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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 means of fractional extraction with a mixed aliphatic-aromatic amine, and more particularly phenylmethylamine or a mixture of solvents containing substantial amounts of aliphatic-aromatic amines. The term "mixed aliphatic-aromatic amines" as used herein comprehends one or a mixture of two or more aliphatic-aromatic amines in which at least one aryl and at least one alkyl radical are directly bonded to the same amino nitrogen. Specific examples of other aliphatic-aromatic amines that may be employed in my process are phenyl diethylamine and phenyl butylamine.

It is recognized in the art that mineral oils, such as petroleum, comprise essentially a mixture of hydro-carbons 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}, hydro-aromatics 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.

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 an 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 paraffinicity or naphthenicity of the oil, and such relationship may be expressed by the viscosity-gravity constant as hereinafter described.

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

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

$$G=0.24+0.755a+0.022\log(V'-35.5)$$

in which "G" is the specific gravity at 60° F., "V" and "V'" are respectively Saybolt universal viscosities at 100° F. and 210° F., and "*a*" is a constant known as the viscosity-gravity constant. Viscous fractions from each of the different types of crude have different viscosity-gravity constants. While, in general, viscous fractions from a single crude have substantially the same viscosity-gravity constant, such constant is lower for fractions of the paraffinic crudes than is the constant 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 viscous oils, since when a given crude is distilled, the fractions thereof collected, and the specific gravity and the viscosity of each of the viscous fractions determined, such specific gravities and viscosities substituted in the formula, and the viscosity-gravity constants of the fractions calculated, it will be found that such constants are substantially the same.

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

While the above figures indicate the viscosity-gravity constants of specific oils from several types of crudes, it is to be understood that for any particular type of crude such constant may be within a range between values above and below the constant of the typical crude given. For example, viscous oils resulting from the distillation of Mid-Continent crudes have viscosity-gravity constants ranging from about .835 to about .855, whereas the viscous fractions resulting from the distillation of Pennsylvania type crudes range from about .805 to about .828, and in most instances, are below .820. Oils are increasingly paraffinic as their 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 a mixed aliphatic-aromatic amine. 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 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 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 the solvent at a temperature such that complete solution is effected and a homogeneous liquid obtained. I then cool the mixture to a temperature at which separation of the liquid into a two-layer system will take place. The upper layer will contain a relatively small amount of the solvent dissolved in the paraffinic portion of the oil while the lower layer will contain the more naphthenic portion of the oil dissolved in the solvent. Or, I may agitate the mixture of solvent and oil at temperatures at which the liquids 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 counter-current 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 compositions and different physical characteristics.

Before removing the solvent from the upper and more paraffinic layer, I may add a further quantity of 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.

Where substantial quantities of waxy hydrocarbons belonging to the true paraffin series (C_nH_{2n+2}) are present, such hydrocarbons remain in the upper or more paraffinic layer and may cause such layer to be solid or semi-solid. Such layer may be separated into solid and liquid hydrocarbons by any of the well-known dewaxing processes such as by cold-settling 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 example:

100 parts of a Mid-Continent distillate having a viscosity of 305 seconds Saybolt universal at 100° F., a specific gravity of 0.909 at 60° F., and a viscosity-gravity constant of 0.853 was mixed with 300 parts of phenylmethylamine and heated to slightly above the temperature of complete miscibility, which was approximately 17° C. The homogeneous liquid which resulted was cooled with agitation to −5° C., and allowed to settle, whereupon a two layer system formed. After separation, the layers were each freed of solvent by vacuum distillation. The undissolved oil fraction comprising 58.2% of the stock had a viscosity of 209 seconds Saybolt universal at 100° F., a specific gravity of 0.878, and a viscosity-gravity constant of 0.822. The dissolved oil fraction comprising 41.8% of the stock had a viscosity of 695 seconds Saybolt universal at 100° F., a specific gravity of 0.948 and a viscosity-gravity constant of 0.898.

From the above example it will be noted that by extraction of an oil with phenylmethylamine, 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.

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 oils which by distillation will not produce such products.

Hereinabove, mixtures of solvents have been referred to. It is to be understood that in such mixtures the constituents 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 mixed aliphatic-aromatic amines.

For brevity, in the appended claims "mixed aliphatic-aromatic amines" is employed in a generic sense to include one or a mixture of aliphatic-aromatic amines in which at least one aryl and at least one alkyl radical is directly bonded to the same amino nitrogen or a mixture of solvents containing substantial amounts of mixed aliphatic-aromatic amines.

Also, herein and in the appended claims, 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 a mixed aliphatic-aromatic amine.

2. In the art of refining mineral oils, the process which comprises adding a mixed aliphatic-aromatic amine 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 mixed aliphatic-aromatic amine 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 mixed amine.

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 mixed aliphatic-aromatic amine thereby to effect solution of a portion richer in naphthenic hydrocarbons in the mixed aliphatic-aromatic amine, separating the solution so formed from the remainder of the oil, and removing the mixed amine from both portions of the oil, thereby to obtain fractions of the oil respectively richer in paraffinic and naphthenic hydrocarbons.

5. The process for separating mineral oils containing paraffinic and naphthenic hydrocarbons into fractions which comprises bringing the oil into contact with a mixed aliphatic-aromatic amine thereby to effect solution of a portion of the oil richer in naphthenic hydrocarbons in the mixed aliphatic-aromatic amine, separating the solution so formed from the remainder of the oil, and distilling the said mixed amine from both of the portions of the oil, thereby to obtain fractions of the roll respectively richer in paraffinic and naphthenic hydrocarbons.

6. 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 mixed aliphatic-aromatic amine, and separating the oil so treated into portions respectively richer in paraffinic and naphthenic hydrocarbons.

7. In the art of refining mineral oils, the process which comprises bringing a mixed aliphatic-aromatic amine 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.

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

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

10. The method of producing paraffinic lubricating oil from mixed base crude which comprises distilling the crude and bringing a portion thereof into contact with phenylmethylamine, thereby partially dissolving the oil, separating the phenylmethylamine solution of oil so treated, and removing the phenylmethylamine from the treated oil.

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

12. 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 phenylmethylamine and separating the oil so treated into portions respectively richer in paraffinic and naphthenic hydrocarbons.

13. 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 phenylmethylamine, and separating the oil so treated into portions respectively richer in paraffinic and naphthenic compounds.

14. In the art of refining mineral oils, the process which comprises adding phenylmethylamine 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.

15. In the art of refining mineral oils, the process which comprises bringing phenylmethylamine 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.

16. The process of decreasing the viscosity-gravity constant of a viscous mineral oil which comprises extracting the oil with a mixed aliphatic-aromatic amine.

17. The process of decreasing the viscosity-gravity constant of a viscous mineral oil at least 0.015 which comprises extracting the oil with phenylmethylamine.

18. The process of treating a viscous mineral oil of viscosity-gravity constant between substantially 0.850 and 0.875 to reduce the viscosity-gravity constant by at least 0.015, which comprises fractionally extracting said viscous oil with phenylmethylamine.

19. The process of treating a viscous mineral oil of viscosity-gravity constant higher than 0.850 to produce an oil having a viscosity-gravity constant less than 0.830 which comprises fractionally extracting said viscous oil with phenylmethylamine.

20. The process of treating a viscous mineral oil of viscosity-gravity constant higher than 0.835 to produce an oil having a viscosity-gravity constant of less than 0.828 which comprises fractionally extracting said viscous oil with phenylmethylamine.

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