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OIL TREATING PROCESS

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Fig. 1.

TYPES OF CRUDE

Appalachian (Penna.)
Paraffins 80-92%
Naphthenes 5-28%
Aromatics 4-2%

Mid-Continent
Paraffins 60%
Naphthenes 26-29%
Aromatics 7-11%

Coastal
Paraffins 50%
Naphthenes 35-38%
Aromatics 10-14%

Astrolite, Gulf, South
Paraffins 35%
Naphthenes 50-60%
Aromatics 5-15%

Fig. 2.

Fig. 3.

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This invention pertains to an improved process of refining mineral oil by means of paraffinic and naphthenic solvents which separate the oil into relatively paraffinic and naphthenic fractions.

The present application embraces matter divided from my copending application Ser. No. 633,463, filed July 30, 1932, entitled "Processes and apparatus for separation of mineral oils". One manner of carrying out this process is described in my United States Letters Patent 1,912,349, issued May 30, 1933.

Through my invention it is possible to separate a residual mineral oil into its several components, or constituents, and more particularly into a lubricating oil fraction containing substantially all of the high-boiling paraffins and into another fraction containing substantially all of the non-paraffinic or so-called "naphthenic" values of the original oil. This last fraction may be broadly termed a tarry portion.

As noted in my application above identified, a clean separation of the paraffinic and non-paraffinic fractions of a mixed-base oil may be obtained by the simultaneous treatment of the original oil with a suitable paraffinic solvent such as propane and a general solvent for the naphthenic values, such as nitrobenzene, the residual solvent capacity of which for paraffinics is compensated for or reduced to a minimum by the paraffinic solvent chosen.

According to the present invention, there is provided a process of separating a mineral oil containing paraffinic and naphthenic constituents into two liquid phases, one of which is relatively paraffinic and the other of which is relatively naphthenic, which comprises commingling the mineral oil to be separated with a paraffinic solvent of the group consisting of liquefied, normally gaseous hydrocarbons, and petroleum ether, with a naphthenic solvent mixture containing naphthenic solvent having as broad a solvent power as nitrobenzene for all non-paraffinic constituents of the oil, and another naphthenic solvent which has a relatively limited solvent power, controlling the temperature of the mixture at a point where the broad and limited solvents are miscible to but a limited extent with the paraffinic solvent and thus cause an effective separation of the oil into layers, and separating the layers thus produced. The process is particularly advantageous in connection with the treatment of residual oils which contain upwards of 40 per cent. of non-paraffinic constituents including naphthenes, aromatics, and asphaltenes, enabling the direct and clean separation of the paraffinic or lubricating fractions of a mineral oil from the non-paraffinic (naphthenic) or tarry fractions of the oil, the several non-paraffinic constituents being removed in a unitary operation.

The combining of solvents should be done under conditions such that the tendency or capacity of the solvent for paraffinics to dissolve non-paraffinics in addition to the paraffinic values, normally dissolved therein, is compensated for or balanced by a like capacity of the solvent for non-paraffinics to dissolve paraffinics as well as the naphthenics or non-paraffinics.

In the flow sheet of the drawing accompanying the present application and forming a part thereof, there is shown—

In Fig. 1 a schematic representation of the distribution of the constituents of mineral oil in the different types of crude mineral oils. In Fig. 2 there is shown an idealized representation of a Mid-Continent crude, together with a graphical representation of the solvent effect of a variety of individual solvents on the several constituents of the oil.

In Fig. 3 there is disclosed a graphical representation of flow sheet indicating the combination of preferred paraffinic and non-paraffinic solvents and the substitutes, or equivalents, preferably, as utilised in the process of the present invention.

Referring to the drawing, there is shown in Fig. 1 a representation of illustrative crude oil stocks in which the non-paraffinic constituents may vary from as little as 8 per cent. of the crude oil stock to as much as 65 per cent. of the crude oil stock. It is in the treatment of the latter type of oil that the present invention is particularly useful.

Referring to Fig. 2, there is shown diagrammatically how different solvents vary in their capacity to dissolve the several types of non-paraffinic constituents of crude oil stocks. For instance, sulphur dioxide and furfural are both extremely limited solvents which only dissolve a minute proportion and a limited range of constituents. Solvents like nitrobenzene, nitrotoluene and cresylic acid dissolve substantially all the non-paraffinic constituents, including naphthenes, aromatics and asphaltenes, and when used in a single solvent system, also dissolve a substantial proportion of paraffinic oil. However, in the double solvent, counterflow system employing both paraffinic and naphthenic solvents, the paraffinic solvent produces a clean...
separation of paraffinic oil from non-paraffinic oil fraction.

This is best illustrated in Fig. 3, where it is shown that the oil to be treated is introduced, in the preferred form of the invention, at the middle of the system so that the fresh paraffinic solvent rises, after washing the naphthenic extract, and the mixture of non-paraffinic solvents settles through the crude oil, after washing the paraffinic fraction at the upper end of the system. In the drawing, there are shown various examples of suitable solvents which may be combined according to the present invention. For instance, when a small proportion of a limited, non-paraffinic solvent is combined with a large proportion of a broad, non-paraffinic solvent, such as cresylic acid, a non-paraffinic solvent is obtained which may be used with a paraffinic solvent, such as propane, to produce a good separation of the lubricating constituents of a residual oil from the non-paraffinic constituents of the oil. The broad solvents which dissolve all the non-paraffinic constituents including naphthenes, aromatics and asphaltenes may thus be made particularly effective by incorporating therewith suitable amounts of limited solvents which dissolve only certain small proportions of some of the non-paraffinic constituents.

While propane has been described as a preferred paraffinic solvent it is to be noted that it is most efficient when used with any of nitrobenzene, nitrotoluene or the organic tar acids and their derivatives. Further, its use may be extended by proper proportioning of the non-paraffinic or "naphthenic" solvent members. The higher boiling paraffinic solvents tend to lower the critical solution temperature of the two-solvent system and when solvents are employed of the class of pyridine, aniline, and furfural resulting in high critical solution temperature with propane, the higher boiling paraffinic solvents may be substituted to lower the C. S. T. (critical solution temperature) and so increase the solubility of oil in the naphthenic solvent.

It will be appreciated that the present invention comprehends as an integral part of the process thereof, that solvents of medium or average solvent capacity for either paraffins or non-paraffins of so-called "naphthenics" of mineral oils may be used together in suitable proportions to provide mutually immiscible two-solvent-layers. It will be appreciated further, from the data herein, that the solvent effect of the several solvents of medial solvent capacity may be duplicated or approximated by the proper combination of broad solvents, as presented above, with limited solvents.

It is to be noted that the capacity of the solvent materials, either for paraffins or non-paraffins, may be compensated for by the use of appropriate solvents for non-paraffins and paraffins, respectively, so that a clean, clear separation of the paraffinic or lubricating constituents of a mineral oil may be separated from the non-paraffinic or tar-forming naphthenic constituents.

The various combinations of individual solvents to effect or give rise to composite solvents approximating the preferred paraffinic and non-paraffinic solvents, is shown in Fig. 3 and has been discussed in more detail heretofore. From the foregoing it will be seen that an important feature of the present discovery resides in the fact that non-paraffinic solvents of progressively greater general solvent power for all of the constituents of mineral oils as well as the non-paraffinic constituents thereof, may be combined with other solvents for non-paraffinic, or certain constituents thereof, to form restricted solvents which may be used with paraffinic solvents of restricted solvent capacity for non-paraffinic whereby to complement the same and permit the securing of effective and clean separation of the paraffinic values of an oil from the non-paraffinic values thereof. As an important feature of this method it is to be noted that the composite solvents for the non-paraffinics must be substantially immiscible or insoluble in the solvents used for dissolving the paraffinics in a mineral oil. Further, the said solvent for paraffinics and the solvent for non-paraffinics, or "naphthenics", must be characterized by such differences in their specific gravities that the formation of two-layer systems is furthered and made possible so as to permit the ready and efficient separation of the solvent systems and their respective dissolved mineral oil fractions from each other.

Thus by employing a paraffinic solvent in combination with a mixture of non-paraffinic solvents, one of which has a broad solvent capacity for all non-paraffinic oils, as well as some solvent capacity for paraffinic oils, and one having a relatively limited solvent capacity, not only may an efficient separation of the oil be obtained, but also the critical solution temperature may be controlled at a suitable temperature for satisfactorily rapid separation of the oil into layers.

It is to be understood that this invention is not to be limited by any theory of operation expressed or by any example given, and that it includes modifications and variations falling within the appended claims.

What I claim is:
1. Process of separating a mineral oil containing paraffinic and naphthenic type constituents into two liquid phases, one of which is relatively paraffinic and the other of which is relatively naphthenic, which comprises commingling the mineral oil to be separated with a paraffinic solvent of the group consisting of liquefied, normally-gaseous hydrocarbons and petroleum oils, and with a naphthenic solvent mixture containing a selective naphthenic solvent having as broad a solvent power as nitrobenzene for all non-paraffinic constituents of the oil, and another naphthenic solvent which has a relatively limited solvent power, controlling the temperature of the mixture at a point where the broad and limited solvents are miscible to but a limited extent with the paraffinic solvent and cause an effective separation of the oil into layers, and separating the layers thus produced.
2. Process as claimed in claim 1 wherein the limited solvent has a markedly higher miscibility temperature with the paraffinic solvent and oil than the broad solvent.
3. Process as claimed in claim 1 wherein said paraffinic solvent is liquefied propane.
4. Process as claimed in claim 1 wherein the oil treated is a residual oil, and wherein the residual oil is introduced to the presence of both paraffinic and naphthenic solvents between the points where the solvents are introduced.

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