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Panzer

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[54] LUBRICATING OIL COMPOSITIONS OF IMPROVED THERMAL STABILITY

[72] Inventor: **Jerome Panzer**, Roselle Park, N.J.

[73] Assignee: **Esso Research and Engineering Company**

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[58] **Field of Search** ..... 252/45, 47.5, 51.5 A

[56] **References Cited**

UNITED STATES PATENTS

2,312,750	3/1943	Cohen	252/45 X
2,337,473	12/1943	Knowles et al.	252/45 X
3,172,892	3/1965	Le Suer et al.	252/51.5 A
3,309,316	3/1967	McNinch	252/47.5
3,352,782	11/1967	Brasch	252/47.5
3,498,915	3/1970	Coleman	252/45 X

Primary Examiner—Daniel E. Wyman
Assistant Examiner—W. Cannon
Attorney—Pearlman and Stahl and Ernest V. Haines

[57] **ABSTRACT**

Mineral lubricating oil compositions are prepared containing oil-soluble additives for sludge control, having improved high temperature oxidation stability and thus permitting longer periods of service before it becomes necessary to drain the used oil and replace it with fresh oil. The novel additive mixture is prepared by reacting elemental sulfur with long chain (C_{16+}) oil-soluble olefinically unsaturated monomeric or polymeric hydrocarbons, e.g. polyisobutylene, and using such sulfurized compounds in conjunction with conventional ashless dispersants with or without using additional ashless dispersants which have previously been reacted with elemental sulfur. Many of the hydrocarbons used as starting materials, in their unsulfurized state, have heretofore been used as viscosity index improvers in lubricating oil compositions.

13 Claims, No Drawings

LUBRICATING OIL COMPOSITIONS OF IMPROVED THERMAL STABILITY

BACKGROUND OF THE INVENTION

The present invention relates to the use in mineral lubricating oil compositions of a combination of oil-soluble sulfurized olefinic compounds with the so-called ashless dispersants which are likewise oil-soluble and have been used in lubricating oil compositions for some years.

Numerous addition agents have heretofore been prepared for use in automotive mineral lubricating oils, including the so-called heavy duty oils which are also employed in railroad diesel engines and gas engines. The prior researchers have been successful in finding various types of oil-soluble organic compounds which exhibit specialized and specific properties of a beneficial nature when they are incorporated into these mineral lubricating oils. For many years now, organic compounds have been added in minor amounts to lubricating oils for the purpose of lowering their pour point, of improving their viscosity index, of affording increased resistance to oxidation, of imparting antiwear properties, of inhibiting sludge formation and of dispersing sludge when it is formed during use of the oils. The use of such additives at the present time enjoys widespread commercial acceptance. Good oxidation stability and good dispersing along with good detergency have become essential requirements for automotive lubricants. This is particularly so in connection with lubricating oils used in so-called heavy duty engines such as gas engines and railroad diesel engines. Additionally, the additives employed must necessarily be accepted from the standpoint of lack of wear or attack on the specialized types of bearings employed in internal combustion engines at the present time. Copper-lead-containing bearings are unusually susceptible to wear and corrosion problems. Suitable compounded oils must exhibit low corrosion and low bearing wear with respect to the specialized bearings which they contact in order to be acceptable commercially.

In the past, it has been proposed to add sulfurized polyisobutylene of relatively low molecular weight (boiling range 175°–260° C.) or of higher molecular weights, or derivatives thereof, to lubricating oils. See, for example, U.S. Pat. Nos. 2,279,688; 2,312,750; 2,330,858; 2,535,705 and 2,658,900. Also, it has been proposed in the past to employ sulfurized ashless dispersants in lubricating oils, see U.S. Pat. Nos. 3,390,086 and 3,309,316; whose disclosures are incorporated herein by reference. By the incorporation of elemental sulfur into a conventionally used olefinically unsaturated hydrocarbon, namely polyisobutylene, and by the incorporation of elemental sulfur into a conventional ashless dispersant, it was possible to increase the effectiveness of these materials for their intended purpose even in the case of lubricating oil compositions being subjected to extremely high temperatures during use. The thermal stability of the lubricating oils containing a combination of such additives, along with unsulfurized ashless dispersants, was greatly enhanced and resulted in the expended and more diversified, use of lubricating oils than when such oils contained either of these types of additives alone; because of the enhanced oxidation stability or resistance to oxidative degradation achieved by the introduction of the elemental sulfur into these compounds.

It has now been discovered that the use of sulfurized oil-soluble olefinically unsaturated long chain hydrocarbons in conjunction with a conventional ashless dispersant (with or without the use of a sulfurized ashless dispersant) gives rise to lubricating oils which have unusually high oxidation stability at high temperatures and which exhibit a heretofore unattainable degree of resistance to sludge formation and an excellent dispersion of the sludge that is formed. What this amounts to is that the versatility of lubricating oils as to their scope of use, where such oils contain this combination of additives, has been increased markedly because of the enhanced high temperature characteristics achieved by so compounding these oils. Another advantage lies in the fact that even when using

such compounded oils at lower temperatures or at temperatures ordinarily encountered in the automotive engines, the life of the oil is increased over that heretofore attainable and so such oils may be employed for longer periods of time necessitating fewer oil changes and longer engine running periods between changes. Whereas, heretofore, a heavy diesel engine operating under severe high temperature conditions would require an oil change after 1,500 hours of operation, because of oxidation breakdown of the oil and excessive sludge build-up due to high temperature conditions in the oil, it is now possible to increase the life of that same oil used under the same conditions by as much as 50 percent through the use of the combination of a sulfurized oil-soluble unsaturated hydrocarbon in combination with an ashless dispersant and, optionally, a sulfurized ashless dispersant.

The materials which may be treated with elemental sulfur or with sodium polysulfide, which is the chemical equivalent of elemental sulfur, are many and varied in number and constitute a great many of those oil-soluble unsaturated polymeric aliphatic hydrocarbon compounds possessing olefinic unsaturation which have heretofore customarily and conventionally been employed as viscosity index improvers in lubricating oils. It has now been discovered that the introduction into these olefinically unsaturated aliphatic hydrocarbon compounds, as well as into similar compounds not possessing V.I. improving properties, of elemental sulfur enhances their properties when used in lubricating oils. The ashless dispersants, used in combination, are well-known conventional and commercially available compounds. They may be employed in the form in which they are commercially available. They may be sulfurized, i.e. subjected to a reaction with elemental sulfur as described and claimed in the aforementioned U.S. Pat. No. 3,390,086 whose disclosure is incorporated hereinto by reference and used in conjunction with the conventional ashless dispersants of commerce.

Among the many varied types of olefinic unsaturated hydrocarbons which are used as starting compounds which are to be treated with elemental sulfur or its chemical equivalent such as sodium polysulfide are:

1. long chain (C_{16}–C_{30}) alpha monoolefin monomers or mixtures thereof;
2. homopolymers of C_3 to C_{18} alpha monoolefins;
3. copolymers of C_2 to C_{18} alpha monoolefins with different C_3 to C_{18} alpha monoolefins; and
4. terpolymers of three different monomers of (3) or of two different monomers (3) with a diolefin such as methylene norbornene or butadiene or with still a third alpha monoolefin.

Exemplary of the reactants that may be employed as starting materials are the following: (copolymers are shown thus: monomer - monomer) C_{18+} alpha olefin mixtures, octadecene-1, hexadecene-1, tetradecene-1, C_{16}–C_{18} alpha olefins, polypropylene, polyisobutylene, ethylene-propylene, ethylene-isobutylene, ethylene-propylene-isobutylene, ethylene-propylene-butadiene-1-3, n-octene-1-isobutylene, propylene-pentene-2, ethylene-propylene-n-dodecene, ethylene-isobutylene-n-decene, ethylene-propylene-1,4-hexadiene, ethylene-propylene-dicyclopentadiene, ethylene-propylene-methylene norbornene. The number average molecular weights of the polymers, copolymers, or terpolymers generally range between about 300 and about 150,000, preferably between about 900 and about 70,000, and they are soluble in lubricating oils. These polymeric products are plastic solids, waxy or elastomeric depending on their molecular weights. Their physical properties and appearance are not the criteria that determine their efficacy, when sulfurized, and used in lubricating oils. The more highly amorphous (non-crystalline) products are preferred.

In general, crystalline contents of less than 25 wt. percent in the polymers are desirable and when such polymers are sulfurized, their use in lubricating oils affords viscosity index improving properties as well as oxidative and sludge inhibiting properties to the oils.

The polymerization reactions used to produce the polymeric hydrocarbon products are all well known to the art and the polymers are well-known commercial articles sold on the open market. The polymeric hydrocarbons are formed by polymerizing, copolymerizing, or terpolymerizing the olefinic monomers using Friedel-Crafts type catalysts, the so-called metallo alkyl, or coordination catalysts, or the Ziegler type catalysts. The homopolymers, i.e. polyisobutylene, most generally are produced by using Friedel-Crafts type catalysts such as boron trifluoride or aluminum chloride at low temperatures. Representative U.S. Pats. disclosing such products and their methods of preparation are Nos. 2,239,501; 2,534,095; 2,781,410; and 2,825,721 whose disclosures are incorporated herein by reference. The copolymers and terpolymers are usually produced by the use of coordination of metallo alkyl type catalysts. Representative U.S. Pats. disclosing suitable starting materials of these types, which may be sulfurized, are: Nos. 2,691,647; 2,975,159; 2,933,480; 3,051,690; and 3,389,087 whose disclosures are incorporated herein by reference. See also Canadian Patent No. 718,417 and French Pat. No. 1,537,571.

The ashless sludge dispersants are conventionally used in lubricating oils and are produced by condensing primary or secondary aliphatic amines, such as polyalkylene polyamines, with one or more long chain (C_{40}–C_{250}) alkenyl substituted mono or dicarboxylic acids or anhydrides thereof. The alkenyl substituted dicarboxylic acid or anhydride is conventionally prepared and the final product, before condensation with the polyamine, has a number average molecular weight generally between about 700 and about 5,000, preferably between about 800 and about 2,000. Preferably, the alkenyl radical is derived from polyisobutylene or from a polypropylene. Alkenyl monocarboxylic acids for use in the present invention also will have molecular weights in the range of from about 700 to about 5,000, preferably between about 800 and about 2,000. The methods of preparation of the dicarboxylic acid materials are disclosed in U.S. Pat. No. 3,172,892, which disclosures are incorporated herein by reference.

The alkenyl monocarboxylic acids can be prepared by halogenating a polymer of a C_2 to C_5 mono-olefin such as polyethylene, polypropylene, or polyisobutylene, with sufficient halogen such as chlorine to provide one to two atoms of halogen per molecule of the olefin polymer, after which the halogenated polymer thus obtained is condensed with an alpha, beta-unsaturated aliphatic monocarboxylic acid of from three to eight carbon atoms, e.g. acrylic acid, crotonic acid, methacrylic acid, etc. Thus, chlorinated polyisobutylene when reacted with acrylic acid will provide polyisobutenyl propionic acid. This high molecular weight acid is then reacted with an aliphatic polyamine such as tetraethylene pentamine, diethylene triamine, octaethylene nonamine, or the like, to form an amide reaction product. The mole ratio of high molecular weight acid to polyamine can range from about 1:1 to about 5:1. See British Pat. No. 1,075,121.

The sulfurized derivatives, i.e. the foregoing amino condensation products reacted with elemental sulfur, are described in detail in U.S. Pat. No. 3,390,086, and an alternative method of preparing such sulfurized ashless dispersants is shown in U.S. Pat. No. 3,309,316. These patents are incorporated herein by reference. A specific dispersant which is especially useful is polyisobutenyl propionic acid condensed with tetraethylene pentamine or polyisobutenyl succinic anhydride condensed with tetraethylene pentamine. The sulfurization of these materials with elemental sulfur is also disclosed in U.S. Pat. No. 3,390,086.

The reaction conditions under which the monomeric or polymeric olefinically unsaturated aliphatic hydrocarbons are subjected to reaction with elemental sulfur, or with sodium polysulfide, generally involve the maintenance of temperatures between about 200° and about 500° F., preferably between about 300° and 450° F. for a time ranging between about 30 minutes and about 40 hours, preferably for between about 4 and about 12 hours. The relative amounts of sulfur reacted with the organic compounds may vary considerably but are generally between about 0.2 and about 200 moles of sulfur, preferably between about 1 and about 150 moles of sulfur per mole of olefinically unsaturated compound. This will result in a final product containing a combined sulfur content of between about 1.0 and about 10.0 wt. percent sulfur, preferably between about 1.5 and 7.5 wt. percent sulfur. Also the reaction may be carried out using reactants and reaction conditions shown in U.S. Pat. No. 3,390,086.

The product may also be prepared using a mineral lubricating oil as a reaction medium solvent or base in which the sulfurization reaction is carried out, in which case the final product constitutes a concentrate of the sulfurized olefinically unsaturated aliphatic hydrocarbon of between about 50 and about 80 percent concentration of the sulfurized compound in the base oil.

This is especially useful where the reactant to be sulfurized is normally solid but is oil-soluble also. The ashless dispersant may be added as an oil concentrate in the lubricating oil as a base oil concentrate of 50–70 percent active ingredient concentration.

The amount of the sulfurized olefinically unsaturated aliphatic hydrocarbon which is ultimately contained in the final compounded oil, is sufficient, as a minimum, to act as an antioxidant or oxidation inhibitor and at the same time, if the unsulfurized compound possesses viscosity index improving properties, is generally sufficient, in amount, to serve also as a conventional viscosity index improver. Generally this amount will range between about 0.05 and about 10.0 wt. percent based on the oil composition, preferably between about 0.1 and about 5.0 wt. percent, on the same basis. The ashless dispersant, and, optionally, sulfurized ashless dispersant likewise should be present in sufficient amount to impart to the final oil composition recognized beneficial sludge dispersing properties. This generally also amounts to between about 0.05 and about 10.0 wt. percent, preferably between about 0.1 and about 5.0 wt. percent, on the same basis as before stated.

The lubricating oils are preferably mineral lubricating oil fractions which are derived from naphthenic, paraffinic, aromatic, or mixed crude oils and which are customarily employed as automotive crankcase, diesel engine, gas engine, and heavy duty or railroad diesel engine, oils. Generally, they will have a viscosity at 210° F. of between about 40 and about 90 SUS (Saybolt Universal Seconds) and at 100° F. a viscosity of between about 150 and about 1,000 SUS. The viscosity indices of these oils will generally range between about 0 and about 100 depending upon the specific use to which the oils are to be put. In the case of oils employed in high speed, heavy duty diesel engines, oils of high viscosity indices are often preferred, i.e. of the order of 60–100 or higher, but usually railroad diesel engines employ lubricating oils having viscosities of between about 75 and about 80 SUS at 210° F. and of between about 800 and about 1,250 SUS at 100° F. with viscosity indices ranging between about 55 and about 80.

The final compounded lubricating oil compositions may also contain other conventional additives, in addition to the sulfurized viscosity index improvers, each in association with the ashless dispersant and, optionally, with the sulfurized ashless dispersants. These are conventional additives and they are designed to complement and supplement the properties in the final oil which are attainable through the use of the two types of additives herein described and which, in combined use, show the unexpected high temperature properties. Amounts similar to the amounts specified for the novel additives are likewise employed for the conventional additives such as corrosion inhibitors, (sorbitan monooleate), antioxidants, (N-phenyl alpha naphthylamine), pour point depressants, (unsulfurized wax alkylated naphthalene), viscosity index improvers (unsulfurized polyisobutylene or various polymethyl methacrylates, antiwear agents (the zinc salt of di(C_4–C alkyl)dithiophosphate), detergents (the alkaline earth metal salts of alkyl substituted phenol thioethers or sul-

fides), and dispersants (alkaline earth metal salts of petroleum sulfonic acids or of alkaryl sulfinic acids) and the like.

A number of routine tests were carried out on compounded oils containing the novel additives hereinbefore described on a comparative basis in order to illustrate the beneficial effect of the combined additives. These tests may be described as follows.

The additive compositions prepared in accordance with the following examples were placed into various mineral lubricating oil bases and were subjected to several types of tests in order to determine their stability at high temperature, as well as under conventional conditions, to inhibit the formation of sludge, to determine their oxidation stability ability, their ability to disperse sludge once it is formed and in general to determine their ability to withstand severe oxidative high temperature conditions. Several tests include a determination of their bearing corrosiveness as well. One or more of the following tests were employed.

1. The Sludge Inhibition Bench Test was employed. This involved the use of a sludge-containing used oil which was rendered free of solid sludge by centrifuging for one hour at 1,800 rpm. The supernatant oil was decanted from the insoluble sludge particles but the oil which was had been freed of solid sludge particles did contain oil-soluble sludge precursors which upon heating as applied in the test would tend to form additional oil-insoluble deposits of sludge. In a tared stainless steel centrifuging tube, 10 grams of supernatant used oil containing from 0.5 wt. percent to 5.0 wt. percent active ingredient to be tested was heated to 300° F. for 2 hours in a constant temperature oil bath. Following the heating, the tube was cooled and then centrifuged for one hour at 1,800 rpm. The supernatant oil was decanted again from the tube and any residual deposits of sludge were washed carefully with 99 percent n-pentane to remove all remaining oil. The weight of the solid sludge formed in the test was determined. A blank or comparative run was also run in which no additive was employed in the oil. A substantial decrease in the amount of sludge deposited as compared with the amount deposited in the case of the blank run indicates that the additive had a sludge inhibiting effect. In addition to an actual measurement, in milligrams, of the weight of the sludge so collected, a haze determination was carried out on the centrifuged supernatant oil. This is done by means of a nephelometer light diffraction reading. The lower the number obtained, the less haze because of the lesser number of particles present to scatter the light.

2. Another test employed in the case of some of the comparative runs is known as the Cyclic Temperature Sludge Test. It was carried out for a total number of hours, depending upon the particular test run, for a minimum of 105 hours and in some cases for a maximum of 168 hours. In order to evaluate the sludge handling ability of the additives in lubricating oil in this test, a Ford 6-cylinder engine was used which employed a standard carburetor. It was operated at a standard speed of 1,500 rpm ± 15 rpm under a constant load of 140 ± 2 footpounds of torque. In this test, the temperature of the oil in the crankcase was cyclically and sequentially raised and lowered during the period of total hours of running the test. The cold phase operation, i.e. the lower temperature, was maintained for a period of 5 hours, alternated with a hot phase operation in which the high temperature was maintained for 2 hours. The oil sump temperature in the cold phase was 150° F. ± 5° F. and the hot phase operation was 215° F. ± 5° F. This test was used to determine the oxidation stability and the sludge inhibiting and sludge dispersing tendencies of the novel additive or additives. The base oil employed in this test was free of other additives and would completely breakdown so much so that it was not possible to complete the 240 hours of the run. Even after 100 hours, the top groove fill was excessive and the P.M.-1 rating indicated an extremely dirty piston when using the base oil alone. Using the base oil alone, the test was not, and could not be, continued beyond 100 hours.

3. P In securing some of the following data a test known as the Falex Wear Test was employed. This involves the use of a conventional Falex Wear Test Machine which was operated with the test oils for 30 minutes over 500 pounds per square inch direct pressure, gauge, on a bearing having a rotating steel pin, which bearing was submerged in the test oil. At the end of this time, the steel pin used in the test was weighed in order to determine the amount of wear on the pin in milligrams of lost weight. This test was conducted for the purpose of measuring the amount of wear which the bearings would encounter under extremely severe conditions when operating in a bath of the test oil composition. Pin seizure or borderline pin seizure conditions are avoided, if possible, but if they do occur, the test oil is deemed to have failed in antiwear qualities.

4. Still a further type of test was employed in some instances in securing the data hereinafter presented. It is known as a CRC-L-38 Oil Oxidation Test and is designed to determine the bearing weight loss in milligrams obtained in operating conventional standard single cylinder CLR spark ignition engines. Using the test oil, the engine was run for 40 hours at a relatively high speed, i.e. 3,150 rpm at an oil temperature of about 190°-200° F., with the oil sump temperature being somewhere between 275° and 290° F. and at high load. This test determines, inter alia, the oxidative characteristics of the oil, the copper-lead bearing weight loss, and the corrosion which the bearings undergo using the test oil.

5. Still a further test involved in securing some of the following data is known as the gas engine detergency and cleanliness test. This involves the testing of compounded lubricating oils, under comparative conditions, in a Chevrolet gas engine of 6 cylinders and of 216.5 cubic inch displacement operating on natural gas and having a horsepower rating of 34 at 1,500 rpm. The engine operated at 2.5 percent excess oxygen in the exhaust in order to maximize nitrogen fixation and oil degradation. The test was conducted for a period of 96 hours using a paraffinic base oil containing no additives other than those specified in the following data. This amounted to an SAE 30-grade oil and had an overall viscosity at 100° F. of 540 SUS and at 210° F. of 66 SUS. The paraffinic base stock comprised 90 percent of a solvent neutral 450 SUS at 100° F. and 10 percent of a brightstock of similar characteristic with a viscosity of 150-160 SUS at 210° F. After running for a period of 96 hours, the piston and cylinder, valves, compression grooves, rings and piston undersides were inspected for varnish and sludge and the bearings sometimes were inspected for bearing weight loss, in milligrams. An overall demerit system was employed for inspection and the rating of the various portions of the engines was used in getting the overall merit rating. Zero rating represents a perfectly clean engine and an engine with a 10 rating represents the dirtiest sludge and varnish deposits that it is possible to obtain.

6. Still another test was carried out to determine the oxidation characteristics of the novel compounded lubricating oils. It is known as the Lubricant Stability Test and evaluates the compounded lubricating oils under accelerated oxidation conditions. It is a method designed primarily to evaluate the stability of the lubricating oil compositions under rather severe conditions of temperature (342° F.) for a period of 23 hours during which time the oil is contacted with copper-lead alloy bearing materials and air is bubbled through the test oil with stirring for this length of time. The air is bubbled in at the rate of about 2 cubic feet per hour and the stirrer in the oil is rotated at about 600 rpm. Fresh bearing metal specimens are inserted into the oil every 3 hours. Also, viscosity in Saybolt Universal Seconds at 100° F. is measured and the rate of oxidation of the oil is computed on the basis of the percent increase in viscosity after 23 hours as compared to the same oil viscosity measurement before the test is started. Bearing weight loss, in milligrams, is determined.

The following examples are illustrative of the character and nature of the invention but it is not intended that the invention be limited thereto.

EXAMPLE 1

A mixture of 2,490 grams of polyisobutylene having a number average molecular weight of about 900 was reacted with 480 grams of elemental sulfur at a temperature of about 400° F. for 24 hours and was thereafter filtered through a filter aid. The resulting product contained about 8.71 wt. percent of sulfur.

EXAMPLE 2

A mixture of 830 grams of the same polyisobutylene as used in Example 1 together with 160 grams of elemental sulfur was heated at 250° F. for 24 hours and filtered through a filter aid. The filtrate contained 2.69 wt. percent of sulfur in chemically combined form.

EXAMPLE 3

A mixture of 89.7 wt. percent of polyisobutylene of approximately the same molecular weight as that described in the preceding examples and approximately 10.3 wt. percent of elemental sulfur was heated at 400° F. for 12 hours and filtered. The filtrate product showed an analysis of chemically combined sulfur of about 5.2 wt. percent sulfur.

EXAMPLE 4

The same mixture as employed in Example 3 was heated at the same temperature as in Example 3 for about 20 hours and filtered through a filter aid. This showed a combined sulfur analysis of about 5.4 wt. percent.

Sulfurized products of the foregoing examples were incorporated into a heavy duty base lubricating oil commonly used in gas engines in varying amounts with and without the addition of conventional ashless dispersants and the compounded oil composition was subjected to various automotive lubrication tests, including test (5) previously mentioned, the results of which are set forth in Table I.

The base oil employed in securing the data shown in Table I was the oil blend (SAE–30 grade), previously described, which comprised 90 percent of solvent neutral paraffinic base stock having a viscosity of 450 SUS at 100° F. and 66 SUS at 210° F. plus 10 percent of a solvent neutral brightstock 150–160 SUS at 210° F.

TABLE I

Run No.	Additive	Additive, wt. percent	Lube stability [6] test, percent vis. increase at 100° F.	Cu-Pb bearing [6] wt. loss, mgs.	L–38 [4] bearing wt. loss, mgs.	Gas engine [5] overall demerit
1	None (base oil)	None	51	−285	>1,000	0.63
2	Example 1	5	17.7	+17	16	0.36
3	Example 1	3	15.0	+2	109	0.06
	PIBA-TEPA*	2				
4	Example 2	5	16.7	+18		
5	Example 3	4	18.0	−69	54	0.08
	PIBA-TEPA	3				
6	Example 4	4	14.8	−1	104	0.11
	PIBA-TEPA	3				

*PIBA–TEPA as used in the foregoing table is the conventional amide condensation product of about 2.8 moles of polyisobutenyl propionic acid with each mole of tetraethylene pentamine.

EXAMPLE 5

About 2,000 grams of polyisobutylene having a number average molecular weight of about 130,000, as a 20 percent concentration in a solvent neutral 150 base lubricating oil, was heated with 20 grams of elemental sulfur at a temperature of about 300° F. for 8 hours. The final product had a sulfur content of 1.08 wt. percent based on the weight of the polyisobutylene.

A base oil blend was prepared in the weight ratio of 9 parts of solvent neutral lubricating oil stock of 100 SUS at 100° F. viscosity which was admixed with each part of solvent neutral 450 SUS at 100° F. viscosity lubricating oil stock. This blend also contained about 1.2 percent of the zinc salt of di(C_4–C_5 alkyl)dithiophosphate, as an antiwear additive, and lesser but effective amounts of a commercially available overbased calcium alkaryl sulfonate and of a commercially available pour point depressant which was a 75–25 percent mixture of wax alkylated naphthalene and dilorol fumarate-vinyl acetate copolymer.

Cyclic Temperature Sludge Tests (2) were carried out as a series of comparative runs with all runs employing the above described base oil compounded as therein described. The test results were as follows:

TABLE II

Run No.	Additive, Wt. %	Hours 63	105	147	168
7	10.6 wt. % sulfurized polyisobutylene	5.4			
8	10.6 wt. % unsulfurized polyisobutylene plus 3.8 wt. % PIBSA/TEPA	9.23	5.5		
9	10.6 wt. % sulfurized polyisobutylene plus 3.8 wt. % PIBSA/TEPA	9.94	9.45	6.8	5.6
10	1.0 wt. % sulfurized polyisobutylene plus 10.0 wt. % unsulfurized polyisobutylene plus 3.8 wt. % PIBSA/TEPA	9.94	9.38	5.9	

*PIBSA/TEPA is the conventional amide condensation ashless dispersant produced in accordance with the teachings of U.S. Pat. No. 3,172,892.

The numbers in the foregoing Table give sludge ratings wherein 10 represents a perfectly clean engine and 0 represents the worst possible dirty engine. From these data, it is obvious that a beneficial synergistic sludge inhibition effect is achieved through the combined use of sulfurized polyisobutylene and a conventional ashless dispersant (Run 9).

A base oil blend was prepared of the same two lube oil stocks in the same weight ratios. The same additives, in the same amounts, were added to the blended base except that the dithiophosphate antiwear agent was omitted and 3.8 wt. percent of the ashless dispersant PIBSA/TEPA as the acetic acid addition salt (see U.S. Pat. No. 3,172,892) was added.

Comparative Falex Antiwear Tests (3) were carried out using this compounded base oil at 500 lbs. per square inch pressure for 30 minutes. The following data were obtained:

TABLE III

Run No.		(Mgs.) Bearing Weight Loss
11	Base oil + 10.6% unsulfurized polyisobutylene	Broken Pin
12	Same as Run 11 + 1.2% zinc	

	di (C_4-C_5 alkyl) dithiophosphate	5.5
13	Base oil + 10.6% sulfurized polyisobutylene (Example 5)	7.0

These data indicate that the product of Example 5 also exhibits substantial antiwear activity (Run 13) as an additional desired property even though it does not appear to have superior qualities in this regard when compared to the use of conventional commercially available antiwear agents (Run 12).

The sulfurized polyisobutylene of Example 5 was further comparatively tested in the Sludge Inhibition Test (1) wherein a used lubricating oil containing sludge precursors but free of suspended sludge was employed to determine the sludge inhibiting properties of the compound. The following test results were obtained:

TABLE IV

Run No.		Mgs. of Sludge Per 10 Grams Used Oil
14	Used Oil	12.0
15	0.4 wt. % PIBSA.TEPA.HAc* + Used Oil	3.5
16	Same as Run 15 + 1% polyisobutylene	3.4
17	Same as Run 15 + 1% sulfurized polyisobutylene (Example 5)	1.5

*Prepared according to U.S. Patent 3,172,892.

These data illustrate the sludge inhibiting synergism in using the combination of an ashless dispersant (PIBSA.TEPA. HAc) with sulfurized polyisobutylene (Run 17) in contrast to the use of the dispersant alone (Run 15) or the unsulfurized polyisobutylene (Run 16) of Example 5.

EXAMPLE 6

About 200 grams of ethylene/propylene copolymer having a number average molecular weight of about 100,000 was treated in a light lubricating oil serving as a solvent, with about 8 grams of elemental sulfur at a temperature of about 356° F. for 9 hours. After filtration to remove any unreacted sulfur the filtrate was found to contain 2.87 wt. percent of combined sulfur based upon the ethylene/propylene copolymer starting reactant.

Used lubricating oil containing sludge precursors but being free of undissolved sludge was subjected to the sludge inhibition test (1) under comparative conditions, in which 1 percent of the starting unsulfurized ethylene/propylene copolymer was used in one instance and 1 percent of the sulfurized ethylene/propylene copolymer was used in the other instance. The unsulfurized copolymer was found to have produced 20.1 milligrams of sludge per 10 grams of used oil while the sulfurized copolymer produced 20.3 milligrams of sludge on the same basis. However, the same two tests were repeated using the same amount of sulfurized and unsulfurized copolymer but in each case with 0.4 wt. percent of conventional ashless dispersant being present, namely the amide condensation product of polyisobutenyl succinic anhydride with tetraethylenepentamine. The sulfurized copolymer, in that combination, showed only 1.7 milligrams of sludge during the sludge inhibition test whereas the unsulfurized copolymer, in such combination, showed 3.2 milligrams of sludge. On a comparative basis, the same oil containing 0.4 wt. percent of the ashless dispersant but no copolymer additive, of either type, showed a final solid sludge formation of 3.5 milligrams per 10 grams of used oil.

EXAMPLE 7

A mixture of C_{20}^+ alpha monoolefins in the amount of about 200 grams was reacted with about 10 grams of sulfur at a temperature of about 176° F. for 12 hours. The final product contained about 4.61 wt. percent of combined sulfur. This material was subjected to the same sludge inhibition test (1) as the product of Example 6 employing a used lubricating oil, and the same comparative tests were run including the comparative test using the conventional ashless dispersant alone described in Example 6. The results were as follows:

TABLE V

	Sludge, Milligrams Per 10 Grams Used Oil
1% C_{20+} alpha olefins (sulfurized)	15.4
1% C_{20+} alpha olefins (unsulfurized)	15.1
1% C_{20+} alpha olefins (sulfurized) plus 0.4 wt. % ashless dispersant*	7.0
1% C_{20+} alpha olefins (unsulfurized) plus 0.4 wt. % ashless dispersant	10.1
0.4 wt. % ashless dispersant (alone)	9.8

*Same dispersant as used in Example 6.

EXAMPLE 8

A polyisobutylene of about 300 number average molecular weight in the amount of 300 grams was reacted with 32 grams of elemental sulfur at a temperature of about 355° F. for 8 hours. After stripping the product with nitrogen gas for 1 hour, the product was found to contain about 5.2 wt. percent of combined sulfur.

The same used oil was employed in the sludge inhibition test (1). The product of Example 8 was added to the used oil and the sludge inhibition test carried out. On the same comparative basis as described in the two preceding examples, the following results were obtained:

TABLE VI

	Sludge, Milligrams Per 10 Grams Used Oil
1% sulfurized polyisobutylene of Example 8	9.4
1% unsulfurized polyisobutylene (reactant of Example 8)	11.3
1% sulfurized polyisobutylene plus 0.4 wt. % conventional ashless dispersant as described in Example 6	1.4
1% unsulfurized polyisobutylene plus 0.4 wt. % ashless dispersant	2.7
0.4 wt. % ashless dispersant (alone)	2.8

EXAMPLE 9

Polyisobutylene having a number average molecular weight of about 900, in the amount of 500 grams, was reacted with 50 grams of elemental sulfur at a temperature of about 482° F. for about 6 hours. After stripping the reacted mixture for about 1 hour under nitrogen gas, the product was analyzed and found to contain 3.15 percent of combined sulfur.

Used lubricating oil containing sludge precursors was used as the base test oil for a comparative series of sludge inhibition tests (1) as previously described which gave the following results:

TABLE VII

	Sludge, Milligrams

	Per 10 Grams Used Oil
1 wt. % polyisobutylene (reactant of Example 9)	11.3
1 wt. % sulfurized polyisobutylene (Example 9 product)	11.3
2 wt. % unsulfurized polyisobutylene plus 0.4 wt. % ashless dispersant*	4.5
2 wt. % sulfurized polyisobutylene plus 0.4 wt. % conventional ashless dispersant	0.7
0.4 wt. % ashless dispersant (alone)	3.4

*Same dispersant as used in Examples 6–8.

From the above examples it is apparent that the combination of sulfurized olefinically unsaturated hydrocarbons and conventional ashless dispersants has a synergistic effect on the inhibition of oxidation inhibition of sludge formation, and a corrosion and wear protection of sensitive bearing materials.

The Lube Stability Test (5) data illustrate the effectiveness of the sulfurized materials as oxidation inhibitors and in reducing Cu-Pb bearing corrosion. The presence of ashless dispersants does not change this effectiveness (by itself the dispersant would provide no such protection), while the combination of the two types of additives provides a degree of engine cleanliness (gas engine test 5) that cannot be achieved by either alone.

The L–38 Test (4) data show that the sulfurized materials provide Cu-Pb bearing protection.

The Cyclic Temperature Sludge Test (2) demonstrates the ability of the combined additives to provide less sludge and varnish then can be obtained by either one alone. Results from this test correlate with passenger car engine performance. Reduction of wear in the Falex Test (3) is important because of its relationship to passenger car engine wear.

The Bench Sludge Inhibition Test (1) shows synergism and is important because its results correlate with the Cyclic Temperature Sludge Test (2).

What is desired to be secured by Letters Patent follows.

I claim:

1. A lubricating oil composition comprising a major proportion of a mineral lubricating oil,

a minor sludge inhibiting amount of at least one oil-soluble sulfurized hydrocarbon produced by sulfurizing an oil-soluble olefinically unsaturated hydrocarbon having a number average molecular weight between about 200 and about 150,000 and selected from the group consisting of monomeric alpha monoolefins of at least 16 carbon atoms per molecule; homopolymers of C_2–C_{18} alpha monoolefins; copolymers of C_2–C_{18} alpha monoolefin with a different C_3–C_{18} alpha monoolefin; and terpolymers of a C_2–C_{18} alpha monoolefin, a different C_3–C_{18} alpha monoolefin and a third monomer which is either a third and still different C_3–C_{18} alpha monoolefin or a C_4–C_{18} diolefin,

and a minor sludge dispersing amount of at least one oil-soluble ashless sludge dispersant selected from the group consisting of condensation products of aliphatic polyamines with long chain alkenyl aliphatic monocarboxylic acids, dicarboxylic acids and dicarboxylic acid anhydrides wherein the alkenyl radical has from about 40 to 250 carbon atoms.

2. A lubricating oil composition as in claim 1 wherein the amount of sulfurized hydrocarbon and the amount of ashless sludge dispersant are each between about 0.05 and about 10.0 wt. percent of the total oil composition.

3. A lubricating oil composition as in claim 1 wherein the hydrocarbon subjected to sulfurization is at least one C_{16}^+ monomeric alpha monoolefin.

4. A lubricating oil composition as in claim 3 wherein the hydrocarbon subjected to sulfurization is a mixture of C_{20}^+ monoolefin monomers.

5. A lubricating oil composition as in claim 1 wherein the hydrocarbon subjected to sulfurization is at least one homopolymer of a C_2–C_{18} alpha monoolefin.

6. A lubricating oil composition as in claim 5 wherein the hydrocarbon subjected to sulfurization is a polyisobutylene.

7. A lubricating oil composition as in claim 1 wherein the hydrocarbon subjected to sulfurization is at least one copolymer of a C_2–C_{18} alpha monoolefin with a different C_3–C_{18} alpha monoolefin.

8. A lubricating oil composition as in claim 7 wherein the hydrocarbon subjected to sulfurization is a copolymer of ethylene and propylene.

9. A lubricating oil composition as in claim 1 wherein the hydrocarbon subjected to sulfurization is at least one terpolymer of a C_2–C_{18} alpha monoolefin, a different C_3–C_{18} alpha monoolefin and a third monomer which is either a third and still different C_3–C_{18} alpha monoolefin or a C_4–C_{18} diolefin.

10. A lubricating oil composition as in claim 1 which also contains a minor sludge inhibiting amount of at least one sulfurized ashless dispersant wherein said ashless dispersant is as set forth in claim 4.

11. A lubricating oil composition as in claim 1 wherein the alkenyl radical is derived from polyisobutylene.

12. A lubricating oil composition as in claim 1 wherein said condensation product is obtained from tetraethylene pentamine and polyisobutenyl succinic anhydride.

13. A lubricating oil composition as in claim 1 wherein said condensation product is obtained from tetraethylene pentamine and polyisobutenyl propionic acid.

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