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TWO-STAGE CATALYTIC HYDROGEN PROCESSING OF A LUBE OIL

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10 Claims

ABSTRACT OF THE DISCLOSURE

Lubricating oil of reduced pour point is prepared without materially decreasing the flashpoint for a given viscosity level by contacting a mineral oil with hydrogen in a first step in the presence of a sulfur-resistant catalyst (e.g., nickel molybdate on alumina) under moderate conditions and further contacting in a second step with hydrogen in the presence of a calcium-exchanged, crystalline aluminosilicate catalyst containing a platinum group metal to effect a more severe treatment of the oil.

This invention relates to a process employing two distinct catalyst types in separate treating zones to produce high quality lubricating oil stocks from raw, heavy mineral lubricating oil distillates. More particularly, this invention concerns a hydroisomerization-hydrocracking catalytic conversion process for the production of refined mineral lubricating oils having substantially reduced pour points without substantial reduction of flash point for a given viscosity oil.

Many of the present day refining techniques employed to produce high quality lubricating oils having low pour points possess certain undesirable features. For example, dewaxing methods for reducing the pour point of raw lubricating oil distillates, such as solvent dewaxing, have high refrigeration requirements and low filter rates, resulting in high process costs. Other techniques, such as urea adduction encounter great difficulties in continuous operations due to handling and plugging problems. Catalytic processes are known which produce low pour point petroleum stocks; however, the products of such processes to date likewise possess extremely low flash points (e.g., below 225° F.) which is undesirable.

The present invention concerns a two-stage hydroisomerization-hydrocracking process wherein a raw, heavy lubricating oil derived by distillation from a waxy mineral crude oil having a high pour point, e.g. for instance, at least about 50° F., is converted into refined mineral lubricating oil of substantially reduced pour point, without substantially reducing the flash point for a given viscosity level. According to the process of the present invention a raw, heavy lubricating oil distillate is contacted in a first stage with hydrogen in the presence of a sulfur-resistant, desulfurization-denitrogenation or hydrogenation-type catalyst under moderate or hydrotreating conditions. The hydrotreated oil from the first stage, if desired after stripping to remove materials boiling below the lubricating oil range is further contacted in a second stage with hydrogen in the presence of a platinum group metal-containing hydroisomerization-hydrocracking catalyst of special composition to effect a more severe treatment of the oil. The effluent from the second stage may be fed, for instance, to a stream stripper to remove excessive hydrocracked components boiling below the lube oil range, and the finished mineral lubricating oil having a reduced pour point, for example, of about -25 to +25° F., recovered.

The mineral lubricating oil distillates treated by the process of the present invention are essentially raw, heavy

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lubricating oil distillates, for instance, a lubricating oil fraction obtained by the vacuum distillation of a waxy mineral crude oil. These lubricating oil feedstocks often possess a viscosity in the range of about 35 to 90 SUS at 210° F., and a pour point of at least about 50° F., frequently at least about 70° F.

The hydrogen treatment in the first stage of the present process is conducted at temperatures of about 600 to 800° F., preferably about 650 to 750° F. The other reaction conditions generally include pressures of about 1000 to 4000 p.s.i.g., preferably about 1000 to 2500 p.s.i.g.; weight hourly space velocities (WHSV) of about 0.1 to 1, preferably about 0.2 to 0.5; and molecular hydrogen to feed oil ratios of about 500 to 5000 s.c.f./b., preferably about 1000 to 2500 s.c.f./b.

The hydrogenated oil from the first hydrogenation stage preferably after stripping, is subjected to a second, more severe hydrogenation operation. The catalyst in the second reactor is especially chosen to effect hydroisomerization and hydrocracking. Temperatures in the second stage range from about 850 to 1000° F., with temperatures of about 900 to 975° F. being preferred. Other reaction conditions often include pressures of about 300 to 2000 p.s.i.g., preferably about 400 to 1000 p.s.i.g., weight hourly space velocities of about 0.25 to 2, preferably about 0.3 to 0.5, and molecular hydrogen to feed oil ratios of about 1000 to 10,000 preferably about 2000 to 6000, s.c.f./b.

The desulfurization-denitrogenation type catalysts used in the first stage of the present process can be any of the sulfur-resistant or sulfur-active, non-precious metal hydrogenation catalysts, such as those conventionally employed in the hydrogenation of heavy mineral oils. Examples of suitable catalytic ingredients are tin, vanadium, members of Group VI-B in the Periodic Table, i.e., chromium, molybdenum and tungsten, and metals of the iron group, i.e., iron, cobalt and nickel. These metals are present in catalytically effective amounts for instance, about 2 to 30 weight percent and may be present in the elemental form or in the form of oxides or sulfides, the sulfide form being the preferred form. Mixtures of these materials or compounds of two or more of the oxides or sulfides can be employed, for example, mixtures or compounds of the iron group metal oxides or sulfides with the oxides or sulfides of Group VI-B constitute very satisfactory catalysts. Examples of such mixtures or compounds are nickel molybdate, tungstate or chromate (or thiomolybdate, thio-tungstate or thiochromate) or mixtures of nickel or cobalt oxides with molybdenum, tungsten or chromium oxides. As the art is aware and as the specific examples below illustrate, these catalytic ingredients are generally employed while disposed on a suitable carrier of the solid metal oxide type, e.g., a predominantly calcined or activated alumina. Commonly employed catalysts have about 1 to 10% of an iron group metal and 5 to 25% of a Group VI-B metal (calculated as the oxide). Advantageously, the catalyst is sulfided nickel-molybdena supported on alumina. Such preferred catalysts can be prepared by the method described in U.S. Patent 2,938,002.

The platinum group metal-containing hydroisomerization-hydrocracking catalyst used in the second state of the present invention, unlike the catalyst employed in the first stage, is not normally sulfur-resistant and contains a major amount of a calcium-exchanged crystalline aluminosilicate having pores of about 8 to 14 angstrom units in size and a silica-to-alumina mole ratio of about 2 to 3:1; and a minor catalytic amount, say about 0.1 to 5, preferably about 0.3 to 2 weight percent of a platinum group metal. If desired, a minor amount, for instance about 5 to 20 or more weight percent of other suitable carrier

materials, for example a solid metal oxide, such as silica, silica-alumina, clay etc. may be added to the second stage catalyst composition.

The crystalline aluminosilicate component of the second stage catalyst may be synthetic or naturally-occurring and has a pore size of about 8 to 14 A., preferably about 9 to 13 A. Usually, with a given material, the pores are relatively uniform in size, and the silica-to-alumina mole ratio is about 2 to 3:1. The aluminosilicate is at least about 50%, preferably at least about 70%, calcium-exchanged. That is, at least about 50% to the cations present in the aluminosilicate are replaced by calcium. Calcium exchange is commonly carried out by exchange of the cations of the synthetic or naturally-occurring aluminosilicates with calcium ions, for instance through contact with an aqueous solution of calcium chloride and subsequently calcining the aluminosilicate, for instance at a temperature of about 500 to 1500° F. preferably about 700 to 1100° F.

The platinum group metals of the second stage catalyst include such Group VIII metals as, for example, platinum, palladium, rhodium or iridium. The platinum group metal may be present in the metallic form or as a sulfide, oxide or other combined form. The metal may interact with other constituents of the catalysts, but if during use the platinum group metal is present in the metallic form, then it is preferred that it be so finely divided that it is not detectable by X-ray diffraction means, i.e., that it exists as crystallites of less than about 50 A. in size. The platinum group metal may be added before or after the calcination of the calcium-exchanged crystalline aluminosilicate, by, for example, ion exchange or impregnation. In any event, after the platinum group metal is added, the catalyst is dehydrated and activated at the calcination temperature described above.

An available method for adding the platinum group metal by ion exchange comprises treating the crystalline aluminosilicate with an aqueous solution containing complex water-soluble, metal-amine cations, both organic and inorganic, of the metal to be deposited in the crystal structure. These complex cations ion-exchange with the cations present in the crystalline aluminosilicate. The exchanged material is then removed from the solution, dried and activated or calcined, for example, by heating the material to a temperature of about 500° F. in a flowing stream of inert dry gas or vacuum. The activation may be effected at a temperature below the temperature at which the complex cations are destroyed. The activated material may then be subjected to heat treatment to a temperature not exceeding about 1200° F. and preferably not exceeding about 925° F. in vacuum or inert atmosphere whereby the complex cation is destroyed and the metal is reduced in the material. Should the thermal treatment be insufficient to reduce the metal of the complex cations to the elemental state, chemical reduction either alone or in combination with thermal reduction may be employed. Through the operation excessive temperatures and extremes of acidity are to be avoided since they may tend to destroy the crystal structure of the crystalline aluminosilicate.

The platinum group metal may also be added by impregnation. The crystalline aluminosilicate, either with or without previous evacuation can be soaked in either a dilute or concentrated solution, usually aqueous chloroplatinic acid, ammonium hexathio-cyanoplatinate (IV) or hexathiocyanate platinic acid, often in an amount just sufficient to wet the material and be completely absorbed.

The catalysts of either stage of the process of this invention can, if desired, be formed into macrosized particles by tableting or extruding. Generally, these particles are about $\frac{1}{32}$ " to $\frac{1}{2}$ " in diameter and about $\frac{1}{16}$ " to 1" or more in length. Although these macrosized particles are usually formed after dehydration and before calcination, this, of course, is optional and can be done at any time found most convenient,

The process of the present invention is illustrated by the following example which is not to be considered as limiting.

EXAMPLE I

A waxy-raw, mixed base lubricating oil distillate having the properties of the feedstock in Table I, below, was contacted with hydrogen in the presence of a calcined nickel-molybdena on alumina catalyst at a temperature of 700° F., a pressure of 1500 p.s.i.g., a weight hourly space velocity of 0.25 and a hydrogen rate of 1500 s.c.f./b. of oil. The catalyst, which contained 2.3 percent nickel and 15.6 percent molybdenum as oxides supported on activated alumina was pretreated with hydrogen sulfide at 350° F. for two hours using one s.c.f.-H₂S/hr./100 grams of catalyst. The hydrocarbon product from this first stage was flashed to remove light gaseous products and further treated in a second stage at a temperature of 950° F., a pressure of 500 p.s.i.g., a weight hourly space velocity of 0.35 and a hydrogen rate of 5000 s.c.f./b. of feed in the presence of a calcined platinum-containing, crystalline aluminosilicate $\frac{1}{16}$ " extrudate catalyst. The catalyst contained about 0.8% platinum supported on a carrier which was composed of a calcium-exchanged, crystalline sodium aluminosilicate having a pore size of about 10 A. and a silica-to-alumina mole ratio of about 2.5:1 and about 15 weight percent clay which was added as a binder prior to extrusion. The catalyst analyzed 0.766% platinum 8.55% calcium and 1.57% sodium. The effluent product from the second stage was steam stripped to remove lighter hydrocarbon components. The properties of the feedstock compared to that of the first stage and final products are as follows:

TABLE I

	Oil A Feed- stock	Oil B 1st stage product	Oil C Final product
Gravity, ° API.....	23.8	29.1	36.0
Flash, °F.....	485	350	255
Viscosity, SUS at 210° F.....	82.4	68.0	153.6
Pour, ° F.....	120+	120+	0
Nitrogen, p.p.m.....	1,300	94	10

¹ At 100° F.

These data illustrate the major reduction in pour point of the second stage product resulting from the process of this invention. The product from the first stage reactor (Oil B) may be seen to have undergone substantial hydrocracking but no reduction in pour point, while the product from the second stage reactor (Oil C), following steam stripping to remove lighter hydrocarbon components, has a pour point of 0° F., down 120° from the pour point of the feedstock.

It is claimed:

1. A process of producing a hydrocarbon lubricating oil having a reduced pour point without a materially decreased flashpoint for a given viscosity level, which comprises contacting a raw, mineral lubricating oil distillate from a waxy mineral crude oil having a pour point of at least about 50° F., with hydrogen in the presence of a sulfur-resistant hydrogenation catalyst at a temperature of about 600 to 800° F. and further contacting the resulting hydrogenated oil with hydrogen in the presence of a hydroisomerization-hydrocracking catalyst at a temperature of about 850 to 1000° F., said hydroisomerization-hydrocracking catalyst comprising a major amount of an at least 50% calcium-exchanged crystalline aluminosilicate having a pore size of about 8 to 14 A., and a silica-to-alumina mole ratio of about 2 to 3:1 and a minor, catalytic amount of a platinum group metal.

2. The process of claim 1 wherein said crystalline aluminosilicate is at least 70% calcium exchanged.

3. The process of claim 2 wherein the contact of said raw mineral lubricating oil distillate with hydrogen is conducted at a pressure of about 1000 to 4000 p.s.i.g., a weight hourly space velocity of about 0.1 to 1 and a hydrogen feed rate of about 500 to 5000 s.c.f./b.

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4. The process of claim 3 wherein the contact of said hydrogenated oil with hydrogen is conducted at a pressure of about 300 to 2000 p.s.i.g., a weight hourly space velocity of about 0.25 to 2 and a hydrogen feed rate of about 1000 to 10,000 s.c.f./b.

5. The process of claim 4 wherein the mineral lubricating oil distillate has a viscosity of about 35 to 90 SUS at 210° F. and a pour point of at least about 70° F.

6. The process of claim 5 wherein the sulfur-resistant catalyst contains molybdenum and an iron group metal.

7. The process of claim 6 wherein the iron group metal is nickel.

8. The process of claim 5 wherein the platinum group metal is platinum.

9. The process of claim 8 wherein the contact of said raw mineral lubricating oil distillate with hydrogen is conducted at a temperature of about 650 to 750° F., a pressure of about 1000 to 2500 p.s.i.g., a weight hourly space velocity of about 0.2 to 0.5 and a hydrogen feed rate of about 1000 to 2500 s.c.f./b. and the resulting hydrogenated oil is further contacted with hydrogen at a

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temperature of about 900 to 975° F., a pressure of about 400 to 1000 p.s.i.g., a weight hourly space velocity of about 0.3 to 0.5 and a hydrogen feed rate of about 2000 to 6000 s.c.f./b.

10. The process of claim 9 wherein the sulfur-resistant catalyst contains molybdenum and nickel.

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