquid obtained. I then adjust the temperature of the solution so that separation of the liquid into a two-layer system will take place. Such temperature is generally at least 35° F. below the miscibility temperature of the oil and solvent. One layer will contain a relatively small amount of the solvent dissolved in the paraffinic portion of the oil (raffinate), while the other layer will contain the more naphthenic portion of the oil (extract) dissolved in the major quantity of the solvent. Or, I may agitate the mixture of solvent and oil at temperatures at which the same are only partially miscible, and thereby effect solution of the naphthenic portion of the oil in the solvent. In either of the above procedures I may take advantage of the principles of countercurrent extraction.

After the extraction proper, I effect separation of the two layers which form, by any suitable procedure, as for example, by decantation. I then remove from each of the separated layers, the portion of solvent which each contains, by suitable procedure, such as by vacuum distillation, thereby to obtain two oils of similar distillation ranges but of different chemical composition and different physical characteristics.

Before removing the solvent from the undissolved or more paraffinic layer, I may add a further quantity of the solvent and repeat the extraction, thereby to remove additional naphthenic constituents from said layer. The extraction step may be repeated any desired number of times, each repetition producing an oil of higher paraffinicity as evidenced by its lower viscosity-gravity constant.

A countercurrent relationship in these successive extractions may be established in the conventional manner by employing the partially spent solvent containing dissolved naphthenic oil from the succeeding stages of a batch-countercurrent extraction system to extract additional quantities of oil in the preceding stages, or in a continuous countercurrent system, the oil and solvent may be simply flowed in countercurrent contact with one another.

Where substantial quantities of waxy hydrocarbons belonging to the true paraffin series (C_nH_{2n+2}) are present, such hydrocarbons remain in the undissolved or more paraffinic layer and may cause such layer to be solid or semi-solid, after the removal of the solvent therefrom. In some cases, the extraction and separation of the layers may be effected at temperatures above the melting point of the waxy hydrocarbons, so that substantial entrainment of oil in the molten or liquid wax is avoided. Such layer may be separated into solid and liquid hydrocarbons by any of the well-known dewaxing processes such as by cold-settling, filtering, or by centrifuging. In many instances it may be advantageous to dewax the oil prior to extraction. However, it is to be understood that in accordance with my invention, dewaxing may be effected either prior or subsequent to extraction.

My invention will be further understood from the following specific examples:

I. 100 parts by volume of a lubricating distillate from a Gulf Coast crude oil having a viscosity of 612 seconds Saybolt universal at 100° F., a specific gravity of 0.9303 at 60° F., and a viscosity-gravity constant of 0.874, was mixed with 100 parts by volume of nitrothiophene, and heated to slightly above the temperature of complete miscibility, i. e., about 176° F. The homogeneous liquid which resulted was cooled, with agitation, to 130° F. and allowed to settle, whereupon a two-layer system was formed. After separation, the layers were each freed of solvent by vacuum distillation. The resulting undissolved oil fraction (raffinate) comprising 56.8% of the stock had a viscosity of 426 seconds Saybolt universal at 100° F., a specific gravity of 0.9007, and a viscosity-gravity constant of 0.840. The dissolved oil fraction (extract) comprising 43.2% of the stock was more naphthenic in character than the initial oil stock.

II. 100 parts by volume of the same lubricating oil distillate was mixed with 200 parts by volume of nitrothiophene, and heated to slightly above the temperature of complete miscibility, i. e., about 176° F. The homogeneous liquid which resulted was cooled, with agitation, to 130° F. and allowed to settle, whereupon a two-layer system formed. After separation, the layers were each freed of solvent by vacuum distillation. The resulting undissolved oil fraction (raffinate) compriisng 44.2% of the stock had a viscosity of 393 seconds Saybolt universal at 100° F., a specific gravity of 0.8899, and a viscosity-gravity constant of 0.827. The dissolved oil fraction (extract) comprising 55.8% of the stock was more naphthenic in character than the initial oil stock.

From the above examples, it will be noted that by extraction of an oil with a nitrogen-containing derivative of thiophene, such as nitrothiophene, there may be obtained oil fractions which are respectively more paraffinic and more naphthenic than the original oil. By repetition of the extraction process upon the undissolved fraction, oils of even greater paraffinicity will result. The quantity of solvent to be employed will vary, depending upon the character of the thiophene derivative and the stock, the temperature at which the extraction is to be carried out, and the quality of refined oil desired.

While, in the above examples, I have shown the use of a thiophene derivative such as nitrothiophene for extracting hydrocarbon oils, other thiophene derivatives may be suitably employed, for example, amino-thiophene, thiophene nitrile, chloro-nitrothiophene, chloro-amino-thiophene, chloro-thiophene nitrile, the esters of the thiophene carboxylic acids, thienone and acetothienone.

My process is practically independent of the particular nature or source of the crude oil or oil fraction to be extracted. There may be produced by my process oil products of desired characteristics from oil which by distillation will not produce such products.

When, in the appended claims, oil is referred to as being "viscous", it is to be understood that the oil is of substantial viscosity, i. e., of the order of 50 seconds Saybolt universal at 100° F., or more.

What I claim is:

1. In the art of refining mineral oils, the process which comprises separating an oil containing paraffinic and naphthenic hydrocarbons into fractions respectively richer in paraffinic and naphthenic compounds by extracting said oil with a nitrogen-containing derivative of thiophene.

2. In the art of refining mineral oils, the process which comprises adding a nitrogen-containing derivative of thiophene to an oil containing paraffinic and naphthenic hydrocarbons, heating the mixture to such temperature as to effect solution, cooling the solution to form a two-layer system,

and separating the upper layer from the lower layer.

3. In the art of refining mineral oils, the process which comprises adding a nitrogen-containing derivative of thiophene to an oil containing paraffinic and naphthenic hydrocarbons, heating the mixture to such temperature as to effect solution, cooling the solution to form a two-layer system, removing the lower layer, and similarly retreating the upper layer with said solvent.

4. In the art of refining mineral oils, the process which comprises bringing a mineral oil containing paraffinic and naphthenic hydrocarbons into contact with a nitrogen-containing derivative of thiophene, thereby to effect solution of a portion richer in naphthenic hydrocarbons in the solvent, separating the solution so formed from the remainder of the oil, and removing the solvent from both portions of the oil, thereby to obtain fractions of the oil respectively richer in paraffinic and naphthenic hydrocarbons.

5. The process of separating mineral oils containing paraffinic and naphthenic hydrocarbons into fractions, which comprises bringing the oil into contact with a nitrogen-containing derivative of thiophene, thereby to effect solution of a portion of the oil richer in naphthenic hydrocarbons in the solvent, separating the solution so formed from the remainder of the oil, and distilling the solvent from both of the portions of the oil, thereby to obtain fractions of the oil respectively richer in paraffinic and naphthenic hydrocarbons.

6. In the art of refining mineral oils, the process which comprises bringing a mineral oil containing paraffinic and naphthenic hydrocarbons into contact with a nitrogen-containing derivative of thiophene, thereby to effect solution of a portion of the oil richer in naphthenic hydrocarbons in the solvent, separating the solution so formed from the remainder of the oil, and retreating the oil remaining with additional amounts of the solvent.

7. In the art of refining hydrocarbon oil, the process which comprises bringing an oil containing paraffinic and naphthenic hydrocarbons into countercurrent contact with a nitrogen-containing derivative of thiophene, thereby to effect solution of a portion of the oil richer in naphthenic hydrocarbons in the solvent, separating the solution so formed from the remainder of the oil and removing the solvent from the solution and the oil.

8. The method for producing paraffinic lubricating oil from mixed base oil, which comprises bringing the oil into contact with a nitrogen-containing derivative of thiophene, thereby partially dissolving the oil, separating the solution of oil so treated, and removing the solvent from the treated oil.

9. In the art of refining mineral lubricating oil containing paraffinic and naphthenic hydrocarbons, the step of fractionally extracting the oil with a nitrogen-containing derivative of thiophene, to effect separation of fractions respectively richer in paraffinic and naphthenic compounds.

10. The process of treating a viscous fraction of a crude oil of one type containing paraffinic and naphthenic hydrocarbons to procure a fraction having the quality of a corresponding fraction of a crude oil of different type having a greater content of paraffinic hydrocarbons, which comprises extracting the viscous fraction with a nitrogen-containing derivative of thiophene, and separating the oil so treated into portions respectively richer in paraffinic and naphthenic hydrocarbons.

11. The process of treating a viscous fraction of a mixed base crude oil to procure a fraction having the quality of a corresponding fraction of a paraffinic base crude, which comprises extracting the viscous fraction with a nitrogen-containing derivative of thiophene, and separating the oil so treated into portions respectively richer in paraffinic and naphthenic compounds.

12. In the art of refining mineral oils, the process which comprises bringing a nitrogen-containing derivative of thiophene into intimate contact with a viscous hydrocarbon oil of a quality other than that of a Pennsylvania type viscous oil, and containing paraffinic and naphthenic components, thereby to dissolve from the oil substantial amounts of its naphthenic components, thereafter removing the solvent and oil dissolved therein from that portion of the oil which remains undissolved, thereby to produce an oil such as is normally obtained from Pennsylvania type crude by distillation.

13. In the art of refining mineral oils, the process which comprises separating an oil containing paraffinic and naphthenic hydrocarbons into fractions respectively richer in paraffinic and naphthenic compounds by extracting said oil with nitrothiophene.

14. In the art of refining mineral oils, the process which comprises bringing a mineral oil containing paraffinic and naphthenic hydrocarbons into contact with nitrothiophene thereby to effect solution of a portion richer in naphthenic hydrocarbons in the solvent, separating the solution so formed from the remainder of the oil, thereby to obtain fractions of the oil respectively richer in paraffinic and naphthenic hydrocarbons.

15. The process of treating a viscous fraction of a crude oil of one type containing paraffinic and naphthenic hydrocarbons to procure a fraction having the quality of a corresponding fraction of a crude oil of a different type having a greater content of paraffinic hydrocarbons, which comprises extracting the viscous fraction with nitrothiophene, and separating the oil so treated into portions respectively richer in paraffinic and naphthenic hydrocarbons.

16. The method for producing a paraffinic lubricating oil from a mixed base oil, which comprises bringing the oil into contact with nitrothiophene, thereby partially dissolving the oil, separating the solution of the oil so treated, and removing the solvent from the treated oil.

17. In the process of decreasing the viscosity-gravity constant of a viscous mineral oil, the step of extracting the oil with a nitrogen-containing derivative of thiophene.

18. In the process of decreasing the viscosity-gravity constant of a viscous mineral oil, the step of extracting the oil with nitrothiophene.

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