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SOLVENT TREATMENT OF HYDROCARBON OILS

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This invention relates to extraction methods of refining mineral oils and has particular reference to methods for extracting such oils by means of solvents whereby fractions of different chemical composition though of the same distillation range, are obtained.

It is well known in the art that mineral oils such as petroleum comprise essentially a mixture of various groups or homologous series of compounds such, for example, as paraffins, olefins, hydroaromatics, polymethylenes and other series of compounds of chain and/or ring structure and in which the hydrogen to carbon ratio is less than in the aforementioned series.

Crude petroleum oils are generally classified into three types, namely, paraffinic, naphthenic and mixed base, which contain the various series of hydrocarbons mentioned heretofore, in varying proportions. Probably the best known example of a paraffinic base crude oil is one obtained from the oil fields of Pennsylvania. In this type crude there is a relatively high proportion of hydrocarbons having a chain structure and a high hydrogen to carbon ratio, whereas in the naphthenic 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, for example, as are obtained from the Mid-Continent oil fields, are intermediate between the paraffinic and naphthenic base type crude oils. The paraffinic type crude oils and their distillates may be distinguished from the naphthenic type crude oils and their distillates by certain arbitrary constants used extensively in the oil refining industry.

The first of these constants is known as the viscosity index and is a coefficient based on the change of viscosity with temperature. This is described by Dean and Davis, Chemical and Metallurgical Engineering, vol. 36, page 618, 1929.

The second of the constants referred to is the viscosity-gravity constant. This is a constant expressing a relation between viscosity and specific gravity and is described by Hill and Coates in Industrial and Engineering Chemistry, vol 20, page 641.

The more paraffinic oils are characterized by relatively lower viscosity-gravity constants and relatively higher viscosity indices, while the more naphthenic oils are characterized by higher viscosity-gravity constants and lower viscosity indices.

An object of the invention is to provide a method for separating viscous mineral oils into fractions by means of solvents.

Another object of the invention is to provide a method for increasing the paraffinicity of mineral lubricating oils.

Still another object of the invention is to provide a new extracting agent for separating viscous mineral oils into paraffinic and naphthenic fractions.

Other objects of the invention will be apparent from the following description.

We have now found that oils containing both paraffinic and various naphthenic hydrocarbons may be fractionally extracted with a selective solvent such as morpholine (tetrahydroparoxazine) and derivatives thereof such as those derivatives in which one or more hydrogen atoms in the morpholine molecule is substituted by alkyl groups. As examples of such derivatives may be mentioned ethyl tetrahydroparoxazine, 1 methyl tetrahydroparoxazine, 1 butyl tetrahydroparoxazine and others. The various series of hydrocarbons possess a different solubility in such solvent, the naphthenic hydrocarbons being much more soluble therein than the paraffinic hydrocarbons. When mineral oil containing both series of hydrocarbons is extracted with a solvent of the class above set forth, it is possible to effect a partial separation of the paraffinic from the naphthenic hydrocarbons and to obtain a fraction which is more paraffinic than the original oil and one which is more naphthenic. For example, from an oil of the mixed base type such as is frequently found in the Mid-Continent area it is possible to produce an oil of a more paraffinic type such as is generally found in the Pennsylvania oil fields. However, regardless of the source, it is possible to obtain by our process oils which are respectively more paraffinic and more naphthenic than the oils normally obtained from such source by distillation.

In accordance with our invention, the oil to be treated is first mixed with morpholine or a suitable derivative of morpholine at such temperature that complete solution is effected. When the temperature of the mixture is reduced, a separation of the liquid into a two-layer system will take place. One layer will contain a relatively small amount of the solvent dissolved in the paraffinic portion of the oil. This is called raffinate. The other layer will contain the more naphthenic portion of the oil dissolved in the major quantity of the solvent. This is called the extract. This procedure may be conducted batchwise or counter-currently. After the extraction, separation of the solvent from the oil may be effected by any one of a number of

methods such as distillation, extraction with water and sulfuric acid, or precipitation with carbon dioxide or a carbon dioxide containing gas. The two layers formed as a result of the extraction operation are of course, separated prior to the removal of the solvent. This separation may be accomplished by any suitable procedure, for example, by decantation. The extraction step may be repeated any desired number of times, each extraction producing an oil of higher paraffinicity, as may be evidenced by its higher viscosity index. Dewaxing may be effected either prior or subsequent to the extraction procedure.

The invention will be more clearly understood from the following specific examples.

Example 1.—100 parts by volume of a lubricating distillate obtained from a Mid-Continent oil, the characteristics of which are given in Table I, was extracted three successive times with 100 parts by volume of commercial morpholine. The mixture was first heated to a temperature of 140° F. and then allowed to cool to 120° F. whereupon a two-layer system was formed. Cooling was continued to approximately 80° F. and the two layers then separated by decantation. The solvent was removed from the two layers by washing with water, which was followed by a wash of 2% sulfuric acid and then a final water wash. A 52% yield by volume of raffinate fraction was obtained. Tests on the original oil and the raffinate fraction are tabulated below:

TABLE I

	Original oil	Raffinate
Gravity	26.7	31.4
Vis./100	286.3	202.7
Vis./210	49.5	46.5
VI	73	101
VGC	0.838	0.810
Percent carbon residue	0.05	0.015
NPA color	+4	2½

Example 2.—100 parts by volume of the same lubricating stock was treated with four successive portions of 50 parts by volume of morpholine. The extract was decanted before mixture of the raffinate with each successive portion of morpholine. Each batch of solvent was mixed with the oil at a temperature of 180° F. and allowed to cool to approximately 80° F. The two layers were separated by decantation and the morpholine separated from both the raffinate and the extract by distillation at atmospheric pressure. The yield of raffinate was 67% by volume. Tests on both the raffinate and the extract are shown in Table II.

TABLE II

	Raffinate	Extract
Gravity	29.3	19.5
Vis./100	216.1	671
Vis./210	47.1	57.5
VI	98	3
VGC	.824	.884
Color	2½	+7
Percent carbon residue	0.01	0.07

Example 3.—100 parts by volume of 300 vis. Gulf Coast lubricating distillate, the characteristics of which are set forth in Table III, was mixed with four successive portions of 50 parts by volume of morpholine in the manner described in connection with Example 2. The mixing temperature was 180° F. The mixture was allowed to cool to approximately 80° F. prior to separation of the two layers by decantation. The yield of raffinate was 52% by volume. The solvent was removed from both the raffinate and extract by distillation at room temperature. Tests on the original oil, raffinate and extract are all shown in Table III.

TABLE III

	Original oil	Raffinate	Extract
Gravity	20.5	24.7	16.4
Flash	380	385	375
Fire	420	425	430
Vis./100	307.3	249.2	405.0
Vis./210	46.8	45.9	48.8
VI	18	50	−10
VGC	.887	.855	.916
Color	3	1+	4½+
Pour	B-30	B-30	
Percent carbon residue	0.03	0.01	

(B—below)

TABLE III.—Continued

	Original oil	Raffinate
Demulsibility—130° F	220	1620
Demulsibility—180° F	1620	1620
Steam emulsion No	154	68

Tests after Brown-Boveri ageing

	Original oil	Raffinate
Sludge (mgms./200 cc. oil)	90	11.
Acid No	0.50	0.05.
Corrosion of copper strip	Positive	Negative.
Steam jet test	25 minutes	5 minutes.

From the foregoing data it is obvious that extraction of an oil with morpholine provides an efficient means of separating the oil into fractions which are respectively more paraffinic and more naphthenic than the original oil. By repetition of the extraction process upon the raffinate fraction, oils of still greater paraffinicity may be obtained. The temperature at which the extraction is most advantageously carried out, the quantity of solvent to be used and the method of separating the solvent from the oil may vary considerably, depending upon the stock being treated and the equipment available with which to carry out the process but in general the ratio of solvent to oil will range from 1 to 5 parts of solvent by volume to 1 part of oil and the temperature of extraction from 125° F. to 200° F. Separation of the solvent and oil into two distinct phases generally occurs at about 120° F. but this may vary greatly depending on the nature of the stock being treated.

In addition to the methods of separating the solvent from the oil described in the specific examples, morpholine may be readily separated from oil at ordinary temperature by first contacting the morpholine with carbon dioxide, forming a solid carbamate which may be easily separated by filtration. Both the carbon dioxide and morpholine may be recovered as such by simply heating the solid carbamate to a temperature of approximately 200° F.

It will also be noted from the data in Example 3 that treatment of a 300 vis. Gulf Coast oil with morpholine produces a raffinate suitable as a high quality turbine oil. The sludging characteristics as shown by the Brown-Boveri test are commensurate with high quality turbine oils commercially available. A considerable improvement in the carbon residue and color of the raffinate is

obtained which adds materially to the desirable properties of oils treated by our method.

While the foregoing examples show the use of morpholine as a selective solvent for hydrocarbon oils, derivatives of morpholine, particularly those in which the hydrogen is replaced by an alkyl group, may also be suitably employed alone or mixed with each other or with morpholine. The process is applicable to oils from all types of crude.

We claim:

1. In the solvent refining of mineral oils, the process which comprises separating an oil containing paraffinic and naphthenic hydrocarbons into fractions respectively higher in paraffinic and naphthenic compounds by extracting said oil with compounds selected from the group consisting of morpholine and its derivatives.

2. In the solvent refining of mineral oils, the process which comprises adding compounds selected from the group consisting of morpholine and its derivatives to an oil containing paraffinic and naphthenic hydrocarbons, heating the mixture to such temperature as to effect solution, cooling the solution to form fractions respectively higher in paraffinic and naphthenic compounds and separating the two fractions.

3. Process in accordance with claim 2 where the added compound is morpholine.

4. In the solvent refining of mineral oils, the process which comprises adding compounds selected from the group consisting of morpholine and alkyl derivatives of morpholine to an oil containing paraffinic and naphthenic hydrocarbons, heating the mixture to such temperature as to effect solution, cooling the solution to form fractions respectively higher in paraffinic and naphthenic compounds, removing the fraction rich in naphthenic compounds and similarly retreating the fraction rich in paraffinic compounds with said solvent.

5. Process in accordance with claim 4 where the added compound is morpholine.

6. In the solvent refining of mineral oils, the process of producing a more paraffinic lubricating oil from a base oil of lesser paraffinicity which comprises bringing the oil into contact with compounds selected from the group consisting of morpholine and alkyl derivatives of morpholine, thereby partially dissolving the oil, separating the solution of oil so treated into fractions respectively more paraffinic and less paraffinic and removing the solvent from the treated oil.

7. Process in accordance with claim 6 where the compound is morpholine.

8. In the solvent refining of mineral oils, the process which comprises bringing mineral oil containing paraffinic and naphthenic hydrocarbons into contact with compounds selected from the group consisting of morpholine and alkyl derivatives of morpholine, thereby effecting solution in the solvent of a portion relatively higher in naphthenic hydrocarbons, separating the solution so formed from the remainder of the oil and removing the solvent from both portions of the oil, thereby obtaining fractions of the oil respectively of higher paraffinic and naphthenic hydrocarbon content.

9. Process in accordance with claim 8 where the oil is brought into contact with morpholine.

10. Process in accordance with claim 8 where the solvent is removed from both portions of the oil by distillation.

11. Process in accordance with claim 8 whereby the solvent is removed from both portions of the oil by reacting the solvent with carbon dioxide or a carbon dioxide-containing gas whereby a substantially insoluble product is formed.

12. In the solvent refining of mineral oils, the process which comprises separating an oil containing paraffinic and naphthenic hydrocarbons into fractions respectively more paraffinic and more naphthenic than the original oil by extracting said oil with morpholine.

13. Process in accordance with claim 12 where the morpholine is removed from both fractions by distillation.

14. Process in accordance with claim 12 where the morpholine is removed from both fractions by contacting the fractions with carbon dioxide or carbon dioxide containing gas whereby relatively solid insoluble compounds are formed.

15. In the solvent refining of mineral oils, the method of increasing the viscosity index of mineral lubricating oil distillate comprising extracting the oil with compounds of the group consisting of morpholine and alkyl derivatives of morpholine whereby to separate fractions of respectively higher and lower viscosity index.

16. Method in accordance with claim 15 where the compound is morpholine.

17. In the solvent refining of mineral oils, the method of increasing the viscosity index of mineral lubricating oil comprising extracting the oil with compounds selected from the group consisting of morpholine and derivatives thereof in which hydrogen is replaced by alkyl groups whereby to separate fractions of respectively higher and lower viscosity index.

18. Method in accordance with claim 17 where the compound is ethyl tetrahydroparoxazine.

19. Method in accordance with claim 17 where the compound is 1 butyl tetrahydroparoxazine.

20. In the solvent refining of hydrocarbon oils, the process which comprises separating an oil containing paraffinic and non-paraffinic hydrocarbons into fractions respectively higher in paraffinic and non-paraffinic compounds by extracting said oil with solvent containing one or more compounds selected from the group consisting of morpholine and its derivatives.

21. Process in accordance with claim 20 where the solvent contains morpholine.

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