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SOLVENT EXTRACTION, SOLVENT DEWAXING AND HYDROTREATING A LUBE OIL

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ABSTRACT OF THE DISCLOSURE

Oxidation inhibitor susceptibility of distillate mineral lubricating oils is enhanced by the steps of treating a distillate lubricating oil fraction by solvent extraction to remove aromatic constituents, solvent dewaxing the raffinate to remove waxy components, and then hydrotreating the dewaxed material over a nickel-molybdenum-activated alumina catalyst at about 550 to 775° F. and about 800 to 5000 p.s.i.g. hydrogen partial pressure, and preferably at about 625 to 725° F. and about 0.5 to 2 WHSV. The catalyst can be sulfided. Oils obtained by this process have great inhibitor susceptibility and as a result can be protected against oxidation breakdown for a long period of time. Conventional antioxidants, such as sulfur compounds, phosphorous compounds, and amine and phenol derivatives, are effective in the oils.

This invention relates to the treatment of mineral lubricating oils in order to improve their additive susceptibility characteristics. More specifically, this invention relates to the treatment of a distillate mineral lubricating oil by a series of processing steps including solvent extraction, solvent dewaxing and hydrotreating with a nickel-molybdenum catalyst in order to obtain a lubricating oil of improved oxidation inhibitor susceptibility.

It is well known that mineral oil based liquid lubricants suffer from the effect of oxidation when used in high temperature applications. The oxidation products may include organic acids and complex condensation and polymerization products which are undesirable. In order to inhibit oxidation, it is customary to add an oxidation inhibitor to a lubricating oil. Small amounts of inhibitor are normally effective in preventing oxidation for a limited period of time. However, oxidation inhibition for the longer periods of time required in normal use is often unobtainable by merely adding larger quantities of inhibitor. A frequent experience is that inhibitors when present in large amounts will not give inhibition for a significantly longer period than they give when used in much smaller amounts. In other words, the susceptibility of the oil to an inhibitor is normally relatively low and the oil is not too responsive to larger amounts of inhibitor.

It is an object of this invention to provide an oil of improved oxidation inhibitor susceptibility in order that long term oxidation resistance can be obtained by simply adding an increased amount of oxidation inhibitor. It is a further object to provide a novel combination of oil and oxidation inhibitor having improved long term oxidation resistance.

It has been found that high oxidation inhibitor susceptibility can be obtained by solvent extraction of a distillate lubricating oil fraction to remove aromatic constituents, solvent dewaxing the resulting material to remove waxy components and yield an oil of low pour point, and then hydrotreating the product over a nickel-molybdenum-activated alumina catalyst. An oil obtained according to this process has a great inhibitor susceptibility and as a result can be protected against breakdown due to oxidation for a long period of time.

In refining of mineral oils a 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 fractions if desired may be used in the process of this invention.

The first step of my method is the solvent extraction of a desired lube fraction to remove aromatic constituents. Solvent extraction is a conventional step and may be accomplished according to any one of a number of well known methods. The solvents used in this step 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 vary from about 1 to 2:1. The extraction temperature may vary from about 100 to 200° F. with the preferred temperature being about 130 to 170° F.

In the second step, the raffinate from the solvent extraction is solvent dewaxed in order to remove waxy components and yield an oil of low pour point. In a typical dewaxing operation, a preferential solvent for the liquid oil constituents is used to separate the waxy from the non-waxy 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 suitable 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 may vary from about 0.5:1 to 2:1. The dewaxing operation is carried out at a temperature sufficiently low enough to obtain the desired amount of wax removal. Normally the filter temperature will range from about −30° F. to +20° F. with the preferred range being from about −20° F. to +10° F.

After the dewaxing operation it may be desirable to adjust product viscosity and boiling range by a distillation step. At this point a close distillation cut can be made on a smaller volume of oil which contains less wax and aromatics.

The next step in my process is hydrotreating using a nickel-molybdena activated alumina catalyst. The temperature used in the hydrotreating may be from about

550 to 775° F. with the preferred range being about 625 to about 725° F. The oil to be hydrogenated is contacted with added molecular hydrogen in the presence of the solid nickel-molybdena catalyst. Any suitable hydrogenation reactor may be employed. For example hydrogen and oil may be contacted with either a stationary or moving catalyst bed. The hydrogen rate may often vary from about 300 to about 5000 s.c.f./b. (standard cubic feet per barrel of oil), with the preferred rate being from about 500 to about 2000 s.c.f./b. The hydrogen partial pressure ranges from about 800 to 5000 p.s.i.g. with the preferred range being from about 1000 to 2500 p.s.i.g. The space velocity should normally range from about 0.25 to 4 WHSV (weight hourly space velocity, pounds of oil per pound of catalyst per hour) and preferably from about 0.5 to 2 WHSV.

The catalyst used in the hydrotreating step of this process is a calcined or activated catalyst comprising catalytic amounts of nickel and molybdenum on activated alumina. The catalyst may contain about 1 to 30 weight percent molybdenum and about 1 to 15 weight percent nickel. The preferred composition is about 8 to 20 weight percent molybdenum and 2 to 10 weight percent nickel. The catalyst may be formed by impregnating activated alumina with nickel and molybdenum compounds in an aqueous medium. The aqueous medium may be a solution or a slurry containing either water insoluble compounds or water soluble compounds such as nickel acetate, nickel nitrate, nickel chloride, nickel perchlorate, molybdenum bromide, molybdenum trioxide, ammonium para molybdate etc. After deposition of the molybdenum and nickel compounds, the catalyst can be dried and calcined or activated, e.g. at a temperature in the range of about 600 to 1300° F. or higher.

A preferred form of the catalyst consists of an activated alumina base having minor, catalytically effective amounts of molybdenum and nickel deposited thereon by double impregnation. The total amount of catalytically active components in the doubly impregnated catalyst can vary considerably while being sufficient to afford a substantial catalytic effect. The finely divided alumina base which is doubly impregnated may first be impregnated by adding nickel and molybdenum components in an aqueous medium. The impregnated material is calcined for instance at temperatures of about 600 to 1300° F. or more. After calcination the catalyst is again impregnated with nickel and molybdenum, dried and calcined at about 600 to 1300° F. or more.

The catalyst of the invention is particularly active when the activating metals, for instance in the oxide form, are converted to the sulfides. To convert the metal oxides to the sulfides, the calcined alumina catalyst may be sulfided by passing hydrogen sulfide, either pure or diluted with another gas such as hydrogen, over the catalyst at temperatures usually below about 800° F., preferably about 300 to 600° F. for a time sufficient to convert a significant portion of the oxides of the metal components to their respective sulfides.

Treatment of an oil according to the foregoing process yields a lube oil having generally improved antioxidant additive susceptibility. Thus any conventional antioxidant will normally be more effective in relatively large quantities in oils treated according to this invention. Typical of the antioxidants which have increased effectiveness due to this invention are sulfur compounds, phosphorous compounds and amine and phenol derivatives. Examples of sulfur compounds are sulfurized fatty oils and olefins, sulfurized terpenes, aromatic sulfides such as dibenzyl sulfides and phenol sulfides such as dibutyl phenol sulfides. Suitable phosphorous compounds are organic phosphites such as triphenyl or tributyl phosphite and alkyl phosphates. Typical phosphorous and sulfur compounds are zinc dithiophosphate. Typical amines are diphenylamine and diamines such as tetramethyl diaminodiphenylmethane. Phenol derivatives which may be used advantageously are for example beta-naphthol pyrogallol, alizarin and the oil soluble alkylated phenols. The oil-soluble, alkylated phenols are preferred and ordinarily contain 1 to 5 alkyl groups each of 1 to 6 or more carbon atoms. Particularly preferred alkylated phenols are the alkylated cresols such as dibutyl p-cresol. In general, antioxidants provided the oils of the present invention will be present in amounts of about 0.1 to 5% by weight, preferably about 0.7 to 3%.

The process of this invention and improved properties of oils treated according to the invention are illustrated by the following example.

Example

A neutral lube distillate obtained as a side stream from the vacuum distillation of a Mid-Continent based crude was employed as the starting material. The neutral lube distillate tested as follows:

Gravity ° API	30.3
Flash point, ° F.	385
Viscosity (cs.) at 210° F.	3.655
Aniline point, ° C.	90.2

This raw, vacuum sidestream was solvent extracted using phenol in a phenol-to-oil ratio of 1.63 to 1. A 64.3% yield of waxy raffinate was obtained and the waxy raffinate was solvent dewaxed using a 60–40 mixture of methyl ethyl ketone and toluene as the solvent for selective crystallization of the paraffinic components. The solvent-to-oil dilution used in the solvent dewaxing was 1.45 to 1. the oil solvent mixture was filtered at −15° F. to yield 78.7% dewaxed raffinate. The dewaxed raffinate was then fractionated to yield a 55.2% oil fraction of desired viscosity and boiling range. This material is identified as Oil A in Table I. Oil A was then hydrogen-treated under the following process conditions using two alternate catalyst types. These catalyst types were (1) cobalt-molybdenum on activated alumina containing 3% CoO and 10% MoO_3 and (2) nickel-molybdenum on activated alumina containing 4% NiO and 16% MoO_3. In the case of both catalysts, the catalytic metal oxides were converted to their sulfide form by treatment with H_2S at 350° F. at a rate of 6 standard cubic feet per hour per catalyst charge of 150 grams.

Hydrogen partial pressure, p.s.i.g.	1500
Temperature, ° F.	650
Space velocity, WHSV	1.0
Hydrogen rate, s.c.f./b.	1500

The products were put through a steam stripping operation using a steam rate of 10 lbs./bbl. to remove any hydrocracked components. The products from this operation are Oil B (the product from the hydrogenation using the cobalt-molybdenum catalyst) and Oil C (the product from the hydrogenation using the nickel-molybdenum catalyst). Properties of these oils along with Oil A are listed in Table I.

TABLE I

	Oil A	Oil B	Oil C
Gravity, °API	32.4	32.7	33.0
Flash point, ° F	415	405	395
Fire, ° F	460	445	465
Viscosity, cs. at 100° F	25.98	25.08	24.73
Viscosity, cs. at 210° F	4.539	4.462	4.447
Pour point, ° F	+10	+5	+10
Color, ASTM	L1.5	L0.5	L0.5
Specific dispersion	105.5	104.2	102.8
Refractive index at 20° C	1.4749	1.4737	1.4728
Iodine number	8.6	3.4	2.7

These oils were then formulated with an oxidation inhibitor. The specific oxidation inhibitor used was dibutyl-paracresol (DBPC) and two additive levels of this oxidation inhibitor were used with each oil. These oils were then evaluated for oxidation resistance in the Turbine

Oil Stability Test (TOST), ASTM D–943. Oxidation life was determined as hours running time to 2.0 acid number. Data on acid number and ASTM color throughout the oxidation runs are presented below:

Hours TOST time	Oil B—Hydrogenated over cobalt-moly catalyst containing—				Oil C—Hydrogenated over nickel-moly catalyst containing—			
	0.4% DBPC		1.0% DBPC		0.4% DBPC		1.0% DBPC	
	Acid No.	Color	Acid No.	Color	Acid No.	Color	Acid No.	Color
1,000	0.08	L2.0	0.08	L3.0	0.05	2.5	0.07	L2.0
1,344	0.08	L3.0	0.17	L2.0	0.07	L3.5	0.10	L5.5
1,680	0.09	L3.5	0.20	L6.5	0.08	4.5	0.12	
2,016	0.10	L4.0	0.22	L6.5	0.08	5.0	0.18	
2,160			10.5	Dark				
2,342	21.6	Dark			18.72	Dark	0.12	
2,520							0.02	
2,688							0.07	L5.0
3,024							0.10	L2.0
3,192							0.06	
3,360								L3.5
3,528							0.09	L5.0
TOST induction period (hours)	2,060		2,050		2,045		3,500+	

These data illustrate the greatly enhanced susceptibility to oxidation inhibitors of Oil C which was hydrogenated over the nickel-moly type catalyst. As would be expected, this superiority is especially evidenced at the higher concentration level of oxidation inhibitor.

It is claimed:

1. A method of producing a mineral oil of lubricating viscosity having enhanced susceptibility to oxidation inhibitors consisting essentially of subjecting a distillate mineral lubricating oil fraction to solvent extraction at a temperature of about 100 to 200° F. with a solvent selective for aromatic hydrocarbons, and at a solvent to oil volumetric ratio of about 1:1 to 2:1 to produce a raffinate of reduced aromatic content, solvent dewaxing said raffinate with a solvent consisting essentially of a mixture of an aromatic hydrocarbon of 6 to 8 carbon atoms and an alkyl ketone of 3 to 8 carbon atoms at a solvent to oil volumetric ratio of 0.5:1 to 2:1 and a temperature of from about −30° F. to 20° F. to yield a solvent dewaxed oil, and hydrotreating said dewaxed oil in the presence of a nickel-molybdenum-activated alumina catalyst at a temperature of from about 550 to 775° F. and a hydrogen partial pressure of about 800 to 5000 p.s.i.g.

2. The method of claim 1 wherein the hydrotreating is carried out at a temperature of about 625 to 725° F. and a weight hourly space velocity of about 0.5 to 2 WHSV.

3. The process of claim 2 wherein the catalyst contains from about 2 to 10 weight percent nickel and about 8 to 20 weight percent molybdenum.

4. The process of claim 3 wherein the nickel and molybdenum are present in the form of sulfides.

5. A lubricating composition consisting essentially of a mineral oil of lubricating viscosity prepared according to the method of claim 1 and small amounts of an oil-soluble alkylated phenol as an antioxidant.

6. The composition of claim 5 wherein the oxidation inhibitor is dibutyl para-cresol in an amount of about 0.7 to 3%.

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