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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 our invention, crude petroleum or petroleum products, particularly oils of substantial viscosity, are separated into various fractions by extraction with a mixture of primary and secondary solvents. By primary solvents we mean nitrogen-containing cyclic compounds such as, for example, nitrobenzene, benzonitrile and aniline or their homologues, and by secondary solvents we mean alcoholic or hydroxy compounds containing one or more hydroxyl groups such as "cellosolve" $\text{CH}_2\text{OH}.\text{CH}_2\text{OC}_2\text{H}_5$, methyl cellosolve $\text{CH}_2\text{OH}.\text{CH}_2\text{OCH}_3$, butyl cellosolve $\text{CH}_2\text{OH}.\text{CH}_2\text{OC}_4\text{H}_9$, carbitol $\text{CH}_2\text{OH}.\text{CH}_2\text{OCH}_2.\text{CH}_2\text{OC}_2\text{H}_5$, butyl carbitol $\text{CH}_2\text{OH}.\text{CH}_2\text{OCH}_2.\text{CH}_2\text{OC}_4\text{H}_9$, ethylene glycol $\text{CH}_2\text{OH}.\text{CH}_2\text{OH}$ and diethylene glycol $\text{CH}_2\text{OH}.\text{CH}_2\text{OCH}_2.\text{CH}_2\text{OH}$. We also contemplate as within the scope of our invention, the employment of mixtures of primary solvents together with mixtures of secondary solvents.

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 $\text{C}_n\text{H}_{2n+2}$, 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 paraffinic 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, con-

tain hydrocarbons in proportions intermediate 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 lower viscosity indices.

Our 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 mixture of primary and secondary solvents of the type above noted. The various series of hydrocarbons possess a differential solubility in such mixed solvents, the naphthenic hydrocarbons being much more soluble therein than the paraffinic hydrocarbons. By means of extraction with such mixed solvents, 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 our 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 our process, oils which are respectively more paraffinic and more naphthenic than the oils normally obtained from such source by distillation.

It has been known heretofore to separate hydrocarbon oils into fractions by means of solvents such as sulfur dioxide, furfural, and others. Such separation is accomplished by agitating the oil with the solvent and bringing the mixture to such a temperature, below the temperature of complete miscibility of the oil and solvent, that the mixture separates into two layers, one of which is the undissolved and more paraffinic portion of the oil containing some dissolved solvent and the other of which is solvent containing dissolved naphthenic constituents of the oil. These two layers are separated at this "separation temperature" and the solvent may subsequently be removed from each. We have found it highly advantageous to effect such separation by employing a mixture of primary and secondary solvents of the type above referred to. In general, the primary solvents, i. e., nitrogen-containing cyclic compounds, are highly selective but usually require a separation temperature below, for example, 60° F., due to their relatively low miscibility temperature with the hydrocarbon oils. On the other hand, the secondary solvents, i. e., the alcoholic or hydroxy compounds, have a fair selectivity with respect to hydrocarbon oils and may be employed at higher separation temperatures than the primary solvents, due to their higher miscibility temperatures. It will be understood, that in accordance with our invention, an important aspect thereof is the increase of the miscibility temperature of the oil and the primary solvent by the presence of the secondary solvent, regardless of whatever, if any, selective action such secondary solvent may have upon the oil. By employing a suitable mixture of primary and secondary solvents we are able to separate hydrocarbon oils into fractions at temperatures considerably above those which could be employed with a primary solvent alone. For example, a residual oil from Hobbs Crude (Texas) which, with nitrobenzene alone required a temperature of 40° F. for separation, was satisfactorily separated with a mixture of 83 parts of nitrobenzene and 17 parts of carbitol at a temperature of 75° F. It will be understood, of course, that the quality of the undissolved or more paraffinic oil fraction produced by means of the mixed solvents will frequently be somewhat lower than that of a similar fraction produced with nitrobenzene alone. In general, greater yields are obtained and higher operating temperatures may be employed when a mixture of the aforesaid primary and secondary solvents is utilized. In any event, an economic balance must be struck between the yield and quality of the refined oil, and the cost of producing the same.

Furthermore, in accordance with our invention, we are able to separate hydrocarbon oils into fractions with our mixture of primary and secondary solvents, which could not be economically treated with either class of solvents alone. For example, it is not practical to employ a primary solvent, such as nitrobenzene, in treating very asphaltic oil stocks such as those derived

from some California crude oils, for the reason that the miscibility temperature of the oil and solvent is very low, excessive refrigeration is required, and in certain cases the nitrobenzene may crystallize before separation of fractions can be effected. However, by adding to the primary solvent, e. g., nitrobenzene, a suitable quantity of a secondary solvent, for example 20% of carbitol, we are able to treat in a satisfactory manner, even the very asphaltic California oils.

In accordance with our invention, we first mix the oil to be treated with a suitable proportion of our mixture of primary and secondary solvents at a temperature such that complete solution is effected and a homogeneous liquid obtained. We 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 solvents dissolved in the paraffinic portion of the oil while the lower layer will contain the more naphthenic portion of the oil dissolved in the solvents. Or, we may agitate the mixture of solvents 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 solvents. In either of the above procedures we may take advantage of the principles of countercurrent extraction.

After the extraction proper, we effect separation of the two layers which form, by any suitable procedure, as for example, by decantation. We then remove from each of the separated layers, the portion of solvents 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 solvents from the upper and more paraffinic layer, we may add a further quantity of our mixed solvents 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 the extraction system to extract additional quantities of oil in the preceding stages.

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 our invention, dewaxing may be effected either prior or subsequent to extraction.

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

I. The following example will serve to illustrate the effect of various percentages of secondary solvent, i. e., carbitol, added to the primary solvent, i. e., nitrobenzene. The extraction was carried out by admixing the solvent mixture with the oil stock, heating to approximately the tem-

perature of complete miscibility, and thereafter cooling to about 25° C., and permitting separation of the undissolved oil layer containing a small amount of solvent mixture from the dissolved layer of oil in the major portion of the solvent mixture. The separated layers were then freed of solvent by vacuum distillation. The results of the extraction of a Gulf Coast residuum having a viscosity of 254 seconds Saybolt universal at 100° F., a specific gravity of 0.9129 at 60° F. and a viscosity-gravity constant of 0.864 are tabulated below:

Parts nitrobenzene per			
100 parts stock	150	150	150
Parts carbitol per 100			
parts stock	14.8	31.9	41
Separation temperature			
25° C.	25° C.	25° C.	
Percent yield undissolved oil			
15.0	32.0	40.5	
Vis./100° F. (S. U.)			
158"	163"	168"	
Specific gravity (60° F.)			
0.8581	0.8639	0.8665	
Viscosity-gravity constant			
0.801	0.808	0.812	

II. A residuum having a viscosity of 420 seconds Saybolt universal at 210° F., a specific gravity of 0.9580 at 60° F., and a viscosity-gravity constant of 0.875 was extracted with various combinations of primary and secondary solvents in the manner above set forth. The total volume of the primary and the mixed solvents was maintained constant at 100% based on the oil stock, and the temperature of separation was held constant at 5° C., except in the last instance which was 15° C.

Primary solvent	Secondary solvent	Undissolved oil fraction			
		Percent yield	S. U. vis. at 210° F.	Specific gravity	Vis. grav. constant
Benzonitrile, 100%	00.0%	78.0	251"	0.9285	0.843
Benzonitrile, 80%	Carbitol, 20%	96.2	381"	0.9446	0.858
Nitrobenzene, 100%	00.0%	75.0	250"	0.9273	0.842
Nitrobenzene, 80%	Cellosolve, 20%	94.0	281"	0.9352	0.850
Nitrobenzene, 80%	Cellosolve, 20%	75.0	274"	0.9321	0.847

In accordance with the above examples, it will be seen that if the separation temperature is maintained constant, the yield will be substantially improved, by employing a mixture of a primary and a secondary solvent, over the yield obtained by the use of primary solvent alone. Or, if the yields are maintained constant, as shown in the 3rd and 5th instances of Example II, the operation involving the use of mixed solvents may be carried on at substantially higher temperatures than in the case of the primary solvent alone, thereby rendering the operation easier to handle on account of less separated wax and greater fluidity and more economical with respect to refrigeration.

From the above examples it will be noted that by extraction of an oil with our mixture of pri-

mary and secondary solvents, 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.

Our 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 our process oil products of desired characteristics from oils which by distillation will not produce such products. Our process is, however, particularly adapted to the treatment of naphthenic and asphaltic oils which generally have relatively low miscibility temperatures with the primary solvents, i. e., nitrogen-containing cyclic compounds.

Herein and in the appended claims the term "primary solvent" is to be understood to comprehend nitrogen containing cyclic compounds, while the term "secondary solvent" comprehends organic hydroxy compounds of the type hereinabove disclosed. Also, 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 we claim is:

1. A process for separating from a naphthenic type hydrocarbon oil containing paraffinic constituents, fractions respectively richer in paraffinic and naphthenic hydrocarbons, which comprises contacting said oil with nitrobenzene containing carbitol in sufficient quantity to substantially increase the miscibility temperature of the nitrobenzene with the oil, thereby to effect solu-

tion of a portion of the oil richer in naphthenic hydrocarbons in the solvent mixture, separating the solution so formed from the remainder of the oil and removing solvent from at least one of the fractions of said oil.

2. In a process for separating from a naphthenic type hydrocarbon oil containing a minor portion of paraffinic constituents and having a relatively low miscibility temperature with nitrobenzene, a fraction more paraffinic in character than said oil, the step which comprises extracting said oil with nitrobenzene containing a quantity of carbitol sufficient to substantially increase the miscibility temperature of the nitrobenzene with said oil.

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