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(71) Applicant: Infineum International Limited
Abingdon, Oxfordshire OX13 6BB (GB)

(72) Inventors:
- Noles, Joe R.
Belle Mead NJ 08502 (US)
- Lin, Wangkan
Bridgewater NJ 08807 (US)
- Hartley, Rolfe John
Rockaway NJ 07866 (US)

(74) Representative: Arunasalam, Velautha-Cumaran
Infineum UK Limited
P.O. Box 1
Milton Hill
Abingdon, Oxfordshire OX13 6BB (GB)

(54) Lubricating oil composition

(57) Lubricating oil compositions containing a major amount of oil of lubricating viscosity, an oil soluble molybdenum compound in an amount providing the composition with from 0.001 to 0.1 mass % molybdenum, an oil soluble copper compound in an amount providing the composition with from 0.001 to 0.02 mass % copper to said composition, and an amount of metal hydrocarbyl dithiophosphate providing the composition with from 100 to 550 ppm phosphorus.

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Description

[0001] The present invention relates to lubricating oil compositions. More particularly, the present invention relates to lubricating oil compositions exhibiting improved antioxidant properties with reduced phosphorus and sulfur content.

BACKGROUND OF THE INVENTION

[0002] Lubricating oil compositions used to lubricate internal combustion engines contain base oil of lubricating viscosity, or a mixture of such oils, and additives used to improve the performance characteristics of the oil. For example, additives are used to improve detergency, reduce engine wear, to provide stability against heat and oxidation, to reduce oil consumption, to inhibit corrosion, to act as a dispersant, and reduce friction loss. Some additives provide multiple benefits, such as a dispersant/viscosity modifier. Other additives, while improving one characteristic of the lubricating oil, have an adverse effect on other characteristics. Thus, to provide a lubricating oil having optimal overall performance, it is necessary to characterize and understand all the effects of the various additives available, and carefully balance the additive content of the lubricant.

[0003] To provide improved low temperature valve train wear performance, conventional lubricants are formulated with an antiwear additive. Metal hydrocarbyl dithiophosphates, particularly zinc dialkyldithiophosphates (ZDDP), are the primary antiwear additive used in lubricating oils for internal combustion engines. ZDDP provides excellent wear protection at a comparatively low cost and also functions as an antioxidant. However, there is some evidence that phosphorus in lubricants can shorten the effective life of automotive emission catalysts. Accordingly, industry has limited the amount of phosphorus that lubricants can contain. The proposed category (ILSAC GF-4) is expected to require not more than 0.08 wt. % P and 0.5 wt. % S in the finished oil, and it is expected that future categories will require that the phosphorus content of lubricants be further reduced to below 0.06 wt. %.

[0004] U.S. Patent Nos. 5,346,635 and 5,439,605 describe lubricating oils completely free of phosphorus-containing antiwear additives containing a complex blend of ashless friction reducers, ashless antiwear/extreme pressure additives, antioxidants, metal detergents and polymeric viscosity modifiers and flow improvers, which compositions purportedly provide acceptable properties. These compositions may also contain a molybdenum-containing additive, as a friction modifier.

[0005] Each of WO 96/37,582 and EP 0 855 437 describes lubricating oil formulations that contain, in addition to other specified and required additives, an amount of ZDDP that may provide 600 ppm or less of phosphorus, together with a molybdenum-based friction modifier.

[0006] It has been proposed in many patents and articles (for example, U.S. Patent No. 4,164,473; 4,176,073; 4,176,074; 4,192,757; 4,248,720; 4,201,683; 4,289,635; and 4,479,883) that oil soluble molybdenum compounds are useful as lubricant additives. In particular, molybdenum compounds provide enhanced fuel economy in gasoline or diesel fueled engines (spark- and compression-ignited engines, respectively), including both short and long term fuel economy (i.e. fuel economy retention properties).

[0007] Oil soluble copper compounds are known to be effective antioxidants, as described in U.S. Patent No. 4,867,890.

[0008] It is desirable to formulate reduced phosphorus lubricating oils providing acceptable antioxidative properties, without the use of substantial amounts of relatively expensive ashless (metal-free) antioxidants.

SUMMARY OF THE INVENTION

[0009] In accordance with this invention, there is provided a lubricating oil composition comprising a major amount of oil of lubricating viscosity, an oil soluble molybdenum compound in an amount sufficient to provide the composition with 0.001 to 0.10 mass % of molybdenum; and an oil soluble copper compound in an amount providing the composition with from about 0.001 to 0.02 mass % copper, which composition contains an amount of metal hydrocarbyl dithiophosphate, such as ZDDP, that introduces from 100 ppm to 550 ppm of phosphorus to the lubricating oil composition.

[0010] Preferably, the lubricating oil composition contains no more than 0.5 wt. % of sulfur.

[0011] Preferably, the lubricating oil composition is substantially free (less than about 1 wt. %, preferably less than 0.5 wt. %, more preferably 0 to 0.25 wt. %) of ashless antioxidant.

[0012] Also preferably, the oil of lubricating viscosity has a viscosity of between about 4.0 mm^2/sec and 5.5 mm^2/sec at 100°C and/or the lubricating oil composition (the fully formulated oil) has a Noack volatility of no more than 15 wt. %, such as 8 to 13 wt. %.

[0013] In, an embodiment, the lubricating oil composition of the present invention is a SAE 10W-X, SAE 5W-X, or SAE 0W-X composition, wherein X represents 20, 30 and 40, preferably 5W-X or 0W-X.

[0014] The present invention is based on the discovery that the combination of molybdenum compound and copper compound, in lubricating oil compositions formulated with relatively low amounts of ZDDP, provides an unexpected cooperative antioxidative effect.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0015] To provide a low cost, commercially acceptable product providing excellent overall properties, especially oxidation resistance, the lubricating oil compositions of the present invention comprise a major amount of oil of lubricating viscosity, an amount of a dihydrocarbyl dithiophosphate metal salt, preferably an amount providing 200 to 550 ppm by mass of phosphorus; a molybdenum compound in a preferable amount providing the composition with from about 0.005 to 0.1 mass % molybdenum and an oil soluble copper compound in an amount providing the composition with from about 0.001 to 0.02 mass % copper, wherein all mass percentages and ppm are based on the total mass of the lubricating oil composition or finished oil

[0016] The oil of lubricating viscosity useful in the context of the present invention is selected from the group consisting of Group I, Group II, or Group in, Group IV or Group V base stocks or base oil blends of the aforementioned base stocks. Generally, the viscosity of such oils ranges from about 2 mm^2/sec (centistokes) to about 40 mm^2/sec at 100°C. Preferred are base stocks or base stock mixtures having an intrinsic viscosity of from about 4.0 to about 5.5 mm^2/sec at 100°C. Further preferable are base stocks and base stock mixtures having a volatility, as measured by the Noack test (measured by determining the evaporative loss in mass percent of an oil after 1 hour at 250°C according to the procedure of ASTM D5880), of less than 15%, more preferably less than 12%, most preferably less than 10%, such as 5 - 9%. The most preferred oils for both fuel economy retention and low temperature valve train antiwear performance are:

(a) Base oil blends of Group III, IV or V base stocks with Group I or Group II base stocks, where the combination has a viscosity index of at least 110; and
(b) Group III, IV or V base stocks or base oil blends of more than one Group III, IV and/or V base stock, where the viscosity index is between about 120 to about 140.

[0017] Definitions for the base stocks and base oils in this invention are the same as those found in the American Petroleum Institute (API) publication "Engine Oil Licensing and Certification System", Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998. Said publication categorizes base stocks as follows:

a.) Group I base stocks contain less than 90 percent saturates and/or greater than 0.03 percent sulfur and have a viscosity index greater than or equal to 80 and less than 120.
b.) Group II base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulfur and have a viscosity index greater than or equal to 80 and less than 120.
c.) Group III base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulfur and have a viscosity index greater than or equal to 120.
d.) Group IV base stocks are polyalphaolefins (PAO).
e.) Group V base stocks include all other base stocks not included in Group I, II, III, or IV.

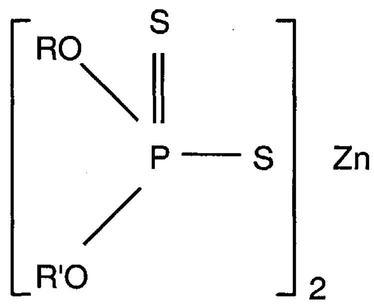
Table 1 -

Analytical Methods for Base Stock	
Property	Test Method
Saturates	ASTM D 2007
Viscosity Index	ASTM D 2270
Sulfur	ASTM D 2622
	ASTM D 4294
	ASTM D 4927
	ASTM D 3120

[0018] The metal dihydrocarbyl dithiophosphate antiwear agents comprise dihydrocarbyl dithiophosphate metal salts wherein the metal may be an alkali or alkaline earth metal, or aluminum, lead, tin, molybdenum, manganese, nickel or copper. The zinc salts are most commonly used in lubricating oil. Although the present specification hereafter makes express mention of ZDDP, dihydrocarbyl dithiophosphate metal salts based on these other metals should be considered equivalent.

[0019] Dihydrocarbyl dithiophosphate metal salts may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohol or a phenol with P_2S_5 and then neutralizing the formed DDPA with a zinc compound. For example, dithiophosphoric acid may be made by reacting mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared where the hydrocarbyl groups on one are entirely secondary in character and the hydrocarbyl groups on the others are entirely primary in character. To make the zinc salt, any basic or neutral zinc compound could be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of zinc due to the use of an excess of the basic zinc compound in the neutralization reaction.

[0020] The preferred zinc dihydrocarbyl dithiophosphates are oil soluble salts of dihydrocarbyl dithiophosphoric acids and may be represented by the following formula:



wherein R and R' may be the same or different hydrocarbyl radicals containing from 1 to 18, preferably 2 to 12, carbon atoms and including radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R and R' groups are alkyl groups of 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylhexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl. In order to obtain oil solubility, the total number of carbon atoms (i.e. R and R') in the dithiophosphoric acid will generally be about 5 or greater. The zinc dihydrocarbyl dithiophosphate can therefore comprise zinc dialkyl dithiophosphates. The zinc dialkylthiophosphate compound can be derived from primary alcohol(s), secondary alcohol(s), or mixtures thereof.

[0021] ZDDP (or other dihydrocarbyl dithiophosphate metal salt) is added to lubricating oil compositions of this invention in an amount within a limited range to gain the beneficial effects and yet comply with low phosphorus regulations. To provide the antiwear advantages of ZDDP but limit phosphorus to a minimum of 100 ppm and a maximum of 550 ppm by mass (calculated as elemental phophorus), the amount of ZDDP should be limited to an amount of from about 0.12 to about 0.7 wt.%, preferably from about 0.24 to about 0.63 wt. %, based on the total weight of the lubricating oil composition (finished oil).

[0022] Lubricating oil compositions of this invention contain an amount of a molybdenum compound, or combination of molybdenum compounds, providing the composition with from about 0.001 to 0.1, preferably from about 0.005 to 0.05 mass % of molybdenum. Any suitable soluble organo-molybdenum compound having anti-wear properties in lubricating oil compositions having reduced phosphorus contents may be employed. The oil-soluble or oil-dispersible molybdenum compound suitable for use in the present invention is typically in the form of a molybdenum additive comprising one or more oil-soluble or oil-dispersible molybdenum compounds. In a preferred embodiment, the molybdenum compound is a molybdenum-sulfur compound.

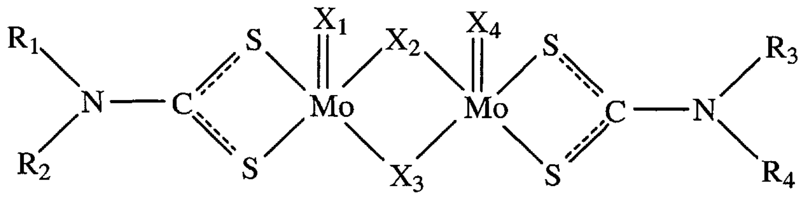
[0023] The molybdenum-sulfur compounds useful in the present invention may be mononuclear or polynuclear. In the event that the compound is polynuclear, the compound contains a molybdenum core consisting of non-metallic atoms, such as sulfur, oxygen and selenium, preferably consisting essentially of sulfur. To enable the molybdenum-sulfur compound to be oil-soluble or oil-dispersible, one or more ligands are bonded to a molybdenum atom in the compound. The bonding of the ligands includes bonding by electrostatic interaction as in the case of a counter-ion and forms of bonding intermediate between covalent and electrostatic bonding. Ligands within the same compound may be differently bonded. For example, a ligand may be covalently bonded and another ligand may be electrostatically bonded.

[0024] Preferably, the or each ligand is monoanionic and examples of such ligands are dithiophosphates, dithiocarbamates, xanthates, carboxylates, thioxanthates, phosphates and hydrocarbyl, preferably alkyl, derivatives thereof. Preferably, the ratio of the number of molybdenum atoms, for example, in the core in the event that the molybdenum-sulfur compound is a polynuclear compound, to the number of monoanionic ligands, which are capable of rendering the compound oil-soluble or oil-dispersible, is greater than 1 to 1, such as at least 3 to 2.

[0025] The oil-solubility or oil-dispersibility of the molybdenum-sulfur compound may be influenced by the total number of carbon atoms present among all of the compound ligands. The total number of carbon atoms present among all of the hydrocarbyl groups of the compound ligands typically will be at least 21, e.g. 21 to 800, such as at least 25, at least 30 or at least 35. For example, the number of carbon atoms in each alkyl group will generally range between 1 to 100, preferably 1 to 40, and more preferably between 3 and 20.

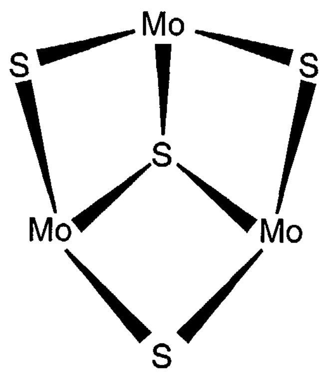
[0026] Examples of molybdenum-sulfur compounds include dinuclear molybdenum-sulfur compounds and trinuclear molybdenum-sulfur compounds.

[0027] An example of a dinuclear molybdenum-sulfur compound is represented by the formula:



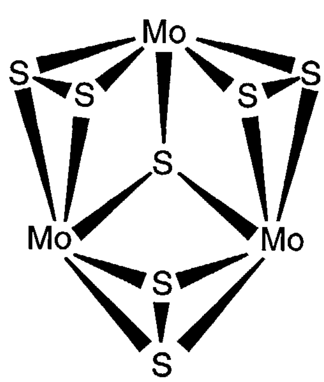
where R_1 to R_4 independently denote a straight chain, branched chain or aromatic hydrocarbyl group having 1 to 24 carbon atoms; and X_1 to X_4 independently denote an oxygen atom or a sulfur atom. The four hydrocarbyl groups, R_1 to R_4, may be identical or different from one another.

[0028] In a preferred embodiment, the molybdenum-sulfur compound is an oil-soluble or oil-dispersible trinuclear molybdenum-sulfur compound. Examples of trinuclear molybdenum-sulfur compounds are disclosed in WO98/26030, WO99/31113, WO99/66013, EP-A-1 138 752, EP-A-1 138 686 and European patent application no. 02078011. Preferably the trinuclear molybdenum-sulfur compound has a core of the structures depicted in (I) or (II):



(I)

or



(II);

wherein each core has a net electrical charge of +4.

[0029] Preferably, the trinuclear molybdenum-sulfur compounds are represented by the formula $Mo_3S_kE_xL_nA_pQ_z$, wherein:

k is an integer of at least 1;
E represents a non-metallic atom selected from oxygen and selenium;
x can be 0 or an integer, and preferably k + x is at least 4, more preferably in the range of 4 to 10, such as 4 to 7, most preferably 4 or 7;
L represents a ligand that confers oil-solubility or oil-dispersibility on the molybdenum-sulfur compound, preferably L is a monoanionic ligand;
n is an integer in the range of 1 to 4;
A represents an anion other than L, if L is an anionic ligand;
p can be 0 or an integer;
Q represents a neutral electron-donating compound; and
z is in the range of 0 to 5 and includes non-stoichiometric values.

[0030] Those skilled in the art recognize that formation of the trinuclear molybdenum-sulfur compound requires selection of appropriate ligands (L) and other anions (A), depending on, for example, the number of sulfur and E atoms present in the core, *i.e.* the total anionic charge contributed by sulfur atom(s), E atom(s), if present, L and A, if present, must be -12.

[0031] Examples of Q include water, alcohol, amine, ether and phosphine. It is believed that the electron-donating compound, Q, is merely present to fill any vacant coordination sites on the trinuclear molybdenum-sulfur compound. Examples of A can be of any valence, for example, monovalent and divalent and include disulfide, hydroxide, alkoxide, amide and, thiocyanate or derivative thereof; preferably A represents a disulfide ion.

[0032] Preferably, L is monoanionic ligand, such as dithiophosphates, dithiocarbamates, xanthates, carboxylates, thioxanthates, phosphates and hydrocarbyl, preferably alkyl, derivatives thereof. When n is 2 or more, the ligands can be the same or different. In one embodiment of the present invention, k is 4 or 7, n is either 1 or 2, L is a monoanionic ligand, p is an integer to confer electrical neutrality on the compound based on the anionic charge on A and each of x and z is 0. In another embodiment, k is 4 or 7, L is a monoanionic ligand, n is 4 and each of p, x and z is 0.

[0033] The molybdenum-sulfur cores, for example, the structures depicted in (I) and (II) above, may be interconnected by means of one or more ligands that are multidentate, *i.e.* a ligand having more than one functional group capable of binding to a molybdenum atom, to form oligomers. Molybdenum-sulfur additives comprising such oligomers are considered to fall within the scope of this invention. Other examples of molybdenum compounds include molybdenum carboxylates and molybdenum nitrogen complexes, both of which may be sulfurised.

[0034] The lubricating oil compositions of the invention contain an oil soluble copper compound in an amount providing the composition with from about 0.001 to 0.02 mass %, preferably from about 0.008 to about 0.016 wt. %, of copper (calculated as elemental copper). The copper compounds are useful as antioxidants.

[0035] Examples of suitable copper-containing compounds include oil soluble copper compounds mentioned in published European Patent Application Nos. EP 0 024 146 B, EP 0 280 579 A, EP 0 280 580 A and U.S. 4,867,890, the disclosures of all of which are incorporated herein by reference. Thus, for example, the copper may be blended into the oil as an oil-soluble copper salt of a synthetic or natural carboxylic acid. Examples of carboxylic acids from which suitable copper salts may be derived include C_2 to C_{18} fatty acids (e.g., acetic acid, stearic acid and palmitic acid), unsaturated acids (e.g., oleic acid), branched carboxylic acids (e.g., naphthenic acids of molecular weight of from 200 to 500, neodecanoic acid and 2-ethylhexanoic acid), and alkyl- or alkenyl-substituted dicarboxylic acids (e.g., polyalkenyl-substituted succinic acids such as octadecenyl succinic acids, dodecenyl succinic acids and polyisobutenyl succinic acids). In some cases, suitable compounds may be derived from an acid anhydride, for example, from a substituted succinic anhydride.

[0036] The copper compound may be, for example, a copper dithiocarbamate or copper dithiophosphate. Other copper and sulfur-containing compounds, for example, copper mercaptides, xanthates, thioxanthates, are also suitable for use in accordance with the invention, as are copper sulfonates, phenates (optionally sulfurized) and acetylacetonates. Other copper compounds which may be used in accordance with the invention are overbased copper compounds. Examples of such compounds, and of processes for their preparation, are given in U.S. Patent No. 4,664,822 and European Specification No. 0 425 367 A, the disclosures of both of which are incorporated herein by reference. The copper compound may be in cuprous or cupric form.

[0037] The amount of phosphorus, sulfur, molybdenum and copper present in the composition is measured in accordance with the procedures of ASTM D5185.

[0038] Preferably, the lubricating oil compositions of the present invention are substantially free (contain less than about 1 wt. %, preferably less than 0.5 wt. %, more preferably 0 to 0.25 wt.%) of ashless, or metal-free, supplemental oxidation inhibitors. Typical commercial ashless antioxidants include both phenolic and aminic antioxidants.

[0039] Ashless phenolic antioxidants include hindered phenols, alkaline earth metal salts of alkylphenolthioesters having preferably C_5 to C_{12} alkyl side chains, nonylphenol sulfide (NPS), ashless oil soluble phenates and sulfurized phenates and phosphosulfurized or sulfurized hydrocarbons.

[0040] Ashless aminic antioxidants include aromatic amines having at least two aromatic groups attached directly to the nitrogen. Typical oil soluble aromatic amines having at least two aromatic groups attached directly to one amine nitrogen contain from 6 to 16 carbon atoms. The amines may contain more than two aromatic groups. Compounds having a total of at least three aromatic groups in which two aromatic groups are linked by a covalent bond or by an atom or group (e.g., an oxygen or sulfur atom, or a -CO-, -SO_2 or alkylene group) and two are directly attached to one amine nitrogen also considered aromatic amines having at least two aromatic groups attached directly to the nitrogen. The aromatic rings are typically substituted by one or more substituents selected from alkyl, cycloalkyl, alkoxy, aryloxy, acyl, acylamino, hydroxy, and nitro groups.

[0041] Additional additives may be incorporated into the compositions of the invention to enable particular performance requirements to be met. Examples of additional additives that may be included in the lubricating oil compositions of the present invention are ashless dispersants, ash-forming detergents, metal rust inhibitors, viscosity index improvers, corrosion inhibitors, anti-foaming agents, and pour point depressants. Some are discussed in further detail below.

[0042] Dispersants maintain in suspension materials resulting from oxidation during use that are insoluble in oil, thus preventing sludge flocculation and precipitation, or deposition on metal parts. Dispersants useful in the context of the present invention include the range of nitrogen-containing, ashless (metal-free) dispersants known to be effective to reduce formation of deposits upon use in gasoline and diesel engines, when added to lubricating oils. Such ashless dispersants comprises an oil soluble polymeric hydrocarbon backbone having functional groups that are capable of associating with particles to be dispersed. Typically, such dispersants comprise amine, alcohol, amide, or ester polar moieties attached to the polymer backbone often via a bridging group. The ashless dispersant may, for example, be selected from oil soluble salts, esters, amino-esters, amides, imides, and oxazolines of long chain hydrocarbon substituted mono and dicarboxylic acids or their anhydrides; thiocarboxylate derivatives of long chain hydrocarbons, long chain aliphatic hydrocarbons having a polyamine attached directly thereto. Also suitable are Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine.

[0043] Dispersants can be used in the lubricating oil compositions of the present invention in amounts of from about 0.5 to 10.0 wt.%, preferably from about 1 to 3 wt.%. Preferred are polyisobutenyl succinimide dispersants wherein the polyisobutenyl moiety has an Mn of about 500 to 3,000, preferably about 900 to 2,500. A preferred embodiment utilizes polyisobutenyl succinimide dispersants prepared using polyisobutylene prepared from a pure isobutylene stream or a Raffinate I stream to prepare reactive isobutylene polymers with terminal vinylidene olefins. Preferably, these polymers, referred to as highly reactive polyisobutylene (HR-PIB), have a terminal vinylidene content of at least 65%, e.g., 70%, more preferably at least 80%, most preferably at least 85%. The preparation of such polymers is described, for example, in U.S. Patent No. 4,152,499. HR-PIB is known and HR-PIB is commercially available under the tradenames Glissopal™ (from BASF) and Ultravis™ (from BP-Amoco).

[0044] Metal-containing or ash-forming detergents function both as detergents to reduce or remove deposits and as acid neutralizers or rust inhibitors, thereby reducing wear and corrosion and extending engine life. Detergents generally comprise a polar head with long hydrophobic tail, with the polar head comprising a metal salt of an acid organic compound. The salts may contain a substantially stoichiometric amount of the metal in which they are usually described as normal or neutral salts, and would typically have a total base number (TBN), as may be measured by ASTM D-2896 of from 0 to 80. It is possible to include large amounts of a metal base by reacting an excess of a metal compound such as an oxide or hydroxide with an acid gas such a such as carbon dioxide. The resulting overbased detergent comprises neutralized detergent as the outer layer of a metal base (e.g., carbonate) micelle. Such overbased detergents may have a TBN of 150 or greater, and typically from 250 to 450 or more.

[0045] Known detergents include oil-soluble neutral and overbased sulfonates, phenates (including alkylene bridged phenates), sulfurized phenates, thiophosphonates, salicylates, and naphthenates and other oil-soluble carboxylates of a metal, particularly the alkali or alkaline earth metals, e.g., sodium, potassium, lithium, calcium, and magnesium. The most commonly used metals are calcium and magnesium, which may both be present in detergents used in a lubricant, and mixtures of calcium and/or magnesium with sodium. Particularly convenient metal detergents are neutral and overbased calcium sulfonates having TBN of from 20 to 450 TBN, and neutral and overbased calcium phenates and sulfurized phenates having TBN of from 50 to 450.

[0046] In the present invention, overbased detergents are preferred, and when used, may be used in amounts of from about 0.5% to 5% weight percent based on the total weight of the composition. The total base number of the overbased sulfonate detergent is preferably between about 150 to 450. Further preferably, the overbased detergent is overbased calcium sulfonate.

[0047] The viscosity modifier (VM) functions to impart high and low temperature operability to lubricating oil. The VM used may have that sole function, or may be multifunctional. Representative examples of suitable viscosity modifiers are polyisobutylene, copolymers of ethylene and propylene, polymethacrylates, methacrylate copolymers, copolymers of an unsaturated dicarboxylic acid and a vinyl compound, interpolymers of styrene and acrylic esters, and partially hydrogenated copolymers of styrene/ isoprene, styrene/butadiene, and isoprene/butadiene, as well as the partially hydrogenated homopolymers of butadiene and isoprene. Multifunctional viscosity modifiers that further function as dispersants are also known.

[0048] Rust inhibitors selected from the group consisting of nonionic polyoxyalkylene polyols and esters thereof, polyoxyalkylene phenols, and anionic alkyl sulfonic acids may be used.

[0049] Copper and lead bearing corrosion inhibitors may be used, but are typically not required with the formulation of the present invention. Typically such compounds are the thiadiazole polysulfides containing from 5 to 50 carbon atoms, their derivatives and polymers thereof. Derivatives of 1,3,4 thiadiazoles such as those described in U.S. Patent Nos. 2,719,125; 2,719,126; and 3,087,932; are typical. Other similar materials are described in U.S. Patent Nos. 3,821,236; 3,904,537; 4,097,387; 4,107,059; 4,136,043; 4,188,299; and 4,193,882. Other additives are the thio and polythio sulfenamides of thiadiazoles such as those described in UK Patent Specification No. 1,560,830. Benzotriazoles derivatives also fall within this class of additives. When these compounds are included in the lubricating composition, they are preferably present in an amount not exceeding 0.2 wt. % active ingredient.

[0050] A small amount of a demulsifying component may be used. A preferred demulsifying component is described in EP 330,522. It is obtained by reacting an alkylene oxide with an adduct obtained by reacting a bis-epoxide with a polyhydric alcohol. The demulsifier should be used at a level not exceeding 0.1 mass % active ingredient. A treat rate of 0.001 to 0.05 mass % active ingredient is convenient.

[0051] Pour point depressants, otherwise known as lube oil flow improvers, lower the minimum temperature at which the fluid will flow or can be poured. Such additives are well known. Typical of those additives which improve the low temperature fluidity of the fluid are C_8 to C_{18} dialkyl fumarate/vinyl acetate copolymers, polyalkylmethacrylates and the like.

[0052] Foam control can be provided by many compounds including an antifoamant of the polysiloxane type, for example, silicone oil or polydimethyl siloxane.

[0053] The individual additives may be incorporated into a base stock in any convenient way. Thus, each of the components can be added directly to the base stock or base oil blend by dispersing or dissolving it in the base stock or base oil blend at the desired level of concentration. Such blending may occur at ambient temperature or at an elevated temperature.

[0054] Preferably, all the additives except for the viscosity modifier and the pour point depressant are blended with a minor amount of an oleaginous carrier, such as a basestock, to prepare a concentrate or additive package described herein as the additive package, that is subsequently blended into base stock to make the finished lubricant. The concentrate will typically be formulated to contain the additive(s) in proper amounts to provide the desired concentration in the final formulation when the concentrate is combined with a predetermined amount of a base lubricant.

[0055] The concentrate is preferably made in accordance with the method described in US 4,938,880. That patent describes making a pre-mix of ashless dispersant and metal detergents that is pre-blended at a temperature of at least about 100°C. Thereafter, the pre-mix is cooled to at least 85°C and the additional components are added.

[0056] The final crankcase lubricating oil formulation may employ from 2 to 20 mass %, preferably 4 to 18 mass %, and most preferably about 5 to 17 mass % of the concentrate or additive package with the remainder being base stock. The compositions can be used in the formulation of crankcase lubricating oils (i.e. passenger car motor oils, heavy duty diesel motor oils, and passenger car diesel oils) for spark-ignited and compression-ignited engines.

[0057] Generally the viscosity of the additive concentrate is higher than that of the lubricating oil composition. Typically, the kinematic viscosity at 100 °C of the additive concentrate is at least 50, such as in the range 100 to 200, preferably 120 to 180, mm^2s^{-1} (or cSt).

[0058] Thus, a method of preparing a lubricating oil composition according to the present invention can involve admixing an oil of lubricating viscosity and one or more of additives or additive concentrates that comprises two or more of additives and then, admixing other additive components, such as viscosity modifier, and optionally a multifunctional viscosity modifier and pour point depressant.

[0059] Preferably, the lubricating oil compositions of the present invention contain no more than 0.5 wt. % of sulfur, such as 0.01 to 0.3 wt % of sulfur.

In this specification:

[0060] The term "hydrocarbyl" as used herein means that the group concerned is primarily composed of hydrogen and carbon atoms and is bonded to the remainder of the molecule via a carbon atom, but does not exclude the presence of other atoms or groups in a proportion insufficient to detract from the substantially hydrocarbon characteristics of the group.

[0061] The term "comprising" or "comprises" when used herein is taken to specify the presence of stated features, integers, steps or components, but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof. In the instance the term "comprising" or comprises" is used herein, the term "consisting essentially of" and its cognates are a preferred embodiment, while the term "consisting of" and its cognates are a preferred embodiment of the term "consisting essentially of".

[0062] The term "oil-soluble" or "oil-dispersible", as used herein, does not mean that the additives are soluble, dissolvable, miscible or capable of being suspended in the oil in all proportions. They do mean, however, that the additives are, for instance, soluble or stable dispersible in the oil to an extent sufficient to exert their intended effect in the environment in which the oil composition is employed. Moreover, the additional incorporation of other additives such as those described above may affect the solubility or dispersibility of the additives.

[0063] "Major amount" "Major amount" means in excess of 50, such as greater than 70, preferably 75 to 97, especially 80 to 95 or 90, mass %, of the composition.

[0064] "Minor amount" means less than 50, such as less than 30, for example, 3 to 25, preferably 5 or 10 to 20, mass %, of the composition mass % of the composition.

[0065] The term 'molybdenum-sulfur compound' means a compound having at least one molybdenum atom and at least one sulfur atom, preferably the compound has at least one sulfur atom that is bonded to one or more molybdenum atoms and also bonded to one or more non-molybdenum atoms, such as carbon, more preferably the compound has at least one sulfur atom that is bonded to one or more molybdenum atoms only, such as represented by cores [Mo_2S_4], [Mo_3S_4] and [Mo_3S_7]. Atoms selected from oxygen and selenium may replace one or more sulfur atoms in such cores. Advantageously, the core consists of molybdenum and sulfur atoms alone. Accordingly, the term 'molybdenum-sulfur additive' means an additive comprising one or more molybdenum-sulfur compounds.

[0066] All percentages reported are mass % on an active ingredient basis, *i.e.* without regard to carrier or diluent oil, unless otherwise stated.

[0067] The abbreviation SAE stands for Society of Automotive Engineers, who classify lubricants by viscosity grades.

[0068] This invention will be further understood by reference to the following examples, wherein all percentages are by weight of active ingredient, unless otherwise noted, and which include preferred embodiments of the invention.

EXAMPLES

[0069] The following lubricating oils were prepared and the antioxidative properties were tested using MHT-4 (Medium High Temperature-4) TEOST (Thermal Engine Oil Stability Test) in accordance with the procedures of ASTM 06335. Each of the lubricating oil samples contained identical amounts of identical mineral oil base stock, dispersant, detergent, organic friction modifier and antifoam agent. Each sample contained 0.64 wt. % of ZDDP, which provided each sample with a phosphorus content of 510 ppm. The amount of copper compound (copper oleate), molybdenum compound (molybdenum dithiocarbamate) and supplemental ashless antioxidant (nonylphenol sulfide or "NPS") is shown in Table 2.

[0070] The amount of copper compound and molybdenum compound are reported as wt.% of elemental copper and molybdenum introduced, respectively. MHT-4 TEOST results are reported as mg of weight gain (of deposit). Lower weight gain indicates improved antioxidative properties.

Table 2

Example	C1	C2	I1	C3	C4	C5
Cu (mass %)	0	0.016	0.008	0.016	0	0
Mo (mass %)	0	0	0.011	0.011	0	0.019
NPS (wt. %)	0	0	0	1.18	1.18	0
Description	Baseline	Cu	Cu/Mo	Cu/NPS	NPS	Mo
TEOST (mg)	68.9	63.5	46.9	65.8	63.7	51.2

[0071] Example 11 represents the lubricating oil compositions of the present invention. As shown by the data presented in Table 2, in lubricating oil compositions having a reduced phosphorus content, a combination of a copper compound and a molybdenum compound provided antioxidative properties that were superior to those provided by an equivalent amount of either the copper compound or the molybdenum compound used individually, as well as a combination of a molybdenum compound and an ashless phenolic antioxidant.

[0072] It should be noted that the lubricating oil compositions of this invention comprise defined, individual, i.e., separate, components that may or may not remain the same chemically before and after mixing. Thus, it will be understood that various components of the composition, essential as well as optional and customary, may react under the conditions of formulation, storage or use and that the invention also is directed to, and encompasses, the product obtainable, or obtained, as a result of any such reaction.

Claims

1. A lubricating oil composition comprising a major amount of oil of lubricating viscosity, an oil soluble molybdenum compound in an amount providing from 0.001 to 0.1 mass % molybdenum to said composition, an oil soluble copper compound in an amount providing from 0.001 to 0.02 mass % copper to said composition, and an amount of metal hydrocarbyl dithiophosphate providing said composition with from 100 to 550 ppm phosphorus.

2. The lubricating oil composition of claim 1, wherein said metal hydrocarbyl dithiophosphate is zinc dialkyl dithiophosphate.

3. The lubricating oil composition of either claim 1 or claim 2, wherein said composition has a Noack volatility of no greater than 15 wt.%.

4. The lubricating oil composition of any of claims 1 to 3, further comprising an ashless dispersant.

5. The lubricating oil composition of claim 4, wherein said dispersant is a polyisobutenyl succinimide.

6. The lubricating oil composition of any of claims 1 to 5, wherein said copper compound is copper oleate.

7. The lubricating oil composition of any of claims 1 to 6, wherein said oil of lubricating viscosity has a viscosity between 4.0 mm^2/sec and 5.5 mm^2/sec at 100°C.

8. The lubricating oil composition of any of claims 1 to 7, wherein said oil of lubricating oil composition is a Group II oil, a Group III oil, a Group IV oil, a Group V oil or a mixture thereof, or is mixture of a Group I oil and at least one of a Group II oil, a Group III, a Group IV oil, or a Group V oil.

9. The lubricating oil composition of any of claims 1 to 8, wherein said oil of lubricating viscosity comprises a Group IV oil.

10. The composition of any of claims 1 to 9, wherein said molybdenum compound is an organo-molybdenum compound.

11. The composition of any of claims 1 to 10, wherein said organo-molybdenum compound is molybdenum dithiocarbamate.

12. A composition of any of claims 1 to 11, which composition is substantially free of ashless antioxidant.

13. The composition of any of claims 1 to 12, further comprising at least one overbased metallic detergent.

14. The composition of claim 13, wherein said at least one overbased metallic detergent is an overbased calcium detergent.

15. A composition of any of claims 1 to 14, which composition contains no more than 0.5 wt. % of sulfur.

16. A concentrate for preparing a lubricating oil composition comprising an oleaginous carrier, an oil soluble molybdenum compound, an oil soluble copper compound and a metal hydrocarbyl dithiophosphate, in such proportions that the lubricating oil composition has 0.001 to 0.1 mass % of molybdenum, 0.001 to 0.02 mass % of copper and 100 to 550 ppm of phosphorus when the oil composition contains 2 to 20 mass % of the concentrate.

17. The use of a molybdenum compound and a copper compound in a lubricating oil composition having 100 to 550 ppm of phosphorus, derived from metal hydrocarbyl dithiophosphate, to improve anti-oxidancy performance of the oil composition.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 25 5866

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	8 January 2004	Dötterl, E

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