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ART OF REFINING

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This invention relates to improvements in the refining of lubricating oils, more particularly of petroleum origin. By "lubricating oils" I mean oils having a viscosity upwards of 70 seconds at 100° F. Saybolt Universal. My invention includes a combined extraction and dewaxing refining operation. My invention also includes improvements in extraction operations and in dewaxing operations. My invention further includes improved refining solvents and improved dewaxing solvents.

The invention relates, more particularly, to improvements in extraction refining operations in which the oil is treated with refining solvents, such as nitrobenzene, phenol and beta beta dichlor ethyl ether, to improvements in dewaxing operations in which the separation of wax is effected in the presence of a benzene, such as benzene or toluene, and to improvements in refining operations combining such extraction and dewaxing operations.

The use of selective solvents, such as those mentioned, to separate raffinates from constituents undesired as components of the particular product in extraction operations and the use of benzenes to assist in the separation of raffinates from wax in dewaxing operations has hitherto been proposed. In such extraction operations as previously practiced, however, the optimum extraction temperatures are usually relatively low, so low as to involve mechanical difficulties as applied to waxy stocks for example. Also, refining solvents of the type mentioned tend to separate from the raffinate in solution with the undesired constituents whereas the benzenes tend to separate from the wax in solution with the raffinate, necessitating stripping of the refining solvent from the raffinate from the extraction operation, with which a minor proportion of the solvent is usually associated, prior to any subsequent dewaxing operation with a solvent because of the diverse effects of the different solvents used in the two operations.

I have discovered that the addition of ethylene glycol monomethyl ether to such refining solvents offers several advantages in such extraction operations, that the addition of this compound to benzene or toluene or mixtures of the two, for example, offers several advantages in such dewaxing operations, and that the presence of this compound during the dewaxing operation enables such extraction and dewaxing operations to be combined in a particularly advantageous manner.

In the improved extraction operation of my invention, the optimum temperature is increased by the addition of ethylene glycol monomethyl ether to refining solvents tending to separate from the raffinate in solution with the undesired constituents. The oil component of the raffinate is less soluble in the mixture of refining solvent and ethylene glycol monomethyl ether than in the refining solvent alone thus permitting increase of the temperature at which the extraction is effected without increase in loss of such oil component in solution with the extract. The extraction efficiency of the refining solvent is improved at higher temperatures and improvement in the extraction operation is thus attained. Also, as applied to waxy stocks for example, it thus becomes possible to carry out the extracting operation at optimum temperature while avoiding mechanical difficulties due to the presence of wax. In this aspect, the invention makes the extraction operation applicable to stocks otherwise impossible to treat by the operation. Addition of ethylene glycol monomethyl ether to the refining solvent decreases its solvent capacity for constituents undesired as components of the refined product but this is offset by an increase in this solvent capacity and in extraction efficiency at higher extraction temperatures, and any remaining net effective decrease in solvent capacity can be made up by increasing the proportion in which the refining solvent is used.

The solvent mixture used in dewaxing operations, in accordance with my invention includes one or more benzenes and ethylene glycol monomethyl ether, and may include, with advantage, a small proportion of a refining solvent of the type mentioned, a proportion corresponding for example to that in which such solvents remain associated with raffinates in extraction operations in which they are used. In the dewaxing solvent mixtures of my invention, the presence in such proportions of such refining solvents improves the dewaxing operation. The dewaxing solvent mixtures of my invention are particularly advantageous as applied to more viscous stocks.

In the combined extraction and dewaxing operation of my invention, the extraction operation and the dewaxing operation are each effected with the aid of solvents, such as those mentioned, and ethylene glycol monomethyl ether is added to the dewaxing solvent mixture. Any necessity for stripping the refining solvent from the raffinate from the extraction operation before it is subjected to the dewaxing operation can thus be avoided, since the proportions of the refining solvent usually retained in association with this raffinate improve the dewaxing operation when the solvent mixture of my invention is used in the dewaxing operation, and important economies with respect to apparatus required as well as in the combined operation itself can thus be secured. Ethylene glycol monomethyl ether is, with advantage, also used with the refining solvent in the combined extraction and dewaxing operation of my invention.

In one way of carrying out the combined ex-

traction and dewaxing refining operation of my invention, for example, the stock from which the refined lubricating oil is to be produced is subjected to extraction with a refining solvent or, with advantage, with a solvent mixture including a refining solvent and ethylene glycol monomethyl ether. In the latter case, the ratio of ethylene glycol monomethyl ether to the refining solvent in the solvent mixture is adjusted, for example, to effect optimum extraction at the chosen extraction temperature. The extraction temperature is chosen with respect to the particular stock, for example, to facilitate the handling of the stock in the extraction operation and to secure satisfactory extraction efficiency. With waxy stocks, for example, a temperature high enough to insure fluidity of the stock notwithstanding the presence of the wax is used. The extract is separated from the raffinate, the bulk of the solvent mixture separating with the extract but a minor proportion of the constituents of the solvent mixture remaining in association with the raffinate. The raffinate with associated constituents of the refining solvent is subjected directly to the dewaxing operation, that is prior to any stripping of the associated solvent constituents from the raffinate. The dewaxing operation is carried out as in conventional practice except that the separation of wax from the raffinate is effected in the presence of a solvent mixture including, for example, benzene or toluene or a mixture of the two, the refining solvent constituents carried over with the raffinate from the extraction operation, and ethylene glycol monomethyl ether. The dewaxing solvent including ethylene glycol monomethyl ether is added to the raffinate from the extraction operation prior to chilling preceding the separation of wax. If the refining solvent used in the extraction operation does not include ethylene glycol monomethyl ether, the full proportion of this compound to be used in the dewaxing operation is added with the dewaxing solvent mixture, but if this compound is used in the refining solvent due allowance is made for that proportion carried over with the raffinate from the extraction operation. Solvent constituents are stripped by distillation from the raffinate from the dewaxing operation following the extraction operation, from the wax separated in the dewaxing operation and from the extract separated in the extraction operation. The distillates from these three stripping operations are combined and redistilled to separate and recover for re-use the several solvent constituents. For example, in an operation using a mixture of nitrobenzene and ethylene glycol monomethyl ether as a refining solvent and a mixture of benzene or toluene or both and ethylene glycol monomethyl ether as the dewaxing solvent mixture, the combined distillates can be separated in a single still equipped to separate a light fraction and an intermediate fraction as well as a residual fraction or in two stills in series. The combined distillates are separated, for example, into a light fraction comprising the benzene or toluene or both together with any water condensed from steam used in the stripping distillations, an intermediate fraction consisting of the ethylene glycol monomethyl ether and a residual fraction consisting of the nitrobenzene, water being separated by gravity from the hydrocarbon component of the light fraction. The raffinate from the dewaxing operation following the extraction operation, after stripping of associated solvent constituents, is the refined lubricating oil product of the combined operation. It may be finished, for example, by contact, at elevated temperature, with an absorbent such as fuller's earth.

My invention will be further illustrated by the two following examples of combined operations involving application of my invention to two different lubricating oil stocks. It will be understood, of course, that these examples of practice of the combined operation also illustrate the extraction operation and the dewaxing operation of my invention.

Example I

An undewaxed Mid-continent neutral oil stock having a viscosity of 201 seconds at 100° F. Saybolt Universal, a pour test of 80° F. and a Conradson carbon of 0.019 was subjected to extraction at 100° F. with 110% (by volume on the charge of raw stock) of a refining solvent mixture consisting of 6 parts nitrobenzene and 5 parts ethylene glycol monomethyl ether to produce a 71.4% yield of a waxy raffinate having a viscosity of 155.8 seconds at 100° F. and 44.3 seconds at 210° F. Saybolt Universal, a pour test of 90° F. and a Conradson carbon of 0.014. The extraction was carried out in six stages with countercurrent contact in each stage. The settling time for separation of raffinate and extract in each stage was ten minutes. The solvent constituents remaining associated with the raffinate amounted to 15.5% (by volume on the charge of raw stock). The raffinate from the extraction including associated solvent constituents, was mixed with 300% (by volume on the charge of raffinate) of a dewaxing solvent mixture consisting of 7 parts benzene and 3 parts ethylene glycol monomethyl ether and chilled to —10° F. Precipitated wax was filtered from the oil-solvent mixture to produce a yield of 86.8% (by volume on the raffinate from the extraction operation, 62.0% on the charge of raw stock) of a raffinate having a viscosity of 190.6 seconds at 100° F. and 45.4 seconds at 210° F. Saybolt Universal, a pour test of —5° F. and a Conradson carbon of 0.014. The viscosity index of the raffinate from the dewaxing operation following the extraction operation was 90.9. The viscosities, pour tests and Conradson carbon contents given with respect to the raffinate from the extraction operation and the raffinate from the dewaxing operation following the extraction operation are values determined from samples after separation of associated solvent constituents. After being stripped of solvent constituents, the raffinate from the dewaxing operation was contacted with 10% (by weight on the raffinate) of fuller's earth (Olmstead) at 180° F. to produce a finished lubricating oil having a viscosity of 190.4 seconds at 100° F. and 45.4 seconds at 210° F. Saybolt Universal, a pour test of 0° F., a Conradson carbon of 0.013, a 2+ color and a viscosity index of 91.

Example II

A Mid-Continent overhead long residuum having a viscosity of 138 seconds at 210° F. Saybolt Universal, a pour test of 90° F. and a Conradson carbon of 2.962 was subjected to extraction at 130° F. with 175% (by volume on the charge of raw stock) of a refining solvent mixture consisting of 4 parts nitrobenzene and 3 parts ethylene glycol monomethyl ether to produce a 53.0% yield of a waxy raffinate having a viscosity of 96.2 seconds at 210° F. Saybolt Universal, a pour test of 100° F. and a Conradson carbon of 0.471. The extraction was carried out in six stages with

countercurrent contact in each stage. The settling time for separation of raffinate and extract in each stage was 30 minutes. The solvent constituents remaining associated with the raffinate amounted to 20.2% (by volume on the charge of raw stock) comprising 17.3% of nitrobenzene and 2.9% of ethylene glycol monomethyl ether. The raffinate from the extraction, including the associated solvent constituents, was mixed with 300% (by volume on the charge of raffinate) of a dewaxing solvent mixture consisting of 55 parts benzene, 22 parts toluene and 23 parts ethylene glycol monomethyl ether and chilled to —20° F. Precipitated wax was filtered from the oil-solvent mixture to produce a yield of 79.4% (by volume on the raffinate from the extraction operation) of a raffinate having a viscosity of 106.9 seconds at 210° F. Saybolt Universal, a pour test of +5° F. and a Conradson carbon of 0.535. The viscosity index of the raffinate from the dewaxing operation following the extraction operation was 87.8. The viscosities, pour tests and Conradson carbon contents given with respect to the raffinate from the extraction operation and the raffinate from the dewaxing operation following the extraction operation are values determined from samples after separation of associated solvent constituents. After being stripped of solvent constituents the raffinate from the dewaxing operation was contacted with 10% (by weight on the raffinate) of acid-treated clay (Terrana) at 450° F. to produce a finished lubricating oil having a viscosity of 105.3 seconds at 210° F. and 1,479 seconds at 100° F. Saybolt Universal, a pour test of +5° F., a Conradson carbon of 0.358, a 4½+ color and a viscosity index of 89.1.

Allyl alcohol, methyl acetate, acetone, methyl ethyl ketone, methyl alcohol, normal propyl alcohol, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether and ethylene glycol monobutyl ether are also useful as modifiers of refining solvents and dewaxing solvents in place of ethylene glycol monomethyl ether. Agents completely miscible with the refining solvent, having little if any solvency for oil and having a selective solvency, even though very slight, for constituents undesired as components of the raffinate, are as a class useful as such modifiers and when I use the term "modifier" herein I mean agents having these properties. The ethylene glycol ethers, however, appear to be advantageous modifiers and I have found ethylene glycol monomethyl ether to be a particularly advantageous modifier. In the combined operation of my invention, one modifier may be used in the refining operation and another, in addition to any part of the first retained in association with the raffinate from the refining operation, may be used in the dewaxing operation.

When I refer to "refining solvents" herein, I mean solvents the bulk of which separates from the raffinate in solution with the constituents undesired as components of the raffinate. When I refer to "dewaxing solvent mixtures" herein, I mean solvent mixtures the bulk of which separates from the wax in solution with the raffinate. When I use the term "a benzene" herein, I mean benzene, toluene or any homologue having the same solvent characteristics with respect to wax and oil.

I claim:

1. In the dewaxing of lubricating oils, the improvement which comprises separating wax from the stock in the presence of a solvent mixture including a benzene and ethylene glycol monomethyl ether.

2. A dewaxing solvent mixture for dewaxing lubricating oils comprising a benzene and ethylene glycol monomethyl ether.

3. In the refining of lubricating oils, the improvement which comprises extracting the stock with nitrobenzene, separating the extract from the raffinate, and separating wax from this raffinate in the presence of a solvent mixture including a benzene, ethylene glycol monomethyl ether and nitrobenzene.

4. In the refining of lubricating oils, the improvement which comprises extracting the stock with a refining solvent, separating the extract from the raffinate, and separating wax from this raffinate in the presence of a solvent mixture including a benzene, an ethylene glycol ether and the refining solvent.

5. In the refining of lubricating oils, the improvement which comprises extracting the stock with a refining solvent, separating the extract from the raffinate and separating wax from this raffinate in the presence of a solvent mixture including a benzene, a modifier of the class described and the refining solvent.

6. In the refining of lubricating oils, the improvement which comprises extracting the stock with a solvent mixture including nitrobenzene and ethylene glycol monomethyl ether, separating the extract from the raffinate, and separating wax from this raffinate in the presence of a solvent mixture including a benzene, ethylene glycol monomethyl ether and nitrobenzene.

7. In the refining of lubricating oils, the improvement which comprises extracting the stock with a solvent mixture including a refining solvent and an ethylene glycol ether, separating the extract from the raffinate, and separating wax from this raffinate in the presence of a solvent mixture including a benzene, an ethylene glycol ether and the refining solvent.

8. In the refining of lubricating oils, the improvement which comprises extracting the stock with a solvent mixture including a refining solvent and a modifier of the class described, separating the extract from the raffinate and separating wax from this raffinate in the presence of a solvent mixture including a benzene, the modifier and the refining solvent.

9. In the refining of lubricating oils, the improvement which comprises extracting the stock with a solvent mixture including a refining solvent and a modifier of the class described, separating the extract from the raffinate and separating wax from this raffinate in the presence of a solvent mixture including a benzene, a modifier of the class described and the refining solvent.

10. In the refining of lubricating oils, the improvement which comprises extracting the stock with a solvent mixture including a refining solvent and a modifier of the class described, separating the extract from the raffinate and separating wax from this raffinate in the presence of a solvent mixture including a benzene, that modifier and another modifier of the class described, and the refining solvent.

EDWARD JOHN MARTIN.