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HYDROCARBON OIL EXTRACTION

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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 products into fractions of different chemical compositions 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 means of fractional extraction with ethylene glycol ethers and their acyl derivatives or mixtures thereof, or mixtures of solvents containing substantial quantities of ethylene glycol ethers and their acyl derivatives.

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}, olefines 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 paraffin base crude oils, such as those obtained from the oil fields of Pennsylvania, there is a relatively high proportion of hydrocarbons 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 these two extremes.

As the use of practically all of the petroleum oils is almost entirely physical, the above described chemical nature of those oils is important in reflecting certain physical characteristics.

The variance in the proportion of the different series of hydrocarbons in paraffinic, naphthenic, and mixed base oils is evidenced by the physical properties of the various oils and particularly by the relationship of the specific gravity to the viscosity of one oil as compared with another. For example, oils derived from a Pennsylvania crude and having a viscosity of 400 seconds Saybolt universal at 100° F., will show a specific gravity at 60° F. of about 0.878, whereas in oil of corresponding viscosity produced from a naphthenic crude, such as one from the Gulf Coast area, will show a specific gravity of about 0.933 at 60° F. The relationship between the viscosity and gravity indicates the degree of the paraffinic or naphthenic character of the oil.

If a given crude petroleum be distilled into successive fractions and the specific gravities and viscosities of the several fractions determined, it will be found that they conform to the general relationship:

$$G=a+\frac{1.0752-a}{10}\log(V-38)$$

in which "G" is the specific gravity at 60° F., "V" is Saybolt universal viscosity at 100° F., and "a" is a constant known as the viscosity-gravity constant. Fractions from each of the different types of crude have different viscosity-gravity constants. Such constants are lower for fractions of the paraffinic crudes than are the constants for fractions of the naphthenic crudes. An article entitled "The viscosity-gravity constant of petroleum lubricating oils" by J. B. Hill and H. B. Coats, which will be found in volume 20, page 641 et seq., Industrial and Engineering Chemistry for June 1928, explains the determination of such constant for several typical oils.

The viscosity-gravity constant is, therefore, an index of the paraffinicity or naphthenicity of an oil, since when a given crude is distilled and fractions thereof are collected, regardless of the fraction upon which the specific gravity and the viscosity are taken, when such specific gravity and viscosity are substituted in the formula and the viscosity-gravity constant of the fraction calculated, the constant will be substantially the same for each of the several fractions of the crude.

The viscosity-gravity constants of the viscous fractions for some of the typical crudes are as follows:

Milltown (Pennsylvania)	0.8067
Burbank (Mid-Continent)	0.8367
Guadalupe (Gulf Coast)	0.8635
Mirando (Gulf Coast)	0.9025

These oils are increasingly paraffinic as the viscosity-gravity constants decrease.

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 ethylene glycol ethers an their acyl derivatives. Ethylene glycol monoalkyl ether, ethylene glycol monoalkyl ether acetate, diethylene glycol monoalkyl ether, and more particularly ethylene glycol monoethyl ether, known as cellosolve, ethylene glycol monoethyl ether acetate, known as cellosolve acetate, ethylene glycol monomethyl ether, known as methyl cellosolve, and diethylene glycol monobutyl ether, known as butyl carbitol, are the selective solvents that I prefer to use, however, other ethylene glycol ethers and their acyl derivatives may be employed, and are considered within the scope of my invention. The various series of hydrocarbons possess a differential solubility in such solvents; the naphthenic hydrocarbons are much more soluble therein than the paraffinic hydrocarbons. By means of extraction with ethylene glycol ethers and their acyl derivatives, and more particularly with one or more of the specific solvents mentioned above, it is therefore, 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, and conversely, to obtain oils from mixed base crudes such as are normally obtained from the naphthenic oils of the Gulf Coast area.

In practicing my invention, I prefer to mix the oil fraction to be treated with a suitable proportion of an ethylene glycol ether or an acyl derivative thereof or a mixture of them, and more particularly with one or more of the specific solvents above mentioned at a temperature sufficiently high so that complete solution is effected and a homogeneous liquid obtained. I then cool the mixture to a temperature sufficiently low to cause a separation of the liquid into a two-layer system, the upper layer being a solution of a relatively small amount of the solvent in the more paraffinic portion of the oil, and the lower layer comprising a solution of the more naphthenic portion of the oil in the solvent. Instead of this heating and cooling to effect extraction, I may simply agitate the mixture of liquids at normal temperatures. Where substantial quantities of solid hydrocarbons belonging to the true paraffin series (C_nH_{2n+2}) are present, these solids or waxes remain in the upper layer and may cause it to be solid or semi-solid. Separation of the two layers is then effected, for example, by decantation, and the solvent removed from each of the separated oil layers by vacuum distillation or other suitable procedure, thereby obtaining two oils of similar distillation ranges but of widely different physical characteristics and correspondingly different chemical compositions.

Before removing the solvent from the upper and more paraffinic layer of oil obtained in the above described process, I may add a further quantity of solvent, and repeat the process for an extraction of additional naphthenic bodies from the oil. The extraction may be repeated any desired number of times, thereby producing oils of progressively increasing paraffinicity as evidences by a decreasing viscosity-gravity constant. In wax-bearing oils, the final undissolved product is a mixture of solid and liquid hydrocarbons. While the exact chemical compositions of these compounds are not known, it is probable that the liquid hydrocarbons are branched chain hydrocarbons of the paraffin series, whereas solid bodies are straight chain paraffin hydrocarbons. This product may be further separated into solid and liquid hydrocarbons by any of the well-known dewaxing processes, such as the cold settling process.

In many instances it will be found of advantage to dewax the oil prior to the extraction process, as this expedites the manual operation of the latter.

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

100 parts of a previously untreated distillate obtained from a Gulf Coast crude oil and having a viscosity of 612 seconds Saybolt universal at 100° F., a specific gravity of 0.9303, and a consequent viscosity gravity constant of 0.874 was mixed with 100 parts of cellosolve acetate and heated to slightly above the temperature of complete miscibility, which in this particular case was 22° C. The homogeneous liquid which resulted was cooled with agitation to 0° C., and allowed to settle whereupon a two layer system formed, which consisted of an upper undissolved oil layer comprising 94.7 parts of the mixture and a lower layer of oil dissolved in cellosolve acetate comprising approximately 105.3 parts of the mixture. After separation, the layers were each freed from cellosolve acetate by

vacuum distillation. The cellosolve acetate dissolved fraction yielded 83 parts of cellosolve acetate and 22.3 parts of oil having a viscosity of 1170 seconds Saybolt universal at 100° F., a specific gravity of 0.9833 and a viscosity gravity constant of 0.942. The undissolved fraction yielded 17 parts of cellosolve acetate and 77.7 parts of an oil having a viscosity of 502 seconds Saybolt universal at 100° F., and a specific gravity of 0.9159, and a viscosity gravity constant of 0.858.

100 parts of a previously untreated distillate obtained from a Gulf Coast crude oil and having a viscosity of 612 seconds Saybolt universal at 100° F., a specific gravity of 0.9303, and a consequent viscosity gravity constant of 0.874 were mixed with 100 parts of cellosolve and heated to slightly above the temperature of complete miscibility, which in this particular case was 60° C. The homogeneous liquid which resulted was cooled with agitation to 40° C., and allowed to settle whereupon a two layer system formed, which consisted of an upper undissolved oil layer comprising 54.3 parts of the mixture and a lower layer of oil dissolved in cellosolve comprising approximately 345.7 parts of the mixture. After separation, the layers were each freed from cellosolve by vacuum distillation. The cellosolve dissolved fraction yielded 291 parts of cellosolve and 54.7 parts of oil having a viscosity of 940 seconds Saybolt universal at 100° F., a specific gravity of 0.9561, and a viscosity gravity constant of 0.906. The undissolved fraction yielded 9 parts of cellosolve and 45.3 parts of an oil having a viscosity of 464 seconds Saybolt universal at 100° F., and a specific gravity of 0.9030, and a viscosity gravity constant of 0.842.

100 parts of a previously untreated distillate obtained from a Gulf Coast crude oil and having a viscosity of 612 seconds Saybolt universal at 100° F., a specific gravity of 0.9303, and a consequent viscosity gravity constant of 0.874 was mixed with 100 parts of methyl cellosolve and heated to slightly above the temperature of complete miscibility, which in this particular case was 120° C. The homogeneous liquid which resulted was cooled with agitation to 98° C., and allowed to settle whereupon a two layer system formed, which consisted of an upper undissolved oil layer comprising 100 parts of the mixture and a lower layer of oil dissolved in methyl cellosolve comprising approximately 100 parts of the mixture. After separation, the layers were each freed from methyl cellosolve by vacuum distillation. The methyl cellosolve dissolved fraction yielded 82 parts of methyl cellosolve and 18 parts of oil having a viscosity of 65.4 seconds Saybolt universal at 210° F., a specific gravity of 0.9738, and a viscosity gravity constant of 0.929. The undissolved fraction yielded 18 parts of methyl cellosolve and 82 parts of an oil having a viscosity of 587 second Saybolt universal at 100° F., and a specific gravity of 0.9212, and a viscosity gravity constant of 0.864.

100 parts of a previously untreated distillate obtained from a Gulf Coast crude oil and having a viscosity of 612 seconds Saybolt universal at 100° F., a specific gravity of 0.9303, and a consequent viscosity gravity constant of 0.874 was mixed with 100 parts of butyl carbitol and heated to slightly above the temperature of complete miscibility, which in this particular case was 22° C. The homogeneous liquid which resulted was cooled with agitation to 0° C., and allowed to settle whereupon a two layer system formed, which consisted of an upper undissolved oil layer comprising 24.5 parts of the mixture and a lower layer of oil dissolved in butyl carbitol comprising approximately 375.5 parts of the mixture. After separation, the layers were each freed from butyl carbitol by vacuum distillation. The butyl carbitol dissolved fraction yielded 297 parts of butyl carbitol and 78.5 parts of oil having a viscosity of 701 seconds Saybolt universal at 100° F., a sepecific gravity of 0.9383 and a viscosity gravity constant of 0.884. The undissolved fraction yielded 3 parts of butyl carbitol and 21.5 parts of an oil having a viscosity of 325 seconds Saybolt universal at 100° F., and a specific gravity of 0.8905, and a viscosity gravity constant of 0.830.

From the above examples it will be seen that by one extraction with the solvent there may be obtained oil fractions which are respectively higher in paraffinicity and naphthenicity than the original oil. By repetition of the extraction process upon the undissolved fraction, oils may be obtained which are increasingly paraffinic, as evidenced by progressively decreasing viscosity-gravity constants.

It is evident that my process is practically independent of the particular nature or source of the crude oil, and that there may be produced thereby oils of desired characteristics from oils which heretofore have not been used as a source of oils of such desired characteristics.

For example, my process may be employed to produce from petroleum of a mixed base type such as would, on normal batch distillation, give a residuum with a viscosity of 150 seconds Saybolt universal at 210° F. with a specific gravity of 0.928 or more, a lubricating stock with a viscosity of 150 seconds Saybolt universal at 210° F., or more, and a specific gravity not higher than 0.910. This latter combination of properties is typical of cylinder stocks produced from Pennsylvania crudes.

In extracting oils containing appreciable amounts of wax, such oils may be dewaxed, for example, by cold settling or centrifuging prior to carrying out the extraction. My process is operable, however, in the absence of preliminary dewaxing.

Hereinabove, mixtures of solvents have been referred to. It is to be understood that in such mixtures the constituent solvents will not react with one another, nor with the oil upon which they are to be used, and that such mixtures will contain substantial amounts of an ethylene glycol ether or an acyl derivative thereof.

For brevity, in the appended claims, the term "ethylene glycol ether" is employed in a generic sense to include one or a mixture of ethylene glycol ethers and their acyl derivatives, or a mixture of solvents which contains substantial quantities of ethylene glycol ethers and their acyl derivatives.

Also where herein and in the appended claims, an oil is specifically 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 an ethylene glycol ether.

2. In the art of refining mineral oils, the process which comprises fractionally extracting an oil containing paraffinic and naphthenic hydrocarbons with an ethylene glycol ether to produce fractions of the oil respectively richer in paraffinic and naphthenic compounds.

3. In the art of refining mineral oils, the process which comprises adding an ethylene glycol ether 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.

4. In the art of refining mineral oils, the process which comprises adding an ethylene glycol ether 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 an ethylene glycol ether.

5. In the art of refining mineral oils, the process which comprises bringing a mineral oil containing paraffinic and naphthenic hydrocarbons into contact with an ethylene glycol ether, thereby to effect solution of a portion richer in naphthenic hydrocarbons in the ethylene glycol ether, separating the solution so formed from the remainder of the oil, and removing the ethylene glycol ether from both portions of the oil, thereby to obtain fractions of the oil respectively richer in paraffinic and naphthenic hydrocarbons.

6. The process for separating mineral oils containing paraffinic and naphthenic hydrocarbons into fractions which comprises bringing the oil into contact with an ethylene glycol ether, thereby to effect solution of a portion of the oil richer in naphthenic hydrocarbons in the ethylene glycol ether, separating the solution so formed from the remainder of the oil, and distilling the ethylene glycol ether from both of the portions of the oil, thereby to obtain fractions of the oil respectively richer in paraffinic and naphthenic hydrocarbons.

7. In the art of refining mineral oils, the process which comprises bringing a mineral oil containing paraffinic and naphthenic hydrocarbons into contact with an ethylene glycol ether, thereby to effect solution of a portion richer in naphthenic hydrocarbons in the ethylene glycol ether, separating the solution so formed from the remainder of the oil, and retreating the oil remaining with additional amounts of an ethylene glycol ether.

8. The method of producing paraffinic lubricating oil from mixed base crude which comprises distilling the crude and bringing a portion thereof into contact with one or more solvents from the group consisting of cellosolve, methyl cellosolve, cellosolve acetate and butyl carbitol, thereby partially dissolving the oil, separating the solvent solution of oil so treated, and removing the solvent from the treated oil.

9. The process of producing a lubricating stock of specific gravity less than .910 and of Saybolt universal viscosity greater than 150 seconds at 210° F. from a crude petroleum which on normal distillation yields a residuum of 150 seconds Saybolt universal viscosity at 210° F. and a specific gravity greater than .928, which comprises producing a residuum from the crude petroleum, and extracting said residuum from said crude petroleum with one or more solvents from the group consisting of cellosolve, methyl cellosolve, cellosolve acetate and butyl carbitol.

10. In the art of refining mineral lubricating oil containing paraffinic and naphthenic hydrocarbons, the step of fractionally extracting the oil with one or more solvents from the group consisting of cellosolve, methyl cellosolve, cellosolve acetate and butyl carbitol, to effect separation of fractions respectively richer in paraffinic and naphthenic compounds.

11. The process of producing a lubricating stock of specific gravity less than .910 and of Saybolt universal viscosity greater than 150 seconds at 210° F. from a crude petroleum which on normal distillation yields a residuum of 150 seconds Saybolt universal vis-

cosity at 210° F. and a specific gravity greater than .928, which comprises separating a residuum from said crude petroleum and bringing such residuum into contact with one or more solvents from the group consisting of cellosolve, methyl cellosolve, cellosolve acetate and butyl carbitol, to effect solution of a portion thereof with the solvent, separating the solvent solution of oil from the portion which does not dissolve therein, and removing the solvent from the oil of said solution.

12. In a process for separating a viscous mineral oil containing paraffinic and naphthenic hydrocarbons into fractions which are respectively richer in naphthenic hydrocarbons and paraffinic hydrocarbons other than wax, the step which comprises extracting the oil with one or more solvents from the group consisting of cellosolve, methyl cellosolve, cellosolve acetate and butyl carbitol.

13. In a process for separating viscous mineral oil liquid at ordinary temperature containing paraffinic and naphthenic hydrocarbons into fractions respectively richer in paraffinic and naphthenic hydrocarbons, the step which comprises extracting the oil with one or more solvents from the group consisting of cellosolve, methyl cellosolve, cellosolve acetate and butyl carbitol.

14. In a process for separating a substantially wax free viscous mineral oil containing paraffinic and naphthenic hydrocarbons into fractions respectively richer in paraffinic and comprises extracting the oil with one or more solvents from the group consisting of cellosolve, methyl cellosolve, cellosolve acetate and butyl carbitol.

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 different type having a greater content of paraffinic hydrocarbons, which comprises extracting the viscous fraction with one or more solvents from the group consisting of cellosolve, methyl cellosolve, cellosolve acetate and butyl carbitol, and separating the oil so treated into portions respectively richer in paraffinic and naphthenic hydrocarbons.

16. 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 one or more solvents from the group consisting of cellosolve, methyl cellosolve, cellosolve acetate and butyl carbitol, and separating the oil so treated into portions respectively richer in paraffinic and naphthenic compounds.

17. In the art of refining mineral oils, the process which comprises adding one or more solvents from the group consisting of cellosolve, methyl cellosolve, cellosolve acetate and butyl carbitol to a viscous oil liquid at ordinary temperatures containing paraffinic and naphthenic hydrocarbons, heating the mixture to a temperature sufficient to effect solution, cooling the solution to a temperature sufficient to form two layers respectively richer in naphthenic hydrocarbons and paraffinic hydrocarbons other than wax, and separating the upper layer richer in paraffinic hydrocarbons from the lower layer richer in naphthenic hydrocarbons.

18. In the art of refining mineral oils, the process which comprises adding one or more solvents from the group consisting of cellosolve, methyl cellosolve, cellosolve acetate and butyl carbitol to a viscous oil liquid at ordinary temperatures containing paraffinic and naphthenic hydrocarbons, heating the mixture to a temperature sufficient to effect solution, cooling the solution to a temperature sufficient to form two layers, separating the solvent and paraffin wax from the upper layer, and separating the solvent from the lower layer to produce one fraction richer in paraffinic and a second fraction richer in naphthenic hydrocarbons than said viscous oil.

In testimony whereof I affix my signature.

LAWRENCE M. HENDERSON.