Description

The present invention relates to lightening a petroleum hydrocarbon oil by purifying the same by a thermal treatment operation to produce materials useful in the fields of, for example, fuels. More specifically, it relates to an improved method for obtaining light fractions useful for fuels and the like from a petroleum hydrocarbon oil by a thermal treatment in which the petroleum hydrocarbon oil is fractionated into useful fractions by a distillation operation.

Heretofore, thermal cracking methods, catalytic cracking methods and hydrogenating cracking methods have been used as methods for lightening petroleum hydrocarbon oils to produce materials useful in the fields of, for example, fuels and the like. In these methods, although hydrocarbon oils can be cracked at a high temperature by a thermal treatment to produce useful light fractions, polymerization reactions occur, simultaneously with the thermal cracking reaction, and polymerized heavy hydrocarbon compounds having a high molecular weight are obtained as by-products. Various proposals have been made for obtaining useful light fractions at a high yield by adding various additives to improve the yield of the light fractions in the above-mentioned methods, namely as follows:

(i) Methods involving adding, as a thermal cracking radical stabilizer, for example, a metal salt of dialkyldithiocarbamic acids, diaryl-dithiocarbamic acids, etc., or organic phosphate esters, benzothiazoles, etc., to petroleum heavy oils (see, for example, JP-A-57-90093); and

(ii) Methods involving adding quinoline, tetrahydroquinoline, or a mixture thereof (see, for example, JP-A-57-21487).

Nevertheless, a method for improving the yield of light material from a petroleum hydrocarbon oil only by a simple distillation operation has not been proposed until now.

Accordingly, the present invention seaks to obviate the above-mentioned problems in the prior art and to provide a method for obtaining light fractions useful in the fields of, for example, fuels and the like, by an ordinary distillation operation not only from heavy residual oils but also from crude oils, without depending upon special catalytic and thermal cracking processes.

In accordance with the present invention, there is provided a method for lightening a petroleum hydrocarbon oil comprising the steps of: adding 1 part by weight or less, preferably 0.001 to 0.1 part by weight, more preferably 0.005 to 0.05 part by weight, of an organic compound having an active mercapto group therein to 100 parts by weight of a petroleum hydrocarbon oil; and carrying out a distillation operation by a thermal treatment.

The organic compounds having an active mercapto group therein usable in the present invention are preferably those which are liquid at normal temperatures. Examples of such compounds are alkyl mercaptans such as octyl mercaptan, dodecyl mercaptan, dimercaptopropane, and dimercaptobutane; polyalkylene ether polythiols such as diethyleneglycol dimercaptan and triethylene glycol dimercaptan; esters of thiocarboxylic acid with monohydric-to polyhydric-alcohols, such as isooctyl thioglycolate, 2-ethylhexyl mercapto propionate, ethyleneglycol dimercaptopropionate, butanediol dimercaptoacetate, trimethylolpropane tris-mercaptoacetate, pentaerythritol tetrakis-3-mercaptoacetate and pentaerythritol tetrakis-3-mercaptopropionate.

The petroleum hydrocarbon oils capable of being lightened according to the present method are not specifically limited. For example, various crude oils such as naphthenic crude oils, paraffinic crude oils, and mixtures thereof, as well as the topping residual oils and the vacuum distillation residual oils thereof, can be lightened. Especially, the present method is preferably applied to petroleum hydrocarbon oils such as crude oils having a low thermal history.

There are no specific limitations to distillation methods for lightening petroleum hydrocarbon oils according to the present invention and any conventional distillation methods can be used when carrying out the present invention. Briefly, the preferable operation conditions are those used by the conventional topping methods of crude oils except that an organic compound having an active mercapto group is added to the petroleum hydrocarbon oil suitably at a preheating step before the distillation operation, to thouroughly mix the additive with the petroleum hydrocarbon oil.

In the practice of the present invention, the yield of light fractions useful in the fields of, for example, fuels and the like, can be increased in conventional distillation methods manely by adding the above-mentioned type of organic compounds having an active mercapto group therein to the petroleum hydrocarbon oils, without making the thermal treatment conditions particularly severe.

The organic compounds having an active mercapto group therein to be used in the present invention very readily react with unsaturated bonds and cause an addition reaction to double bonds at an ordinary temperature or upon slight heating, to saturate the same. Accordingly, when the organic compound having an active mercapto group therein is added, various condensation polymerization reactions caused by radicals generated during the thermal treatment of petroleum hydrocarbon oils are suppressed and the propagation or growth of unsaturated compounds to the giant molecules is prevented.

Example

The present invention will now be explained in detail with reference to, but is by no means limited to, the following Examples.

Example 1 (Distillation of Oman crude oil)

Fractionating tests of the crude oil were carried out by using a distillation apparatus according to ASTM-D2892. The fractionating test results are shown in Table 1. Experiment No. 1 is a comparative test in which an organic compound having an active mercapto group therein was not added to the crude oil. In Experiment Nos. 2 and 3, 0.01 part by weight and 0.10 part by weight of pentaerythritol tetrakis-3-mercaptopropionate were added, as the organic compound having an active mercapto group, to the crude oil, respectively. The crude oil used in the tests was Middle-East mixed crude oil mainly containing Oman crude oil.

Table 1

Experiment No.	1*	2	3
Yield of 360°C-fraction (wt%)	53.2	55.4	55.8

* Comparative Experiment

As is clear from the results shown in Table 1, the economical value of Experiment Nos. 2 and 3 according to the present invention is high when compared to the comparative experiment, i.e. Experiment No. 1, because the difference of 2 to 3% by weight in the yields of the light fractions is large, from the viewpoint of a large scale distillation treatment of crude oil.

Example 2 (Distillation of Topping Residual Oil

Fractionating tests of topping residual oil were carried out by using a distillation apparatus according to ASTM-D 1160. The fractionating test results are shown in Table 2. Experiment No. 1 was a Comparative test, in which an organic compound having an active mercapto group was not used. In Experiment Nos. 2 and 3, the fractionating tests were carried out by adding trimethylolpropane tris-3-mercaptopropionate in an amount of 0.010 part by weight and 0.025 parts by weight, respectively, to 100 parts by weight of the topping residual oil. The topping residual oil used was 360°C-fraction of topping residual oil of Middle-East mixed crude oil mainly containing Khafji crude oil.

Table 2

Experiment No.	1*	2	3
360°C - 530°C (Vol%)	40.5	42.5	41.8

* Comparative Example

As is clear from the results shown in Table 2, an increase in yield of the vacuum light oil of 1 to 2% by volume was obtained in the case of Experiment Nos. 2 and 3, when compared to the Comparative Example (i.e., Experiment No. 1). This increase in the yield is useful for holding the necessary raw materials of the subsequent cracking process.

Example 3 (Distillation of Iranian Heavy Crude Oil)

The fractionating tests were carried out in the same manner as in Example 1, except that a crude oil mainly containing Iranian heavy crude oil was used in lieu of the crude oil mainly containing Oman crude oil.

The results obtained are shown in Table 3.

Table 3

Experiment No.	1*	2
Amount of additive added (wt. part per 100 parts of crude oil)	None	0.015
Yield of 350°C-fraction (Vol%)	56.8	62.5

* Comparative Example

As shown in Tables 1 to 3, the yields of the light fractions were increased, when compared to each Comparative Example, by adding an organic compound having an active mercapto group to the petroleum hydrocarbon oils according to the present invention, followed by carrying out a conventional distillation operation.

Claims

1. A method for lightening a petroleum hydrocarbon oil by distillation, characterised by distilling the petroleum hydrocarbon oil in the presence of an organic compound having a mercapto group therein, added in an amount of 1 part by weight or less per 100 parts by weight of the petroleum hydrocarbon oil.

2. A method as claimed in claim 1, wherein the petroleum hydrocarbon oil is a crude oil or topping residual oil.

3. A method as claimed in claim 1 or 2, wherein the addition amount of the organic compound having an active mercapto group therein is 0.001 to 1 part by weight, based on 100 parts by weight of the petroleum hydrocarbon oil.

4. A method as claimed in any of claims 1 to 3, wherein the organic compound having an active mercapto group therein is pentaerythritol tetrakis-3-mercaptopropionate, trimethylolpropane tris-3-mercaptopropionate, pentaerythritol tetrakis-mercaptoacetate, or trimethylolpropane tris-mercaptoacetate.

Patentansprüche

1. Verfahren zur Gewinnung leichter Komponente aus einem Petroleum-Kohlenwasserstofföl durch Destillation dadurch gekennzeichnet, daß das Petroleum-Hohlenwasserstofföl in Gegenwart einer organischen Verbindung destilliert wird, die eine Mercapto-Gruppe aufweist und in einer Menge von einem Gewischsteil oder weniger pro 100 Gewichtsteile des Petroleum-Hohlenwasserstofföls zugesetzt wird.

2. Verfahren nach Anspruch 1, bei dem das Petroleum-Kohlenwasserstofföl ein Rohöl oder ein Restöl einer leichten Destillation ist.

3. Verfahren nach Anspruch 1 oder 2, bei dem die Zugabemenge der organischen Verbindung, die eine aktive Mercapto-Gruppe enthält, 0,001 bis 1 Gewichtsteile auf der Basis von 100 Gewichtsteilen des Petroleum-Kohlenwasserstofföls beträgt.

4. Verfahren nach einem der Ansprüche 1 bis 3, bei dem die organische Verbindung, die eine aktive Mercapto-Gruppe enthält, Pentaerythritoltetrakis-3-mercaptopropionat, Trimethylolpropantris-3-mercaptoproprionat, Pentaerythritoltetrakis-mecaptoacetat oder Trimethylolpropantris-mercaptoacetat ist.

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* C L M S *

Revendications

1. Procédé d'enrichissement par distillation d'une huile d'hydrocarbures pétroliers, caractérisé en ce qu'on distille l'huile d'hydrocarbures pétroliers en présence d'un composé organique comportant un groupe mercapto, ajouté à raison de 1 partie en poids ou moins pour 100 parties en poids de l'huile d'hydrocarbures pétroliers.

2. Procédé tel que revendiqué dans la revendication 1, dans lequel l'huile d'hydrocarbures pétroliers est un pétrole brut ou une huile résiduelle d'étêtage.

3. Procédé tel que revendiqué dans la revendication 1 ou 2, dans lequel la proportion de composé organique comportant un groupe mercapto actif, ajouté va de 0,001 à 1 partie en poids, par rapport à 100 parties en poids de l'huile d'hydrocarbures pétroliers.

4. Procédé tel que revendiqué dans l'une quelconque des revendications 1 à 3, dans lequel le composé organique comportant un groupe mercapto actif est le tétrakis-3-mercaptopropionate de pentaérythritol, le tris-3-mercaptopropionate de triméthylolpropane, le tétrakis-mercaptoacétate de pentaérythritol ou le tris-mercaptoacétate de triméthylolpropane.