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SEPARATION OF HYDROCARBON MIXTURES INTO CONSTITUENT PARTS

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3 Claims. (Cl. 196—13)

This invention relates to the separation of hydrocarbon mixtures into constituent parts; and more specifically comprises a method for separating such hydrocarbon mixtures into fractions of different molecular weight and/or fractions of dissimilar hydrocarbon structure by means of a selective hydrocarbon solvent.

The term "hydrocarbon mixtures" is intended to include hydrocarbon oils such as heavy gas oils, lubricating distillates, cylinder oils, residual oils, fuel oils and the like, as well as waxy hydrocarbon materials, such as petrolatum and paraffin wax or mixtures of oil and wax, whether obtained from petroleum, or by the cracking, destructive distillation or hydrogenation of shales, coals, lignites, tars, pitches, bitumens and other carbonaceous materials.

Hydrocarbon mixtures may be readily separated into fractions of different boiling point and molecular weight by distillation, fractionation or rectification. They may also be separated into fractions of dissimilar hydrocarbon structure, that is, separated into paraffinic and aromatic or naphthenic fractions by means of selective solvents such as phenol, aniline, liquid sulfur dioxide, nitrobenzene and the like. In many cases, however, the application of heat even under high vacuum to heavy oils in order to distill the lower boiling fractions may be undesirable due to the cracking and polymerization which occurs. The use of the common selective solvents is wasteful and expensive and necessitates subsequent complete elimination of the solvent which is always a non-hydrocarbon material.

I have now found that hydrocarbon mixtures may be separated into their constituent parts according to molecular weight and/or hydrocarbon structure by the incorporation therewith of a selective hydrocarbon solvent. This avoids the necessity for applying heat and has the additional great advantage that the agent of separation is a hydrocarbon itself. The method by which this separation may be effected and the nature of the preferred selective hydrocarbon solvents will be fully understood from the following description.

It has been indicated that separation may be made either according to molecular weight or according to hydrocarbon structure. If a mixture of wide boiling range is selected as the initial material, separation will be principally according to molecular weight and only a small amount of separation according to structure occurs. If separation according to structure is principally desired it is preferable to start with a mixture

of more limited boiling range, say one with a boiling range of not more than 20 to 50° F.

The hydrocarbon mixture to be separated into constituent parts is placed in a suitable vessel which is adapted to be maintained under a pressure sufficient at the temperature employed to retain the light hydrocarbons used to effect the separation in liquid phase. Temperatures between say -40 and 150° F., or even 200° F. are suitable, and pressures varying from slightly above atmospheric to 50 or more atmospheres may be used.

The hydrocarbon mixture is then diluted with from 3 to 15 volumes or more of a selective hydrocarbon solvent, such as, for example, a liquefied normally gaseous hydrocarbon or mixture of liquefied hydrocarbons. If a hydrocarbon oil containing substantial amounts of asphaltic materials is to be treated, it is preferable to add the liquefied hydrocarbon to the oil slowly or stepwise in small quantities, this to avoid a sudden precipitation of such asphaltic materials and the entrapment of globules of oil which results therefrom. Vigorous agitation may be provided to facilitate the mixing of the hydrocarbon mixture with the diluent.

Selective hydrocarbon solvents suitable for the purpose of the present process comprise generally all those hydrocarbons the boiling point of which lies below about 0° C. Among these are methane, ethane, propane, butane, iso-butane, ethylene, propylene, butylene, iso-butylene or any mixture of these. Other hydrocarbons such as acetylene and cyclobutane may also be used. Small quantities of higher boiling hydrocarbons such as pentane, hexane and even higher are not objectionable, but in general the lower boiling hydrocarbons are preferred. The particular hydrocarbon or mixture of hydrocarbons chosen as the agent of separation will depend very largely on the nature of the material to be separated and also on practical and economical considerations of the pressure necessary to maintain the separating agent in the liquid phase at the temperature of working. Thus, for example, methane alone would require a very great pressure, and unless a high degree of separation were desired, its use would hardly be economically justified. Pure methane or methane containing only small quantities of higher hydrocarbons may however be used with satisfactory results. Ethane and propane are the preferred hydrocarbons because these can be maintained in the liquid phase under moderate pressures say about 15 atmospheres, more or less, depending upon the pro-

portion of ethane to propane. The whole or a part of the normally gaseous hydrocarbon may if preferable be pumped into the hydrocarbon mixture in gaseous form and the whole mass then subjected to pressure to effect the liquefaction.

The gases obtained in the cracking of hydrocarbons normally contain small quantities of these lighter hydrocarbons and such gases may be liquefied and used as the diluent. Gases obtained in the stabilization of gasoline furnish an especially suitable source of the preferred hydrocarbons, ethane and propane.

The quantity of liquefied hydrocarbon used naturally depends upon the nature of the material to be separated into constituent parts. If the mixture is a hydrocarbon oil sufficient diluent should be added to cause the formation of two distinct layers. If the mixture is a solid or waxy hydrocarbon the quantity of diluent should at least be sufficient to dissolve the soluble portions of the mass.

Following dilution of the hydrocarbon mixture, the two layers or the two fractions into which the mixture has been divided are separated the one from the other by any suitable means, such as decanting, filtering or otherwise and the liquefied hydrocarbon diluent removed from each part by vaporization or other means. The recovered diluent may be recycled with a fresh portion of material as will be understood. Prior to removing the diluent, either or both portions may be filtered while diluted with the liquefied hydrocarbon through adsorptive media such as clay or charcoal. Filtration in the light hydrocarbon solution is extremely rapid and efficient and results in an improved color and appearance of the separated products.

Although the above described method of separating hydrocarbon mixtures into constituent parts is applicable to all types of hydrocarbons whether liquid, solid, or combinations of liquid and solid, it is particularly adapted to the separation of heavy hydrocarbon oils, especially the lubricating fractions of petroleum oils, into component oils of dissimilar composition and characteristics.

When working with petroleum oils a mixture of propane and ethane provides a very satisfactory selective solvent or separation agent. If such a solvent is used the ethane should be present in an amount preferably above say 15% and below say 85%, although similar or larger quantities may be used. By increasing the proportion of ethane in the selective solvent the volume of heavy oil thrown out in the bottom layer is correspondingly increased. Depending therefore upon what degree of separation is desired the ratio of ethane to propane may be increased or decreased. This of course applies also to other mixtures of hydrocarbons of 2 carbon atoms or less with hydrocarbons of 3 carbon atoms or more. When only 15% ethane is used the bottom layer contains a very small amount of a high molecular weight and high viscosity oil. On the other hand when 85% ethane is used the bottom layer comprises a very large proportion of the oil and has a correspondingly lower viscosity.

When carrying out the process for the purpose of separating the paraffinic from the aromatic and naphthenic hydrocarbons, in which case a fraction of narrow boiling range is preferably chosen as the starting material, it may be advantageous to use selective solvents for aromatic

and naphthenic hydrocarbons such as liquid sulfur dioxide, phenol, aniline, nitrobenzene and the like, in addition to the liquefied hydrocarbons which latter exhibit a selective solvent action for the paraffinic hydrocarbons.

By controlling the proportion of ethane and propane used, the total volume of diluent, and the temperature and pressure at which the process is carried out it is possible to separate heavy hydrocarbon oils into fractions of different viscosity temperature characteristics and to increase the viscosity temperature characteristics of either the lighter fraction or the heavier fraction.

The following example illustrates the application of this process to a cylinder oil. A finished cylinder oil dewaxed to zero pour obtained from a Ranger crude is diluted with 5 volumes of propane and 6 volumes of ethane at a temperature of about 75° F. and under pressure of 20 atmospheres. Two distinct layers are formed which are separated and the liquefied hydrocarbon removed by vaporization. The top layer is found to contain 38% of the original oil, the bottom layer 62%. A comparison of the characteristics of the original oil and the top and bottom layers follows:

	Original oil	Top layer	Bottom layer
Gravity A. P. I.-----	22.9	26.6	20.8
Saybolt viscosity at 100° F.-----	3015	846	6885
Saybolt viscosity at 210° F.-----	146	80	231
Carbon-----	2.479	0.488	3.67
Viscosity index-----	77	96	75

The viscosity index, V. I., indicates the relation between the viscosity at 100° F. and the viscosity at 210° F. and is such that the smaller the difference in viscosity at these two temperatures the higher is the V. I. It is defined by Dean and Davis in Chemical and Metallurgical Engineering, vol. 36, No. 10, October 1929.

To illustrate the effect of varying the proportion of ethane and propane used another portion of the mass oil is diluted with 5 volumes of propane and only 3 volumes of ethane. When the two layers are separated and the propane and ethane are flashed off, the top layer is found to contain 87% of the original oil and the bottom layer only 13%.

This example shows that by decreasing the proportion of ethane used the volume of oil thrown out is reduced. The increase in V. I. of the oil in the top layer over the V. I. of the original oil, however, is correspondingly reduced. For example, in this last example the V. I. of the top layer was only 80 as compared with 96 in the first example.

This invention is not limited by any theory of the mechanism of the separation nor by any details or examples which have been given merely for illustrative purposes, but is limited only by the following claims in which I wish to claim all novelty inherent in the invention.

This application is a division of my copending application, Ser. No. 582,501, filed December 21, 1931.

I claim:

1. In the art of refining mineral oil comprising naphthenic and paraffinic constituents, the step comprising extracting the oil with phenol in the presence of an added liquid having greater solvent power for paraffinic constituents of the oil than for naphthenic constituents thereof.

2. In the art of refining mineral oil comprising

naphthenic and paraffinic constituents, the step comprising extracting the oil with phenol in the presence of an added hydrocarbon having a boiling range substantially below the boiling point
5 of the oil, the said hydrocarbon being adapted to form a two layer system with the phenol and oil.

3. In the art of refining mineral oil comprising

naphthenic and paraffinic constituents, the step comprising extracting the oil with phenol in the presence of an added liquefied normally gaseous hydrocarbon, the said added hydrocarbon being adapted to form a two layer system with the
5 phenol and oil.

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