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PROCESS FOR THE PRODUCTION OF A LUBRICATING OIL

Maurice K. Rausch, South Holland, Ill., assignor to Sinclair Research, Inc., New York, N.Y., a corporation of Delaware

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ABSTRACT OF THE DISCLOSURE

Lubricating oil with an enhanced susceptibility to the action of pour point depressors is prepared by subjecting a solvent-extracted, solvent-dewaxed mineral oil to a two-step hydrogenation, the first step being one of low hydrogen consumption in presence of sulfur insensitive catalyst (e.g., Co-MoO_3/Al_2O_3), the second being one of high hydrogen consumption in presence of platinum group metal-alumina catalyst promoted with about 1 to 15 wt. percent of fluorine.

This invention relates to the preparation of mineral lubricating oils having enhanced pour point depressor susceptibility. More particularly, it relates to a process of subjecting a solvent-extracted, solvent-dewaxed mineral oil to the sequential treatments of hydrorefining and hydrocracking-hydroisomerization to produce a lubricating oil of high susceptibility to the action of pour point depressors.

It is well known in the art to add pour point depressors to mineral lubricating oils in order to permit their flow at low temperatures. The improvement of low temperature flow properties is an increasingly important facet in lubricant manufacture. These demands are felt in such important applications as automotive engine oils where modern close tolerance engines demand a lubricant with good fluidity and low viscosity properties for satisfactory cold starting characteristics. The development of pour point depressing additives has been to some extent responsive to these needs, but the amount of decrease in pour point and improvement in low temperature flow properties of the oils, as effected by the pour point depressor, has normally been relatively low and oils have not been too responsive to larger amounts of depressor. There is being sought, therefore, a method of preparing mineral oil bases which will exhibit increased susceptibility to the pour point depressors, thereby permitting the use of smaller quantities of the additives to achieve the same low temperature flow properties or the use of the same concentrations of additive to achieve superior flow properties.

Various refining and finishing treatments have been explored by the art for generally improving the properties of mineral oil bases. These include acid or caustic treatment, solvent refining, clay treatment, solvent-dewaxing, deasphalting, hydrotreating, etc. Certain of these treatments have also been conducted in ordered sequence to enhance specific properties of the mineral oil bases. Hydrorefining of lubricating oil stocks using a high hydrogen-to-feed ratio over nickel-tungsten or cobalt-molybdenum catalysts, for example, has been followed with a mild hydrofinishing step in the presence of a platinum-alumina catalyst containing a modicum of fluoride promoter, the purpose being to supplant the lower-yield solvent refining steps and to produce lubricating oils of improved stability and oxidation resistance. Another sequence variation has been the use of multiple solvent refinings followed by clay treatments, in turn followed by a very low hydrogen consumption hydrorefining or hydrofinishing process, the purpose of this sequence also being to improve the stability to oxidation of the lubricating oil. No one of the treatments or combinations of treatments previously employed, however, has been effective to produce a mineral oil base with any pronounced increase in pour point depressor susceptibility over bases produced by other treatments.

It has now been found that by subjecting a solvent-extracted, solvent-dewaxed mineral oil base to a two-step hydrogenation treatment comprising hydrotreating under conditions of low hydrogen consumption in the presence of a "sulfur-insensitive" catalyst, followed by hydrotreating under conditions of high hydrogen consumption in the presence of a platinum group metal-alumina catalyst, containing a substantial amount of fluorine promoter, there is obtained a lubricating oil of greatly enhanced pour point depressor susceptibility. Whereas the oils produced by the method of this invention exhibit only a slightly lower pour point prior to the addition of depressor than do oils produced by conventional refining steps, when a pour depressor is added to the oils of the present invention there results a considerably greater decrease in viscosity at low temperatures than effected by depressor addition to conventionally refined oils.

In refining of mineral oils, a wax-bearing reduced crude is normally fractionated to yield a distillate oil, e.g., a light lube oil having a viscosity in the range of about 60 to 100 Saybolt seconds at 100° F., a medium lube oil having a viscosity in the range of SAE 10 to SAE 20 and a heavy lube oil having a viscosity in the range of SAE 40 to SAE 60. Any of these fractions or other distillate lubricant fractions, if desired, may be used in the process of this invention. Solvent extraction can be accomplished according to any one of a number of well known methods. The solvents used will preferentially dissolve aromatic type hydrocarbons, have much less preference for naphthene hydrocarbons and little or no solubility for paraffinic hydrocarbons. The solvent selected for aromatics is normally only partially miscible with the oil undergoing treatment so that two phases are formed: a raffinate phase containing a refined oil of reduced aromatic content and an extract phase containing the selective solvent and aromatic hydrocarbons. Suitable selective solvents are furfural, phenols, liquid SO_2, nitrobenzene, dimethyl formamide and the like. The volumetric ratio of solvent to oil may often vary from about 1 to 4:1. The extraction temperature may be from about 100 to 200° F. with the preferred temperature being about 130 to 170° F.

The raffinate from the solvent extraction is solvent-dewaxed in order to remove any waxy components and lower the pour point of the feedstock. In a typical dewaxing operation, a preferential solvent for the liquid oil constituents is used to separate the waxy from the nonwaxy components. Typical dewaxing solvents contain a mixture of an aromatic hydrocarbon containing from 6 to 8 carbon atoms per molecule, e.g., benzene, toluene, or mixtures thereof, and an aliphatic or alkyl ketone having from 3 to 8 carbon atoms per molecule, such as acetone, methyl ethyl ketone, methyl propyl ketone, methyl isobutyl ketone or mixtures thereof. For example, a frequently used dewaxing solvent comprises a mixture of about 40 to 60 volume percent of an aromatic hydrocarbon such as toluene, and 40 to 60 volume percent of an aliphatic ketone such as methyl ethyl ketone. Useful solvent to oil ratios include from about 0.5:1 to 4:1. The dewaxing operation is carried out at a temperature sufficiently low to obtain the desired amount of wax removal. Normally the filter temperature will range from about —30° to +20° F. with the preferred range being from about —20° to +10° F.

The solvent-extracted, solvent-dewaxed lubricating oil stock to be subjected to the dual hydrogenation treatment of this invention is characterized by an aromatic carbon content of less than about 10 percent, preferably less than 8 percent. The first step of the hydrogenation treatment, which will be referred to hereinafter as the "hydrorefining step," comprises a hydrogen treatment in the presence of a "sulfur-insensitive" catalyst, e.g., an iron-group metal on a predominantly activated alumina support. Preferred catalysts are the nickel-molybdena on alumina and the cobalt-molybdena on alumina hydrogenation catalysts containing catalytically effective amounts of molybdena and cobalt or nickel. The catalytic promoters are usually a minor amount of the catalyst with the alumina being the major component. Advantageously, the catalyst will contain about 1 to 10 weight percent of cobalt or nickel, preferably 2 to 5 percent, calculated as the free metal; about 8 to 20 weight percent of molybdena, calculated as MoO_3, preferably 10 to 15 percent; and the balance being an essentially activated or calcined alumina support. The catalyst is preferably pre-sulfided, e.g., by contact with H_2S at an elevated temperature, before use.

In the initial hydrogen treatment, the rate of hydrogen feed is to be kept relatively low for the hydrorefining process, i.e., from about 500 to 3,000 standard cubic feet per barrel of feed, preferably about 1,000 to 2,500 s.c.f./bbl. Hydrogen consumption is kept within about 50 to 200, preferably about 75 to 150 s.c.f./bbl. Pressures from about 500 to 3,000 pounds per square inch guage, preferably about 1,000 to 2,500 p.s.i.g., temperatures from about 600 to 800° F., preferably from about 650 to 750° F., and a weight hourly space velocity (WHSV) of about 0.25 to 3, preferably about 0.5 to 2 can be employed.

The second hydrogenation treatment of the process, which subjects the feedstock to hydrocracking-hydroisomerization, involves hydrotreating in the presence of a fluoride-promoted platinum-group metal on activated or calcined alumina catalyst. The fluoride and platinum components form a minor amount of the catalyst with the major portion being alumina catalyst. It is often preferred to employ an ammonium fluoride promoted platinum-alumina catalyst. The catalyst may contain about 0.2 to 2, preferably 0.3 to 1, weight percent of platinum group metal, calculated as the free metal, and about 1 to 15, preferably about 2 to 8, weight percent of fluorine, the balance being essentially alumina. Activated or gamma-family aluminas can be employed such as those derived by calcination of amorphous hydrous alumina, alumina monohydrate, alumina trihydrate or their mixtures, at elevated temperatures of, for instance, about 750 to 1500° F., preferably about 850 to 1400° F. Advantageously, the alumina precursor may be a mixture predominating in, for instance, about 65 to 95% by weight, in one or more of the alumina trihydrates: bayerite, nordstrandite or gibbsite, and about 5 to 35% by weight alumina monohydrate (boehmite), amorphous alumina or their mixtures. Catalyst bases of this type are disclosed in U.S. Pats. Nos. 2,838,444 and 2,838,445.

As stated, the second hydrogen treatment requires isomerization of the hydrocarbon feed, as well as hydrocracking. The treatment conditions include pressures of about 500 to 3000 p.s.i.g., preferably about 1000 to 2500 p.s.i.g.; temperatures of about 450 to 700° F., preferably about 500 to 600° F.; a WHSV of about 0.2 to 2, preferably about 0.25 to 0.5, and a ratio of hydrogen to feed of about 3000 to 9000, preferably about 4000 to 7000, standard cubic feet of hydrogen per barrel of feed. Hydrogen consumption is significantly higher than in the hydrorefining step, being about 400 to 1600, preferably about 600 to 1000 standard cubic feet of hydrogen per barrel of feed. After the second hydrogenation step it may be desirable to remove low boiling hydrocracked components and adjust the flash point-viscosity relationship by subjecting the effluent to a distillation step.

Treatment of a solvent-extracted, solvent-dewaxed lube distillate according to the foregoing process yields a lube oil having generally improved pour point depressor susceptibility. Thus, the various conventional pour point depresors will normally be more effective in oils treated according to this invention. Typical of the pour point depressors which have increased effectiveness in the lubricating oils refined by the manner of this invention are condensation products of chlorinated wax and naphthalene, condensation products of chlorinated wax and phenol, polymers of ethylenically-unsaturated monomers such as olefins, ethers, esters, etc. A comprehensive list of materials suitable as pour point depressors appears in "Petroleum Refining With Chemicals" by Kalichevsky and Kobe (1956), published by Elsevier Publishing Company, New York, pages 525–534, herein incorporated by reference.

Particularly effective pour point depressors are the synthetic resins derived by the polymerization of esters of acrylic and methacrylic acids.

Pour point depressors may be added to the oil in various amounts depending on the nature of the particular depressor and on the pour point desired. The acrylic resin pour depressors, for example, may generally be successfully employed in amounts up to about one percent by weight of the oil.

The process of this invention and the improved properties of oils treated according thereto are illustrated by the following examples. Percentages given are by weight.

EXAMPLE I

A raw lube distillate obtained from a mixed base crude was subjected to solvent extraction at 175° F. with phenol at a solvent to oil volume ratio of 1.8/1, followed by solvent dewaxing at −10° F. using a mixture of 50 volume percent of each of methyl ethyl ketone and toluene at a 3:1 solvent to oil ratio. The resulting neutral oil fraction containing about 5% aromatics was then processed in a two fixed bed catalyt reactor system using the following conditions:

	First reactor	Second reactor
Catalyst (sulfided): before use	2.64% CO/ 13.4% MoO_3 on alumina	0.6% Pt/ 4.7% F on alumina
Pressure, p.s.i.g	1,500	1,500
Temperature, ° F	700	550
WHSV	1.0	0.35
Hydrogen/feed, s.c.f./b	1,500	5,000

The effluent from the second reactor was distilled to remove low boiling hydrocracked components, leaving a lube fraction with proper flash point-viscosity relationship for a mixed base lube. Properties of the solvent-extracted, solvent dewaxed feedstock prior to, and after, the two-step hydrogenation compare as follows:

	Solvent-treated feedstock	Hydrogenation product
Gravity, ° API	30.4	34.2
Flash point, ° F	435	405
Viscosity at 100° F., cs	49.77	29.89
Pour Point, ° F	+10	+5

These results indicate that the hydrogenation product has undergone some moderate degree of hydrocracking (viscosity decrease from 49.77 to 29.89 cs.) and a slight degree of hydroisomerization (pour point decrease from +10 to +5° F.).

EXAMPLE II

After adding a small amount of pour depressor (0.5% of Acryloid 150) to the oils of Example I, viscosities at 0° F. were obtained as a measure of low temperature

performance. The effects of the pour depressor additions were as follows:

	Solvent-treated feedstock	Hydrogenation product
Added Acryloid 150, percent	0.5	0.5
Viscosity, cs. at 0° F	16,334	1,763

This major improvement in low temperature flow characteristics is especially surprising in view of the very slight decrease in pour point between the solvent-treated feedstock and the dual hydrogenation product.

EXAMPLE III

In order to further illustrate the superior low temperature flow properties of the hydrogenation product of Example I, a series of blends were made using other solvent-extracted, solvent-dewaxed neutrals from mixed base crudes which had not been further subjected to the hydrogenation treatment of the present invention. These oils have high temperature viscosities bracketing that of the double hydrogenated oil of Example I. The results of these studies are presented below, with the oils listed in increasing order of viscosity at 100° F.

	Oil B [1]	Dual hydrogenation [2]	Oil C [1]	Oil D
Viscosity, cs. at 100° F	21.29	29.89	33.68	49.77
Pour Point, ° F	+10	+5	+5	+10
+0.5% Acryloid 150:				
Viscosity, cs. at 100° F	22.70	31.62	35.31	52.44
Viscosity, cs. at 0° F	3,226	1,763	8,626	16,334

[1] Solvent extracted, solvent-dewaxed.
[2] Product of Example I.
[3] Solvent-extracted, solvent-dewaxed feedstock of Example I.

For a viscosity of 31.62 cs. at 100° F. for a stock which, like Oils B, C and D, is merely solvent-extracted and solvent dewaxed, the viscosity at 0° F. would have to be about 7000 cs. The viscosity at 0° F. of the two-step hydrogenation product of the example, however, is a surprisingly low 1763 cs. Conversely, in order to achieve the low value of 1763 cs. at 0° F., the viscosity at 100° F. of the normal solvent-extracted, solvent dewaxed stock would have to be reduced to about 18.3 cs., whereas the hydrogenated product of the Example I exhibits the much higher value of 31.62 cs. These data illustrate the marked superiority in low temperature flow properties of the product resulting from the sequential steps of hydrorefining and hydrocracking-hydroisomerization as practiced by the manner of the present invention on a solvent-extracted, solvent-dewaxed mineral oil base.

What is claimed:

1. A method of producing a lubricating oil having enhanced susceptibility to the action of pour point depressors which comprises subjecting a solvent-extracted, solvent-dewaxed distillate mineral lubricating oil fraction having an aromatic carbon content of less than about 10 percent to a two-step hydrogenation treatment comprising hydrorefining said lubricating oil fraction in the presence of a sulfur-insensitive catalyst at a temperature of about 600 to 800° F. at a ratio of hydrogen to oil of about 500 to 3000 standard cubic feet per barrel and with a hydrogen consumption of about 50 to 200 standard cubic feet per barrel, and hydrocracking-hydroisomerizing the hydrorefined oil in the presence of a fluoride-promoted, platinum group metal-alumina catalyst at a temperature of about 450 to 700° F., at a ratio of hydrogen to oil of about 3000 to 9000 standard cubic feet per barrel and with a hydrogen consumption of about 400 to 1600 standard cubic feet per barrel.

2. The method of claim **1** wherein the catalyst in the hydrorefining step is an alumina based catalyst containing catalytically-effective amounts of molybdena and a metal selected from the group consisting of cobalt and nickel.

3. The method of claim **2** wherein the hydrorefining step is conducted at a temperature of about 650 to 750° F., at a ratio of hydrogen to oil of about 1000 to 2500 standard cubic feet per barrel, and the hydrogen consumption is about 75 to 150 standard cubic feet per barrel.

4. The method of claim **3** wherein the hydrocracking-hydroisomerization step is conducted at a temperature of about 500 to 600° F., at a ratio of hydrogen to oil of about 4000 to 7000 standard cubic feet per barrel, and the hydrogen consumption is about 600 to 1000 standard cubic feet per barrel.

5. The method of claim **2** wherein the fluoride-promoted platinum group metal-alumina catalyst contains about 0.2 to 2 weight percent of platinum, calculated as the free metal, and about 1 to 15 weight percent of fluorine.

6. The method of claim **5** wherein the alumina-based catalyst employed in the hydrorefining step contains about 1 to 10 weight percent of cobalt, calculated as the free metal, and about 8 to 20 weight percent of molybdena, calculated as MoO_3.

7. The method of claim **1** wherein the hydrorefining step is conducted in the presence of an alumina-based catalyst containing catalytically effective amounts of molybdena and a metal selected from the group consisting of cobalt and nickel, at a temperature of about 650 to 750° F., at a ratio of hydrogen to oil of about 1000 to 2500 standard cubic feet per barrel, and with a hydrogen consumption of about 75 to 150 standard cubic feet per barrel, and further wherein the hydrocracking-hydroisomerization step is conducted in the presence of a fluoride-promoted platinum-alumina catalyst containing about 0.2 to 2 weight percent platinum, calculated as the free metal, and about 1 to 15 weight percent of fluorine, at a temperature of about 500 to 600° F., at a ratio of hydrogen to oil of about 4000 to 7000 standard cubic feet per barrel, and with a hydrogen consumption of about 600 to 1000 standard cubic feet per barrel.

8. The method of claim **7** wherein the alumina-based catalyst employed in the hydrorefining step contains about 1 to 10 weight percent of cobalt, calculated as the free metal, and about 8 to 20 weight percent of molybdena, calculated as MoO_3.

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DELBERT E. GANTZ, Primary Examiner

A. RIMENS, Assistant Examiner

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