

[54] LUBRICATING OIL COMPOSITION

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[58] Field of Search **252/32.7 E, 33, 33.4, 45**

[56] **References Cited**

UNITED STATES PATENTS

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3,377,281	4/1968	Gower.....	252/32.7 E
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[57]

ABSTRACT

Lubricating oil composition comprising a mineral oil of lubricating viscosity containing in combination a basic barium sulfonate, a zinc dialkyldithiophosphate, an estolide of 12-hydroxystearic acid, a sulfurized triisobutylene, an alkylated diphenylamine, a triaryl phosphate ester and an alkyl phosphorus acid ester.

4 Claims, No Drawings

LUBRICATING OIL COMPOSITION

BACKGROUND OF THE INVENTION

Conventional load carrying lubricating oil compositions used in tractors and other heavy equipment generally have consisted of a blended lubricating oil composition comprising a mineral oil of lubricating viscosity and a variety of additives to provide an effective level of extreme pressure, anti-wear, dispersant, detergent and corrosion inhibiting properties. Formerly, many of these lubricants designed for severe load carrying service incorporated sulfurized sperm oil or a derivative of sperm oil as an essential additive to meet the extreme pressure and anti-wear requirements of heavy vehicle service.

The use of sperm oil or, more particularly, sperm oil derivatives in commercial applications, such as in a lubricating oil composition has recently been barred by statute. The wide use of sperm oil and its derivatives in heavy duty lubricating oils attests to its unique effectiveness in these applications. The unavailability of this material has resulted in the initiation of numerous investigations to find a suitable substitute for use in the formulation of heavy duty lubricants.

Among the commercial substitutes for sperm oil derivatives are sulfurized fatty oils, sulfurized methyl esters of fatty acids and mixtures of the foregoing, esters of sulfurized fatty acids with an alcohol other than methyl alcohol and mixtures of sulfurized fatty oils with sulfurized olefins. Many of these substitutes have not been entirely satisfactory. In general, the newly developed lubricants containing a substitute for the sperm oil component suffered from one or more disadvantages including thermal instability, poor oil solubility, poor low temperature properties, and poor extreme pressure properties. In addition, certain of the sperm oil substitutes were considered responsible for the formation of significant sludge residues in the lubricant composition further detracting from their usefulness.

DESCRIPTION OF THE PRIOR ART

U.S. Pat. No. 3,673,090 discloses a sulfurized triisobutylene and its usefulness as an additive in mineral lubricating oils.

U.S. Pat. No. 2,877,181 discloses an estolide of 12-hydroxystearic acid as a stabilizer in a calcium fatty acid base grease.

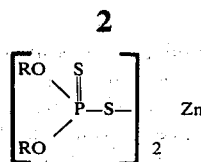
U.S. Pat. No. 3,732,167 discloses a zinc dialkyldithiophosphate as a corrosion inhibitor and a dialkyl diphenylamine oxidation inhibitor in a mineral lubricating oil composition.

U.S. Pat. No. 3,242,079 discloses a basic alkaline earth metal sulfonate and its usefulness as a detergent in a mineral lubricating oil composition.

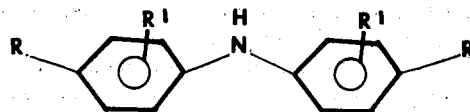
The reference disclosures on the individual components employed in the lubricant of the invention noted above are incorporated in the disclosure of this invention.

SUMMARY OF THE INVENTION

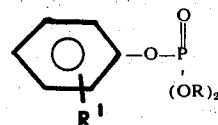
In its broadest aspects, the lubricant of the invention comprises a major portion of a mineral base oil of lubricating viscosity containing in combination 1 to 2.5 percent of a basic barium sulfonate, 0.1 to 0.5 percent of a zinc dialkyldithiophosphate represented by the formula:



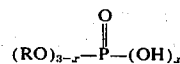
in which R is an aliphatic hydrocarbon radical having from about 1 to 8 carbon atoms, from about 0.5 to 1.5 percent of an estolide of 12-hydroxystearic acid, from about 0.1 to 1 percent of a sulfurized triisobutylene containing from about 30 to 40 percent sulfur, from about 0.1 to 1 percent of a dialkyldiphenylamine represented by the formula:



in which R is an alkyl radical having from 4 to 16 carbon atoms and R' is hydrogen or an alkyl radical having from 1 to 4 carbon atoms, from about 1 to 2 percent of a triarylphosphate represented by the formula:



in which R is an aryl or alkaryl radical having from 6 to 10 carbon atoms and R' is an alkyl radical having from 1 to 3 carbon atoms, and from about 0.1 to 1 percent of an alkyl phosphorus acid ester represented by the formula:



in which R is an alkyl radical having from 10 to 16 carbon atoms and x has the value of 1 or 2.

The effectiveness of the lubricating oil composition of the invention appears to be based on critical combination of additive components. Similar formulated lubricating oil compositions were found to be relatively ineffective or unsatisfactory as a lubricant because of excessive corrosion.

Broadly, the base oil employed in the lubricant of the invention is derived from petroleum and is a hydrocarbon mineral oil of lubricating viscosity. In general, the oil can be a paraffin base, naphthene base or mixed paraffin-naphthene base distillate or residual oil. This base oil has a SUS viscosity at 100°F. between about 50 and 1,000. The base oil comprises a major portion of the lubricant composition, normally amounting to at least 85 percent of the lubricant composition. In a preferred embodiment, the base oil comprises at least 90 percent of the lubricant with the balance consisting of the additive components.

In a preferred aspect of the invention, the base oil comprises a mixture of oils. According to this embodiment, a portion of the base oil will comprise a paraffin base distillate fraction which has been subjected to solvent refining to improve its lubricity and viscosity tem-

perature relationship as well as solvent dewaxing to remove waxy components and to improve the pour of the oil. This paraffin base distillate will have an SUS viscosity at 100°F. from about 70 to 300. When a mixture of base oils is employed in the lubricant composition, as in this embodiment, the paraffin base oil is employed in a concentration from about 40 to 60 percent.

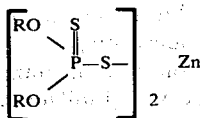
The second component of the base oil mixture is a refined residual fraction which imparts a high flash point and lubricity to the base oil. This fraction comprises a paraffin base residuum which has been propane deasphalted and subjected to centrifuge dewaxing and which has an SUS at 210°F. below about 250, generally in the range of 150 to 180 SUS at 210°F. The refined residual fraction can constitute from about 30 to 50 weight percent of the lubricant composition.

The basic barium sulfonate component of the lubricant of the invention is a barium salt of a long chain sulfonic acid. The acid should contain a minimum of at least 12 aliphatic carbon atoms in the molecule. Suitable sulfonic acids include the aliphatic and aromatic sulfonic acids containing from 12 to 24 carbon atoms. They are illustrated by petroleum sulfonic acids or the acids obtained by treating an alkylated aromatic hydrocarbon with a sulfonating agent, for example, chlorosulfonic acid, sulfur trioxide, oleum, sulfuric acid or sulfur dioxide and chlorine. Specific examples of the sulfonic acids are mahogany acid, dodecyl benzene sulfonic acid, didodecylbenzene sulfonic acid, dinonylbenzene sulfonic acid, octadecyl sulfonic acids and the like.

An important aspect of the barium sulfonate additive is that it is a basic material having a metal ratio of at least 3. In general, the metal weight ratio for the effective basic barium sulfonate is from about 3 to about 6. It is prepared by carbonating a substantially anhydrous mixture of the acid with at least about 3 chemical equivalents of barium metal base per equivalent of acid in the presence of promoting agent. The metal base can be barium oxide, barium bicarbonate or their equivalents and the promoting agent can be alcohol, a phenol, a mercaptan, an amine or the like. The basic barium sulfonates and their method of preparation are disclosed in U.S. Pat. No. 3,242,079.

The basic barium sulfonate of the invention normally contains from about 10 to 15 weight percent, preferably 12 to 14 percent of barium metal calculated as barium oxide.

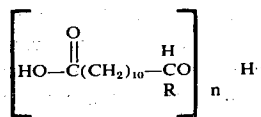
The essential zinc dithiophosphate component of the lubricating oil is represented by the formula:



in which R is a hydrocarbyl radical having from 1 to 8 carbon atoms. The preferred zinc dithiophosphates are those in which R represents an alkyl radical having from 1 to 8 carbon atoms. Examples of suitable compounds include zinc isobutyl 2-ethylhexyl dithiophosphate, zinc di-(2-ethyl-hexyl) dithiophosphate, zinc isoamyl 2-ethylhexyl dithiophosphate. In general, these compounds are employed in the oil composition in a concentration ranging from about 0.1 to 3.0 percent with the preferred concentration ranging from about 0.5 to 1.5 percent. The preparation of these com-

pounds from the reaction of a suitable alcohol or mixture of alcohols with phosphorus pentasulfide is well known.

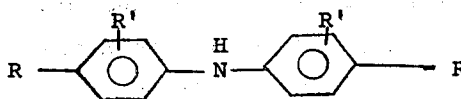
The essential estolide of 12-hydroxy stearic acid is represented by the formula:



wherein R is an alkyl group 2 to 6 carbon atoms and n is an integer having a value of 2 to 12. The estolides are formed by heat treatment of 12-hydroxy stearic acid at temperatures between 200° and 300°F. and subsequent extraction of the estolides from the heat-treated hydroxy stearic acid with an aliphatic hydrocarbon solvent such as hexane or pentane. The preparation of this material is disclosed in detail in U.S. Pat. No. 2,877,181.

The sulfurized triisobutylene component of the lubricant of the invention is prepared by contacting triisobutylene with sulfur at a temperature between about 360° and 500°F. under a pressure of between about 0 and 15 psig utilizing a mole ratio of triisobutylene to sulfur of between 1:4 and 1:2.5 while blowing the reaction mixture with an inert gas during at least a portion of said contacting and continuing the reaction until the free sulfur in the final reaction mixture is less than about 0.3 weight percent and recovering the sulfurized triisobutylene from the reaction mixture. The sulfurized triisobutylene so prepared is characterized by a sulfur content of from about 30 to 40 weight percent sulfur. This additive component is employed in the lubricant at a concentration ranging from about 0.1 to 1 weight percent.

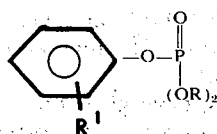
The alkylated diphenylamine component of the lubricating oil composition is represented by the formula:



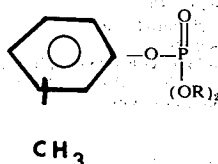
in which R is an alkyl radical having from 4 to 16 carbon atoms and R' is hydrogen or an alkyl radical having from 1 to 4 carbon atoms. More preferred compounds are those in which R is a tertiary alkyl hydrocarbon radical having from 6 to 12 carbon atoms. Examples of suitable compounds include 2,2'-diethyl, 4,4'-tert. dioctyldiphenylamine, 2,2'-diethyl, 4,4'-tert. dioctyldiphenylamine, 2,2'-diethyl-4-tert. octyldiphenylamine, 2,2'-dimethyl-4,4'-tert. dioctyldiphenylamine, 2,5-diethyl, 4,4'-tert.-dihexyldiphenylamine, 2,2,2',2'-tetraethyl, 4,4'-tert. didodecyldiphenylamine and 2,2'-dipropyl-4,4'-tert. dibutyldiphenylamine. Mixtures of the foregoing compounds can be employed with equal effectiveness. The alkylated diphenylamine is normally employed in the oil composition at a concentration ranging from about 0.1 to 2.5 percent weight percent based on the weight of the lubricating oil composition. A preferred concentration is from about 0.25 to 1.0 percent.

The essential triarylphosphate component of the lubricant of the invention is represented by the formula:

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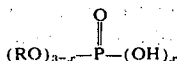


in which R is an aryl or an alkaryl radical having from 6 to 10 carbon atoms and R' is an alkyl radical having from 1 to 3 carbon atoms. The preferred compounds are those in which R is an aryl radical and, more particularly, a phenyl radical. A preferred species of the triaryl phosphate is cresyldiphenyl phosphate corresponding to the formula:



The triarylphosphate component of the lubricant is employed at a concentration from about 1 to 2 weight percent. Highly effective results are realized employing concentration of from about 1.25 to 1.6 percent.

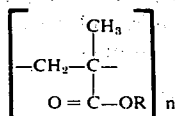
The final essential component of the lubricant of the invention is a mono or dialkyl ester of phosphoric acid. This additive component is represented by the formula:



in which R is an alkyl radical having from 10 to 16 carbon atoms and x has the value of 1 or 2. R is preferably a straight chain aliphatic hydrocarbon radical having from 12 to 14 carbon atoms. This additive component may consist of within the prescribed formula. Particularly effective compounds are the mono- and didodecyl esters of phosphoric acid.

The mono and dialkyl esters of phosphoric acid are employed in the lubricant composition at a concentration ranging from about 0.1 to 1 percent by weight. The preferred concentration of this additive component is an amount from about 0.25 to 0.65 weight percent.

An optional component of the lubricant of the invention for the purpose of improving the pour point of the lubricant is a methacrylate ester polymer having the formula:



wherein R is an alkyl group, a dialkyl aminoalkyl group or a mixture of such groups containing from 1 to 20 carbon atoms and n is a member providing a molecular weight of the polymer in the range from 25,000 to 1,250,000 and preferably from 35,000 to 200,000. Various methacrylate ester polymers of this type are known which impart a lower pour to the lubricant. A

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very effective material of this type is a copolymer of the lower C₄—C₁₄ alkyl methacrylate esters. A commercial methacrylate copolymer of this type corresponds to the formula in which R represents about 32 percent lauryl, 28 percent butyl, 26 percent stearyl and 14 percent hexyl groups and having a molecular weight above 50,000. Another commercial methacrylate copolymer consists of about 75 weight percent Neodol 25 methacrylate and about 25 weight percent Alfol 1620 methacrylate. The methacrylate ester copolymer is employed in the base oil in a proportion ranging from about 0.2 to 5 percent by weight preferably from 0.5 to 1.0 weight percent based upon the oil composition in order to impart the desired pour point. It is understood that other methacrylate ester polymers of the foregoing type can be employed.

An anti-foam agent is optionally employed in the lubricant of the invention. For this purpose, a silicone fluid of high viscosity, such as a dimethyl silicone polymer having a kinematic viscosity of 25°C. of about 1,000 centistokes and above is preferably employed. A very satisfactory anti-foam agent for this purpose is prepared by diluting 10 grams of a dimethyl silicone polymer (100,000 centistokes at 25°C.) with kerosene to provide a solution of 100 cubic centimeters. From 0.005 to 0.025 percent by weight of this concentrate is generally employed in the hydraulic fluid to provide from 50 to 200 parts per million of the silicone polymer based on the hydraulic fluid composition.

A highly effective lubricant of the invention consisted of about 52.6% of a paraffinic mineral oil having an SUS viscosity at 100°F. of about 100, 40.8% of a residual oil having an SUS viscosity at 210°F. of about 160, 1.9% of a basic barium sulfonate characterized by containing about 13% barium, about 0.3% of a zinc dialkyl dithiophosphate in which the alkyl radicals are a mixture of isopropyl and mixed C₄ to C₈ alkyl radicals, about 0.9% of an estolide of 12-hydroxy stearic acid having a neutralization no. below 40 and a hydroxyl number below 25, about 0.5% of sulfurized triisobutylene containing about 36% sulfur, about 0.5% of diethyl di-tert. octyl diphenylamine, about 1.4% cresyldiphenylphosphate, about 0.4% of a mixture of mono and didodecyl esters of phosphoric acid, about 0.7% of a copolymer of lauryl methacrylate and stearyl methacrylate and 150 parts per million of a silicone polymer solution.

Analysis of the foregoing formulated lubricating oil composition show that it contains 0.31 Wt. % barium, 0.27 wt. % phosphorus, 0.46 Wt. % sulfur and 0.046 Wt. % zinc.

The following inspecting values were obtained on this lubricating oil composition:

Gravity, °API	26.9
Fire/Flash COC, °F.	460/440
Kin. Vis, cs, 100°F. (SUS)	85.2 (395)
210°F. (SUS)	10.02 (59.3)
Brookfield Vis, cps 0°F.	6,710
VI	107
Pour, °F. -35	
Aniline Point, °F.	226

The lubricating oil composition of the foregoing example was tested for its oxidation stability and its load carrying and anti-wear properties in the Oxidation Stability Test, Falex BJ 1-1 Test, Timken OK Test, Timken Wear Test and the 4-Ball Wear Test.

The Timken Wear Test is conducted by rotating a hardened and ground flat steel ring mounted on a spindle against a hardened and ground flat steel test block. A stream of the lubricant to be tested is applied over the line of contact between the ring and the test block while the tester is operated at bearing load for 6 hours. The load is obtained by applying a weight of 10 lbs. to the weight platform. Determinations are made from the appearance of the test block surface at the end of the run. At the end of this time, the total weight loss of the block and cup is determined. The contact pressure in psi (pounds per square inch) is determined from the scar diameter. The oil is rejected if the weight loss is greater than 1 mg. and the contact pressure is less than 7,000 psi.

The 4-Ball Wear Test for determining the anti-wear performance of a lubricant is conducted using equipment described in ASTM specification D2266. Test conditions are given in Ford. Spec. M2C134A. This test is conducted by clamping three steel balls in a cup filled with the lubricant being tested. A fourth steel ball held by a chuck which is motor driven is positioned to rotate against the fixed lower balls. On completion of the test, the scar diameter on the lower three balls is measured and compared to the specification standard for this test.

The Falex E.P. Test is conducted in accordance with Ford specification M2C134A, Ford Method BJ 1-1. According to this test, a one quarter inch diameter steel pin (Falex No. 8 Steel) in a drill press type device (Falex Tester) is rotated at 290 rpm within bearing surfaces formed into test blocks (Falex V-shape 96° blocks). The blocks are self-aligning in recesses in the lever arms of the load applying mechanism. The test is conducted at ambient temperatures using 16 ml. of the oil being tested. The load is increased in 250 lb. increments over the 500 lb. initial face load and maintained at each step for 1 minute. Inability to maintain the applied load for 1 minute indicates lubricant failure. The Falex Wear Teeth is a measure gotten in conjunction with the E.P. measurement of pin and block wear and relates to additional load applied to the pin to maintain a prescribed load step. Eighteen teeth are equivalent to 0.001 inches of wear.

The Oxidation Stability Test or "oven test" is conducted according to Ford specification M2C134A. According to this test, 200 ml. of oil are measured into a 400 ml. tall-form beaker. The sample is placed into an electric oven and maintained there for 100 hours at a temperature of $300^{\circ} \pm 5^{\circ}\text{F}$. At the end of this time, 150 ml. of the oil are decanted from the beaker and subjected to a viscosity determination at 210°F . The presence of any sludge formation in the treated oil is also noted.

The Timken E.P. Test is run similar to the Timken Wear Test except that incremental 10 lb. loads are applied for 10 minutes for each load increase using new test specimens at each load until a scoring (failure) occurs. This is evidenced by furrowing of the wear track on the test block. At this point, the load is decreased 5 lbs., a new test piece is used and the OK value determined.

The MHL and Weld Point determination is described in ASTM D-2783. The tester is operated with one steel ball under load rotating against three steel balls held stationary in the form of a cradle. The rotating speed is 1770 ± 60 rpm. The lubricating fluid is brought to

temperature ($65 - 95^{\circ}\text{F}$.) and then subjected to a series of tests of 10 second duration at increasing loads until welding occurs.

The following table gives the composition and test results for a lubricating oil composition of the invention:

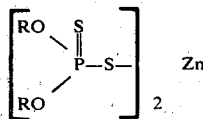
TABLE I

Lubricant Composition, wt. %	
Paraffinic Base Oil, S.U.S. Vis. at 100°F : 100	52.6
Residual Oil, S.U.S. Vis. at 210°F : 158.0	40.8
Basic barium sulfonate, TBN 52	1.9
Zinc isopropyl and mixed $\text{C}_4\text{-C}_8$ alkyl dithiophosphates	0.3
Estolide of 12-hydroxy stearic acid	0.9
Sulfurized triisobutylene 33% S	0.5
Diethyl-tert.-dioctyl diphenylamine	0.5
Cresyldiphenyl phosphate	1.4
Mixed mono- and didodecyl hydrogen phosphate	0.4
Copolymer of lauryl and stearyl methacrylate	0.7
Dimethylsilicone Solution p.p.m.	150
Test Results	
Oxid. Stab. 100 hr./ 300°F .	0.9
Vis. at 210°F ., % Increase	None
Sludge	2,250/2,750
Falex BJ 1-1, lbs.	23.40
Wear Teeth	50
Timken OK, lbs.	0.45
4-Ball Wear, scar. dia., mm	0.44
1 hr./40 kg./ 200°F ./1800 rpm	
2 hr./40 kg./ 200°F ./600 rpm	
Timken Wear Test 6hr./10 lbs. mg. wt. loss	none
psi at 15 lbs.	12,442
MHL (Load Wear Index)	45 Kg.
Incipient Seizure Point	126 Kg.
Weld Load	224 Kg.

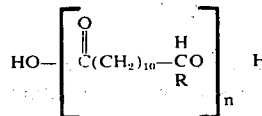
The lubricant of the invention exhibited surprising and unexpected effectiveness in passing the extreme pressure and anti-wear requirements of heavy vehicle service in the absence of any sulfurized sperm oil additive component while maintaining a high level of oxidation stability under severe conditions.

We claim:

1. A lubricating oil composition comprising a major portion of a mineral oil of lubricating viscosity containing from about 1 to 2.5 weight percent of a basic barium sulfonate having a metal weight ratio from about 3 to 6, from about 0.1 to 0.5 weight percent of a zinc dialkyl dithiophosphate represented by the formula:

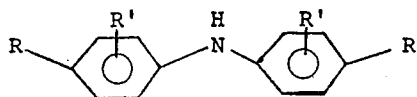


in which R is an aliphatic hydrocarbon radical having from about 1 to 8 carbon atoms, from about 0.5 to 1.5 weight percent of an estolide of 12-hydroxystearic acid represented by the formula:

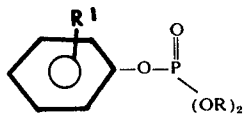


in which R is an alkyl group having from 2 to 6 carbon atoms and n is an integer having a value of 2 to 12, from about 0.1 to 1 weight percent of a sulfurized triisobutylene containing from about 30 to 40 weight percent sul-

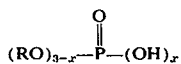
fur, from about 0.1 to 1 weight percent of an alkylated diphenylamine represented by the formula:



in which R is an alkyl radical having from about 4 to 16 carbon atoms and R' is hydrogen or an alkyl radical having from 1 to 4 carbon atoms, from about 1 to 2 weight percent of a triarylphosphate represented by the formula:



in which R is an aryl or an alkaryl radical having from 6 to 10 carbon atoms, and from about 0.1 to 1.0 weight percent of an alkyl phosphorus acid ester represented by the formula:



in which R is an alkyl radical having from 10 to 16 carbon atoms and x has a value of 1 or 2.

2. A composition according to claim 1 in which said mineral oil has an SUS at 100°F. from about 50 to 1,000.

3. A composition according to claim 1 in which about 40 to 60 percent of said composition consists of a paraffin base distillate having an SUS viscosity at 100°F. from about 70 to 300 and about 30 to 50 percent of said composition consists of a refined residual fraction having an SUS at 210°F. below about 250.

4. A composition according to claim 1 in which said basic barium sulfonate is a carbon dioxide neutralized basic barium sulfonate having a barium content of about 12.5 to 13.5 percent, said zinc dialkyldithiophosphate is zinc isopropyl-mixed C₄ to C₈ alkyl dithiophosphate, said estolide is the estolide of 12-hydroxy stearic acid, said sulfurized triisobutylene has from 33 to 38 percent sulfur, said alkylated diphenylamine is 2,2'-diethyl-4,4'-dioctyldiphenylamine, said triarylphosphate is cresyldiphenylphosphate and said alkyl phosphorus acid ester is monolauryl dihydrogen phosphate.

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