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SOLVENT TREATMENT OF OILS

James W. Weir, Los Angeles, Calif., assignor, by mesne assignments, to Edeleanu Gesellschaft, m. b. H., Berlin, Germany, a corporation of Germany

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This invention relates to improvements in the art of refining hydrocarbon oil by solvent extraction and has particular reference to methods of separating crude petroleum oils or their distillates into fractions or components of different chemical composition, whereby oils of relatively high and of relatively low "viscosity index" may be separated from the oil treated.

As is well known, lubricating oils from Mid-Continent, Gulf, Mexico and California crudes have lower viscosity indices (as the term "viscosity index" is defined in the Chemical and Metallurgical Engineering, 1929, volume 36, pages 618–619, Dean & Davis) than have corresponding oils obtained from Pennsylvania crude petroleums. As is also well known, numerous liquid solvents have been proposed and used for the purpose of making this desired separation by virtue of the difference in solvent power possessed by such liquids with respect to the components of the oil having relatively high and relatively low viscosity index.

In the refining of lubricating oil by selective solvent extraction, oil and solvent are mixed in such proportions, and under such conditions, that they are not entirely miscible one in the other. After thorough mixing the mixture is separated by gravity or otherwise and the two layers are found to consist of an upper or "raffinate" layer consisting mainly of "paraffinic" or high viscosity index oil, in which a small percentage of the selective solvent is dissolved, and a lower or "extract" layer consisting mainly of solvent in which the "naphthenic" or low viscosity index fractions of the oil stock are dissolved.

I have observed that in the case of the selective solvent refining processes and solvents heretofore used, the result of the admixture of solvent and oil is in the nature of an unstable emulsion in which the extract constitutes the continuous phase and the raffinate the dispersed phase. In other words, at the completion of the mixing period and the beginning of the settling period, the raffinate or oil phase is in the form of droplets of greater or less diameter distributed through the extract or solvent phase. In order that the two phases may be separated, it is necessary to cause the dispersed raffinate to rise from the extract and agglomerate into a pure raffinate layer. The larger droplets of raffinate separate out of the extract layer fairly rapidly, but the smaller particles are never completely removed in commercial practice. The net result is a loss of desired raffinate which is carried away dispersed in the extract phase, i. e., in the form of mechanical entrainment. This loss may amount to as much as 15 or 20% of the final yield of raffinate.

I have discovered that the phases of the pseudo-emulsion may be reversed, making the extract the dispersed rather than the continuous phase, and that when the treatment is carried out under these conditions raffinate losses are materially reduced.

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

With the phases thus reversed the process of separation consists of the settling and agglomerating of dispersed particles of extract out of a body of raffinate. The only manner in which a distinct layer of extract phase may be formed is for droplets of extract to agglomerate into a continuous layer of uniform composition. It is impossible, under these conditions, for the extract layer to contain entrained raffinate, and when the extract layer is removed from the system, there is absolutely no danger of withdrawing even a small amount of raffinate.

A practical method of reversing the phases in the desired manner is by introducing, along with the oil and solvent, a relatively small quantity of aqueous alkali solution. When the solvent and oil are mixed in any manner such as is usually employed to obtain equilibrium (as by violent agitation, counter-current contacting, etc.), and when aqueous alkali solution is present, the resultant mixture, when delivered to the separator, is found to consist of a continuous raffinate phase containing dispersed therein droplets of extract and droplets of the alkali solution. Upon separation I then have three distinct layers, namely, the oil or raffinate layer, the extract layer, and a layer of aqueous alkali solution. The alkali solution, although it plays an important part in the process, is substantially uncontaminated, and may be reused directly without purification or other treatment.

It is possible, of course, that when my method of treatment is employed, a certain amount of finely divided extract may remain in the raffinate layer (analogous to the raffinate which remains in the extract layer in the conventional processes referred to above). The effect of this contamination of the raffinate layer will be to lower the quality of raffinate (just as, in the older methods, the "contamination" of the extract layer resulted in a loss of yield of raffinate). In the case of my process, however, this contamination, or failure to make complete separation, is less harmful than in the older methods for the reason

that the extract phase represents relatively dilute solutions of oil in solvent. The oil content of the extract layer, per unit volume, is less than that of the raffinate.

The following is an example of the operation of my process:

One volume of dewaxed distillate from a California crude oil, which distillate had an A. P. I. gravity of 19.8 and a Saybolt Universal viscosity of 74 seconds at 210° F., was agitated with two volumes of pyridine containing 5% of water by volume. The temperature of treatment was 70° F. After thorough agitation this mixture was allowed to separate by gravity. It was evident, from close observation of the mixture, that the extract was the continuous phase and that the raffinate was dispersed therein. The yield of raffinate from this treatment was 68% by volume and had a gravity of 25.2° A. P. I.

In contrast to this treatment another identical sample of the same crude was treated with pyridine at the rate of two volumes of solvent to one of oil. This treatment was also made at 70° F. and was carried out in exactly the same manner as the first treatment with the exception that 5% of aqueous sodium hydroxide solution containing approximately 10% by weight of alkali was introduced along with the oil and solvent. The mixture presented a very different appearance from that of the first treatment, the extract being in this case, the dispersed phase. After settling, the raffinate and extract layers were separately withdrawn. A separate small layer of alkaline solution remained. The raffinate yield from this treatment was 76% and had a gravity of 25.1° A. P. I.

In addition to reversing the phases of the oil-solvent mixture (thus preventing raffinate loss), and bringing about a much more rapid separation, the use of an alkali phase has a remarkable effect on the color of the refined oil. An oil which, upon treatment with solvent alone, gives a very dark, opaque, raffinate will give a light colored, translucent, raffinate when treated with the same solvent in the presence of an alkali phase as described. Obviously such an oil will require less adsorbent or other refinement to produce the desired final color than in the case of conventional solvent refinement.

The above-described use of a separate alkali layer is a practicable and advantageous step for employment along with any selective solvent except the few which react chemically with the alkali solution. Examples of such reactive solvents are phenol and cresylic acid. On the other hand alkali may be used satisfactorily with aniline, chloraniline, furfural, pyridine, methyl pyridine, nitrobenzene, aliphatic amines and others, which do not react with alkali.

The term "alkali" as used by me in this connection is to be understood to refer to and include the hydroxides of the alkali metals. I prefer, for the use described, the hydroxide of sodium or of potassium.

The amount of alkaline solution to be used can be varied somewhat at the discretion of the operator. In any case enough must be used to cause the raffinate layer to be the continuous phase and the extract layer the dispersed phase when the two are mixed. In order to do this it is necessary to provide a distinct separate alkali solution phase when in contact with the particular solvent and treating conditions used. It is unnecessary, and undesirable, to have present a large alkaline phase. I have found that a volume of alkaline phase about equal to 5% of the volume of oil charged gives satisfactory results. More or less may be required in some cases, however, depending on the amount of water in the solvent, the nature of the oil, etc.

The concentration, as well as the relative volume of the alkali solution which will give best results with a given oil and solvent is best determined by experiment. If the concentration is too low the desired effect on color bodies will not be obtained. As a general rule, a concentration of about 10% by weight of alkali is satisfactory. The optimum concentration will depend, however, on the nature and amount of solvent used, the type of oil being treated, and the particular hydroxide used. If the solvent is one which is capable of dissolving water to some extent, the concentration and amount of alkaline solution will, of course, be altered as soon as it comes in contact with the solvent, since there will be tendency for a portion of the water of the alkaline layer to go into solution in the solvent. The extent of alteration of the caustic layer due to this cause will obviously depend on the amount of water already contained in the solvent. In view of these facts, it is impossible to give specific directions for the amount and concentration of alkali to cover all cases.

As stated, a generally satisfactory procedure is to provide an alkaline layer which, in contact with the solvent, will contain about 10% by weight of alkali and the volume of which is about 5% of the volume of oil being treated. In determining the proper concentration of the alkaline layer by experiment, it may be observed that this concentration should be such as will produce an extract layer darker than the raffinate layer.

Although I have described an example of treatment in which a single mixing of oil and solvent is employed, it is to be understood that in practice best results are often obtained by means of a series of extractions. The technique of series extraction is well known and need not be described in detail here. Ordinarily, in mixing such a series of extractions, oil and solvent (or extract) flow in counter-current directions through the system. My invention does not embrace the mechanical method of extraction.

I claim:

1. The method of separating high viscosity index from low viscosity index components of petroleum oil which comprises contacting the oil with a selective solvent which does not react with alkali, in the presence of an aqueous alkali metal hydroxide solution in sufficient amount to form three phases, causing the extract phase to be dispersed in a continuous raffinate phase, then separating and separately removing raffinate phase, extract phase and alkali metal hydroxide phase.

2. In the refining of hydrocarbon oil with a selective solvent of the class of pyridine and its homologues by which a fraction of relatively high viscosity index is separated as a "raffinate" liquid phase and another fraction of relatively low viscosity index is separated as an "extract" liquid phase, the step of adding to the oil and solvent undergoing treatment an aqueous alkaline substance capable of existing as a separate layer in equilibrium with the oil and solvent in sufficient amount to form a third phase, thereby causing the extract to be dispersed in a continuous raffinate phase.

3. The method of refining hydrocarbon oil

which comprises contacting the oil with a solution of an alkali metal hydroxide, and simultaneously contacting the oil with a selective solvent with which said alkali metal hydroxide does not react chemically and which is capable, in the proportions and at the temperature used, of separating the oil without reacting chemically therewith into a fraction of relatively high viscosity index and a fraction of relatively low viscosity index.

4. In the art of separating relatively high viscosity index fractions from petroleum oil by means of selective solvents, the improvement which comprises contacting with the oil and solvent before separation of the respective phases a quantity of aqueous alkali metal hydroxide solution unreactive and not wholly miscible therewith, of sufficient strength and volume to cause the extract layer to be the dispersed phase, and the raffinate layer to be the continuous phase resulting from the extraction treatment.

5. The method of separating high viscosity index from low viscosity index components of petroleum oils which comprises contacting the oil with a selective solvent of the class of pyridine and its homologues in the presence of an aqueous alkali metal hydroxide solution, producing thereby a system of essentially three phases, namely an oil-insoluble aqueous alkali metal hydroxide solution, an extract solution and a raffinate solution, then separating and separately removing said three phases.

6. The method of separating high viscosity index from low viscosity index components of petroleum oils which comprises contacting the oil with a substance containing a mixture of pyridine and pyridine homologues as selective solvent in the presence of an aqueous alkali metal hydroxide solution producing thereby a system of essentially three phases, namely an oil-insoluble aqueous alkali metal hydroxide solution, an extract solution and a raffinate solution, then separately removing said three phases.

7. The method of refining hydrocarbon oil which comprises treating the oil with a selective solvent in the presence of a sufficient quantity of an aqueous alkali metal hydroxide solution which is chemically unreactive with the solvent to form a separate layer upon separation of phases.

8. In the method of refining hydrocarbon oil with a selective solvent which does not react with alkali, the addition of a sufficient quantity of an aqueous alkali metal hydroxide solution to form a separate layer upon separation of phases and when in contact with the oil and solvent to cause a reversal of the natural order of the phases in the treating zone so that the raffinate oil phase constitutes the continuous phase and the solvent extract phase is dispersed in the said continuous phase before separation.

JAMES W. WEIR.