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(54) Lubricating oil composition

(57) A lubricating oil composition having a phosphorus content of up to 0.12 wt%, a sulfated ash content of up to 1.2 wt% comprising (a) a major amount of an oil of lubricating viscosity; (b) an alkali metal or alkaline earth metal alkyl salicylate lubricating oil detergent providing from 7-15 mmol salicylate soap per kilogram of lubricating oil composition; (c) one or more dispersants providing the lubricating oil composition with from at least 0.12 wt% to 0.20 wt% atomic nitrogen, based on the weight of the lubricating oil composition, and (d) a dispersant-viscosity modifier.

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Description

[0001] The present invention relates to lubricating oil compositions. More particularly, the present invention relates to lubricating oil compositions for use in engines comprising emission control systems.

BACKGROUND OF THE INVENTION

[0002] Environmental concerns have led to continued efforts to reduce the CO, hydrocarbon and nitrogen oxide (NO_x) emissions of compression ignited (diesel-fueled) and spark ignited (gasoline-fueled) light duty internal combustion engines. Further, there have been continued efforts to reduce the particulate emissions of compression ignited light duty internal combustion engines. To meet the current and upcoming emission standards for vehicles, original equipment manufacturers (OEMs) rely on the use of exhaust gas after-treatment devices. Such exhaust gas after-treatment devices may include exhaust gas recirculation arrangements and cooled exhaust gas recirculation arrangements, catalytic converters, which can contain one or more oxidation catalysts, NO_x storage catalysts, and/or NH_3 reduction catalysts and/or a particulate trap. OEM's are also looking at using selective catalytic reduction (SCR) systems to further reduce NO_x emissions.

[0003] Oxidation catalysts can become poisoned and rendered less effective by exposure to certain elements/compounds present in engine exhaust gasses, particularly by exposure to phosphorus and phosphorus compounds introduced into the exhaust gas by the degradation of phosphorus-containing lubricating oil additives. Reduction catalysts are sensitive to sulfur and sulfur compounds in the engine exhaust gas introduced by the degradation of both the base oil used to blend the lubricant, and sulfur-containing lubricating oil additives. Particulate traps can become blocked by metallic ash, which is a product of degraded metal-containing lubricating oil additives. Thus in addition to designing engines to include a variety of emission control systems, OEM's also require lubricating oil compositions to be formulated to reduce the presence of detrimental materials in the exhaust gas stream. At the same time, the selected lubricating oil composition must provide adequate lubricant performance, including adequate wear protection and detergency.

[0004] European patent application 1 167 497 A2 discloses a lubricating oil composition having restricted sulfur, phosphorous and sulfated ash content comprising an ashless dispersant with a certain nitrogen content, a metal-containing detergent containing an organic acid metal salt selected from the group comprising an alkali or alkaline earth metal salt of an alkyl salicylic acid and an alkali or alkaline earth metal salt of an alkylphenol derivative having a mannich base structure providing a certain sulphated ash content, a zinc dialkyldithiophosphate providing a specified phosphorus amount and an oxidiation inhibitor. Lubricating oils formulated in accordance with this patent application are stated to exhibit good high temperature detergency despite the lower sulfur, phosphorus and sulphated ash levels of the compositions.

SUMMARY OF THE INVENTION

[0005] In accordance with a first aspect of the present invention there is provided a lubricating oil composition having a phosphorus content of up to 0.12 wt%, a sulfated ash content of up to 1.2 wt% comprising, (a) a major amount of an oil of lubricating viscosity; (b) an alkali metal or alkaline earth metal alkyl salicylate lubricating oil detergent providing from 7-15 mmol of salicylate soap per kilogram of lubricating oil composition; (c) one or more dispersants providing the lubricating oil composition with from at least 0.12 wt% to 0.20 wt% atomic nitrogen, based on the weight of the lubricating oil composition, and (d) a dispersant-viscosity modifier.

[0006] In accordance with a second aspect of the present invention there is provided a method of lubricating a vehicle engine comprising an exhaust gas recirculation (EGR) system comprising use in that engine of a lubricating oil composition according to the first aspect of the invention.

[0007] In accordance with a third aspect of the present invention there is provided a method according to the second aspect, wherein the engine further comprises a selective catalytic reduction (SCR) system.

[0008] Unless otherwise stated, all amounts of additives are reported in wt. % on an active ingredient ("a.i.") basis, i.e., independent of the diluent or carrier oil.

Oil of Lubricating Viscosity

[0009] The oil of lubricating viscosity may be selected from Group I, II, III, IV or V base stocks, synthetic ester base stocks or mixtures thereof The base stock groups are defined in the American Petroleum Institute (API) publication "Engine Oil Licensing and Certification System", Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998. The base stock will have a viscosity preferably of 3-12, more preferably 4-10, most preferably 4.5-8 mm^2/s (cSt.) at 100°C.

(a) Group I mineral oil base stocks contain less than 90% saturates and/or greater than 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table A below.

(b) Group II mineral oil base stocks contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table A below.

(c) Group III mineral oil base stocks contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 120 using the test methods specified in Table A below.

(d) Group IV base stocks are polyalphaolefins (PAO).

(e) Suitable ester base stocks that can be used comprise the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, alkenyl malonic acids, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, etc.) Specific examples of these esters include dibutyl adipate, di(e-ethylhexyl) sebacate, din-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid and the like.

[0010] Esters useful as synthetic base stock oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylol propane, pentaerythritol, dipentaerythritol, tripentaerythritol, etc.

[0011] In one embodiment of the present invention, the oil of lubricating viscosity comprises less than 50 wt% of a Fischer-Tropsch base oil, suitably less than 30 wt%, preferably less than 10 wt% and most preferably substantially no Fischer-Tropsch base oil; wherein substantially no Fischer-Tropsch base oil means no more than an impurity amount.

Table A - Analytical Methods for Testing Base Stocks

Property	Test Method
Saturates	ASTM D2007
Viscosity Index	ASTM D2270
Sulfur	ASTM D2622, D4294, D4927, or D3120

Metal Salicylate Detergent

[0012] The present invention requires the presence of at least one alkali metal or alkaline earth lubricating oil salicylate detergent.

[0013] The metal salicylate detergent may be C_8-C_{30} alkyl salicylates or mixtures thereof, with C_{10}-C_{20} alkyl salicylates being particularly preferred. Preferably, the salicylate detergent will be a calcium and/or magnesium salicylate and will have a Total Base Number at 100% active mass (TBN) between 10 and 1000, more preferably between 20 and 850. The most preferred detergent for use in this invention is one or a mixture of overbased calcium alkyl salicylate detergents having a TBN between 300 and 600. In one embodiment, the metal salicylate detergent comprises substantially no magnesium alkyl salicylate detergent.

[0014] In the present invention, the amount of metal salicylate detergent used can vary broadly, but typically will be from about 0.1 to about 5 wt.%, preferably 0.5 to 1.5 wt.% based on the total weight of the composition, so as to provide from 7-15 mmoles of metal salicylate detergent per kilogram of the finished oil composition. Suitably, the amount of metal salicylate detergent used in the present invention provides the composition with at least 8 mmol soap per kilogram of the finished oil composition. Suitably, the amount of metal salicylate detergent used in the present invention provides the composition with no more than 11 mmol soap per kilogram of the finished oil composition.

[0015] Suitably, the metal salicylate detergent provides greater than 0.3 mass%, preferably at least 0.4 mass% metal as sulphated ash to the lubricating oil composition.

[0016] The metal salicylate may be the sole metal lubricating oil detergent present in the lubricating oil compositions of the invention. Alternatively, other metal-containing detergents, such as metal sulfonates or phenates, may be present in the lubricating composition. Advantageously, where the lubricating oil composition comprises a mixture of detergent types, the lubricating oil composition suitably comprises a mixture of metal salicylate and metal sulphonate detergents.

The additional detergents may be either calcium or magnesium metal salts. In one embodiment of the present invention the additional detergents are calcium metal salts and the lubricating oil composition comprises substantially no magnesium metal salts. Preferably, the salicylate detergent provides the majority of the detergent additive in the lubricating oil composition.

[0017] By substantially no magnesium metal salt detergent and substantially no magnesium alkyl salicylate detergent it is meant no more than an impurity amount, such as an amount providing less than 50 ppm magnesium preferably less than 30 ppm magnesium and most preferably less than 10 ppm magnesium.

[0018] Metal salts of organic acids typically used as lubricating oil detergents are present as stable colloidal dispersions of salt in oil. The components are generally made by neutralizing the organic acid with a strong metal base in the presence of process aids. When the component is overbased, the organic acid is neutralized with a strong metal base in the presence of an acidic gas (often carbon dioxide). In consequence both the organic acid and the acidic gas are converted to the metal salt and the component contains metal in an amount in excess of that required to neutralize the organic acid.

[0019] Manufacture of these components is extremely complex and the final composition of the colloidal dispersion is not known with accuracy. For example sulfurized metal phenates are generally described as bis-thiophenates with sulfur linkages of varying lengths. In fact the number of phenolic groups actually linked together is not known with certainty. Similarly, the amount of phenol assumed to convert to a metal salt is often assumed to be 100%. In fact the degree of the neutralization depends on the acidity of the phenol and the acidity of the neutralizing base. Further the equilibria established when the component is made shift whenever the component is blended with other materials containing strong bases. For these reasons, the amounts of carbonate, sulfonate, and phenolic hydroxide present in a lubricant are inferred from the amounts present in the individual components that are blended to make the finished lubricant. And those amounts are in turn inferred from the charge ratios of raw materials used to make the detergents or by resort to analytical methods that can determine detectable moieties allowing inference of the remaining moieties.

[0020] Thus the moles of metal salt of an organic acid present can be determined directly in some cases and in others must be derived. When the salt is a calcium sulfonate, direct analysis is possible using the liquid chromatography method described in ASTM 3712. For other organic acids, the moles of salt must be derived. When this is required titrimetry including two phase titrimetric methods, total acid number (TAN) as determined using ASTM D664, dialysis and other well known analytical techniques allow determination of the organic salt content. Thus for phenates and carboxylates (including salicylates) the total amount of metal must be determined and allocated between organic and inorganic acids using a metal ratio. The total amount of metal present is conveniently determined by inductively coupled plasma atomic emission spectrometry--ASTM D4951. Metal ratio is defined as the total amount of metal present divided by the amount of metal in excess of that required to neutralize any organic acid present, i.e., the amount of metal neutralizing inorganic acids. Metal ratios are quoted by manufacturers of commercial detergents and can be determined by a manufacturer having knowledge of the total amount of salts present and the average molecular weight of the organic acid. The amount of metal salt present in a detergent may be determined by dialyzing the detergent and quantifying the amount of the residue. If the average molecular weight of the organic salts is not known, the residue from the dialyzed detergent can be treated with strong acid to convert the salt to its acid form, analyzed by chromatographic methods, proton NMR, and mass spectroscopy and correlated to acids of known properties. More particularly, the detergent is dialysed and then residue is treated with strong acid to convert any salts to their respective acid form. The hydroxide number of the mixture can then be measured by the method described in ASTM D1957. If the detergent contains non-phenolic hydroxyl groups on the phenolic compound (e.g., alcoholic derivatives of ethylene glycol used in manufacture of commercial phenates or carboxylic acid groups on salicylic acid), separate analyses must be conducted to quantify the amounts of those hydroxyl groups so that the hydroxide number determined by ASTM D1957 can be corrected. Suitable techniques to determine the quantity of non-phenolic hydroxyl groups include analyses by mass spectroscopy, liquid chromatography, and proton NMR and correlation to compounds having known properties.

[0021] A second method for deriving the number of moles of metal salt of an organic acid present assumes that all of the organic acid charged to make the component is in fact converted to the salt. In practice the two methods can give slightly different results, but both are believed to be sufficiently precise to allow determination of the amount of salt present to the precision required to practice the present invention.

[0022] In addition to being constrained by the amount of soap present in the finished oil composition, the total amount of detergent present is limited by the maximum 1.2 wt% sulfated ash content of the finished oil composition.

[0023] The total soap content of the lubricating oil is suitably no more than 1.5 wt%, preferably no more than 1.2wt% and more preferably no more than 1.0 wt%. The total soap content of the lubricating oil composition is suitably at least 0.7 wt%, preferably at least 0.75 wt%.

Ashless Dispersant

[0024] An ashless dispersant generally comprises an oil soluble polymeric hydrocarbon backbone having functional groups that are capable of associating with particles to be dispersed. Typically, the dispersants comprise amine, alcohol, amide, or ester polar moieties attached to the polymer backbone often via a bridging group. The ashless dispersant of the present invention may be, for example, 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; and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine. The most common dispersant in use is the well known succinimide dispersant, which is a condensation product of hydrocarbyl-substituted succinic anhydride and a poly(alkyleneamine). Both mono-succinimide and bis-succinimide dispersants (and mixtures thereof) are well known.

[0025] Preferred groups of dispersant include polyamine-derivatized poly α-olefin, dispersants, particularly ethylene/butene alpha-olefin and polyisobutylene-based dispersants. Particularly preferred are ashless dispersants derived from polyisobutylene substituted with succinic anhydride groups and reacted with polyethylene amines, e.g., polyethylene diamine, tetraethylene pentamine; or a polyoxyalkylene polyamine, e.g., polyoxypropylene diamine, trimethylolaminomethane; a hydroxy compound, e.g., pentaerythritol; and combinations thereof. One particularly preferred dispersant combination is a combination of (A) polyisobutylene substituted with succinic anhydride groups and reacted with (B) a hydroxy compound, e.g., pentaerythritol; (C) a polyoxyalkylene polyamine, e.g., polyoxypropylene diamine, or (D) a polyalkylene diamine, e.g., polyethylene diamine and tetraethylene pentamine using about 0.3 to about 2 moles of (B), (C) and/or (D) per mole of (A). Another preferred dispersant combination comprises a combination of (A) polyisobutenyl succinic anhydride with (B) a polyalkylene polyamine, e.g., tetraethylene pentamine, and (C) a polyhydric alcohol or polyhydroxy-substituted aliphatic primary amine, e.g., pentaerythritol or trismethylolaminomethane, as described in U.S. Patent No. 3,632,511.

[0026] Another class of ashless dispersants comprises Mannich base condensation products. Generally, these products are prepared by condensing about one mole of an alkyl-substituted mono- or polyhydroxy benzene with about 1 to 2.5 moles of carbonyl compound(s) (e.g., formaldehyde and paraformaldehyde) and about 0.5 to 2 moles of polyalkylene polyamine, as disclosed, for example, in U.S. Patent No. 3,442,808. Such Mannich base condensation products may include a polymer product of a metallocene catalyzed polymerization as a substituent on the benzene group, or may be reacted with a compound containing such a polymer substituted on a succinic anhydride in a manner similar to that described in U.S. Patent No. 3,442,808. Examples of functionalized and/or derivatized olefin polymers synthesized using metallocene catalyst systems are described in the publications identified *supra*.

[0027] The dispersant can be further post treated by a variety of conventional post treatments such as boration, as generally taught in U.S. Patent Nos. 3,087,936 and 3,254,025. Boration of the dispersant is readily accomplished by treating an acyl nitrogen-containing dispersant with a boron compound such as boron oxide, boron halide boron acids, and esters of boron acids, in an amount sufficient to provide from about 0.1 to about 20 atomic proportions of boron for each mole of acylated nitrogen composition. Useful dispersants contain from about 0.05 to about 2.0 mass %, e.g., from about 0.05 to about 0.7 mass % boron. The boron, which appears in the product as dehydrated boric acid polymers (primarily $(HBO_2)_3$), is believed to attach to the dispersant imides and diimides as amine salts, e.g., the metaborate salt of the diimide. Boration can be carried out by adding from about 0.5 to 4 mass %, e.g., from about 1 to about 3 mass % (based on the mass of acyl nitrogen compound) of a boron compound, preferably boric acid, usually as a slurry, to the acyl nitrogen compound and heating with stirring at from about 135°C to about 190°C, e.g., 140°C to 170°C, for from about 1 to about 5 hours, followed by nitrogen stripping. Alternatively, the boron treatment can be conducted by adding boric acid to a hot reaction mixture of the dicarboxylic acid material and amine, while removing water. Other post reaction processes commonly known in the art can also be applied.

[0028] The dispersant may also be further post treated by reaction with a so-called "capping agent". Conventionally, nitrogen-containing dispersants have been "capped" to reduce the adverse effect such dispersants have on the fluoroelastomer engine seals. Numerous capping agents and methods are known. Of the known "capping agents", those that convert basic dispersant amino groups to non-basic moieties (e.g., amido or imido groups) are most suitable. The reaction of a nitrogen-containing dispersant and alkyl acetoacetate (e.g., ethyl acetoacetate (EAA)) is described, for example, in U.S. Patent Nos. 4,839,071; 4,839,072 and 4,579,675. The reaction of a nitrogen-containing dispersant and formic acid is described, for example, in U.S. Patent No. 3,185,704. The reaction product of a nitrogen-containing dispersant and other suitable capping agents are described in U.S. Patent Nos. 4,663,064 (glycolic acid); 4,612,132; 5,334,321; 5,356,552; 5,716,912; 5,849,676; 5,861,363 (alkyl and alkylene carbonates, e.g., ethylene carbonate); 5,328,622 (mono-epoxide); 5,026,495; 5,085,788; 5,259,906; 5,407,591 (poly (e.g., bis)-epoxides) and 4,686,054 (maleic anhydride or succinic anhydride). The foregoing list is not exhaustive and other methods of capping nitrogen-containing dispersants are known to those skilled in the art.

[0029] Preferably, the dispersant is a thermally maleated dispersant formed by reacting a polyalkenyl-substituted mono- or dicarboxylic acid, anhydride or ester; and a polyamine, having from greater than about 1.3 to less than about 1.7 mono- or di-carboxylic acid producing moieties per polyalkenyl moiety and wherein said polyalkenyl moiety has a molecular weight distribution (M_w/M_n) of from 1.5 to 2.0 and a number average molecular weight (M_n) of from about 1800 to about 3000. Such preferred dispersants are described, for example, in U.S. Patent Nos. 6,734,148 and 6,743,757.

[0030] The ashless dispersant is suitably present in an amount of from 4 to 10 wt.%, preferably about 5 to 8 wt.% on a 100% active matter basis. The dispersant should provide the lubricating oil composition with at least 0.12 wt % of atomic nitrogen. The dispersant suitably provides the lubricating oil composition with no more than 0.2 wt % atomic nitrogen. Preferably, the dispersant provides the lubricating oil composition with from 0.12 to 0.17 wt% atomic nitrogen.

[0031] The nitrogen content provided to the lubricating oil composition by the dispersant can be determined in accordance with the procedures of ASTM D5762

[0032] Preferred dispersants are borated or non-borated polyisobutenyl succinimide dispersants wherein the polyisobutenyl has a number average molecular weight (Mn) of about 400 to 3,000, preferably about 900 to 2,500.

[0033] An embodiment of the present invention 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 Gfissopal™ (from BASF) and Ultravis™ (from BP-Amoco).

[0034] The dispersant may comprise one dispersant or a combination of dispersants. If the dispersant comprises a combination of dispersants, the mixture suitable comprises a low molecular weight dispersant and a high molecular weight dispersant. A low molecular weight dispersant is a dispersant with a polymeric hydrocarbon backbone having a number average molecular weight (Mn) of about 500 to 1750. A high molecular weight dispersant is a dispersant with a polymeric hydrocarbon backbone having a number average molecular weight (Mn) of about 1800 to 3000. In one embodiment, the total dispersant present in the lubricating oil composition comprises less than 40 mass%, less than 35 mass% or less than 30 mass% of low molecular weight dispersants.

[0035] Polymer molecular weight, specifically $\overline{M}n$, can be determined by various known techniques. One convenient method is gel permeation chromatography (GPC), which additionally provides molecular weight distribution information (see W. W. Yau, J. J. Kirkland and D. D. Bly, "Modern Size Exclusion Liquid Chromatography", John Wiley and Sons, New York, 1979). Another useful method for determining molecular weight, particularly for lower molecular weight polymers, is vapor pressure osmometry (see, e.g., ASTM D3592).

Viscosity Modifier

[0036] The viscosity index of the base stock is increased, or improved, by incorporating therein certain polymeric materials that function as viscosity modifiers (VM) or viscosity index improvers (VII). Generally, polymeric materials useful as viscosity modifiers are those having number average molecular weights (Mn) of from about 5,000 to about 250,000, preferably from about 15,000 to about 200,000, more preferably from about 20,000 to about 150,000. Suitable viscosity modifiers are polyisobutylene, olefin copolymers, such as copolymers of ethylene and propylene and higher alpha-olefins, polymethacrylates, polyalkylmethacrylates, methacrylate copolymers, copolymers of an unsaturated dicarboxylic acid and a vinyl compound, inter polymers 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 and isoprene/divinylbenzene.

Dispersant-viscosity Modifier

[0037] Dispersant-viscosity modifiers are produced from grafting viscosity modifiers, such as those described above, with grafting materials such as, for example, maleic anhydride, and then reacting the grafted material with, for example, amines, amides, nitrogen-containing heterocyclic compounds or alcohol.

[0038] Examples of dispersant - viscosity modifiers include amine, derivatized hydrocarbyl-substituted mono-or dicarboxylic acids in which the hydrocarbyl substituent comprises a chain of sufficient length to impart viscosity index improving properties to the compounds. In general, the dispersant-viscosity modifier may be made from, for example, a polymer of a C_4 to C_{24} unsaturated ester of vinyl alcohol or a C_3 to C_{10} unsaturated mono-carboxylic acid or a C_4 to C_{10} di-carboxylic acid derivatized with an unsaturated nitrogen-containing monomer having 4 to 20 carbon atoms; a polymer of a C_2 to C_{20} olefin with an unsaturated C_3 to C_{10} mono- or di-carboxylic acid derivatized with an amine, hydroxyl amine or an alcohol; or a polymer of ethylene with a C_3 to C_{20} olefin further reacted either by grafting a C_4 to C_{20} unsaturated nitrogen-containing monomer thereon or by grafting an unsaturated acid onto the polymer backbone and then reacting carboxylic acid groups of the grafted acid with an amine, hydroxy amine or alcohol.

[0039] Preferred dispersant-viscosity modifiers comprise an aromatic amine derivatized, maleic anhydride grafted polymer. A preferred aromatic amine is N-phenyl -1,4 - phenylenediamine. Suitably the polymer is an ethylene-propylene copolymer. The polymer preferably has a number average molecular weight Mn of at least 5,000, preferably at least 8,000 and suitably at least 10,000. The polymer may have an Mn as high as 100,000, but is suitably no more than 60,000 and preferably around 40,000.

[0040] Suitable commercially available dispersant-viscosity modifiers include, but are not limited to, HiTec 5777, available from Afton Chemicals, or multifunctional polymethacrylate viscosity modifiers such as the Viscoplex™ or Acryloid™ range of products available from Rohmax GmbH

[0041] The present invention comprises a dispersant-viscosity modifier. It may be present in amounts of from 0.05 to 5 wt. %, preferably about 0.5 to 3 wt.% on an active matter basis.

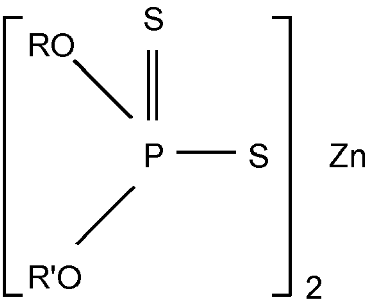
[0042] A lubricating oil composition according to the present invention may additionally comprise one or more standard crankcase lubricating oil additives; examples or which are discussed below.

Antioxidants

[0043] Antioxidants reduce the tendency of base stocks to deteriorate in service which deterioration can be evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces and by viscosity growth. In the present invention they are suitably present in amount of from 0.1 to 5.0 wt.%. Suitable oxidation inhibitors include hindered phenols, alkaline earth metal salts of alkylphenolthioesters having preferably C_5 to C_{12} alkyl side chains, calcium nonylphenol sulfide, ashless oil soluble phenates and sulfurized phenates, phosphosulfurized or sulfurized hydrocarbons, alkyl substituted diphenylamine, alkyl substituted phenyl and napthylamines, phosphorous esters, metal thiocarbamates, ashless thiocarbamates and oil soluble copper compounds as described in U.S. 4,867,890. Most preferred are the dialkyl substituted diphenylamines, wherein the alkyl is C_4-C_{20}, such as dinonyl diphenylamine and the hindered phenols, such as isooctyl-3,5-di-tert-butyl-4-hydroxycinnamate and mixtures of same.

Zinc Dihydrocarbyldithiophosphates

[0044] Zinc dihydrocarbyl dithiophosphates are oil soluble salts of dihydrocarbyl dithiophosphoric acids and may be represented by the following formula:

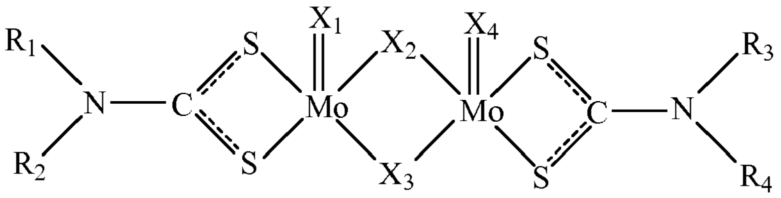


wherein R and R' may be the same or different hydrocarbyl radicals containing from 1 to 18, preferably 2 to 12, carbon atoms and including radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R and R' groups are alkyl groups of 2 to 8 carbon 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 (ZDDP) can therefore comprise zinc dialkyl dithiophosphates. ZDDP is the most commonly used antioxidant/antiwear agent in lubricating oil compositions for internal combustion engines, and in conventional passenger car diesel engines formulated to meet present European ACEA specifications. The lubricating oil compositions of the present invention suitably contain an amount of ZDDP (or other dihydrocarbyl dithiophosphate metal salt) that introduces about 0.02 to 0.12 wt.%, preferably 0.02 to 0.1 wt.%, more preferably 0.05 to 0.08 wt.% of phosphorus into the lubricating oil composition. The phosphorus content of the lubricating oil compositions is determined in accordance with the procedures of ASTM D5185.

Molybdenum Compound

[0045] For the lubricating oil compositions of this invention, any suitable oil soluble organo-molybdenum compound may be employed. The molybdenum compound is thought to function both as an antiwear and antioxidant additive. Preferably, dimeric and trimeric molybdenum compounds are used. Examples of such oil soluble organo-molybdenum compounds are the dialkyldithiocarbamates, dialkyldithiophosphates, dialkyldithiophosphinates, xanthates, thioxanthates, carboxylates and the like, and mixtures thereof. Particularly preferred are molybdenum dialkylthiocarbamates.

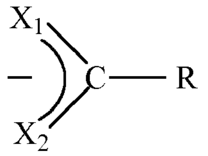
[0046] Suitable molybdenum dialkyldithiocarbamates include dimeric molybdenum dialkyldithiocarbamates such as those having the following formula:



R_1 through R_4 independently denote a straight chain, branched chain or aromatic hydrocarbyl group; and X1 through X4 independently denote an oxygen atom or a sulfur atom. The four hydrocarbyl groups, R_1 through R_4, may be identical or different from one another.

[0047] Another group of organo-molybdenum compounds useful in the lubricating compositions of this invention are trinuclear (trimeric) molybdenum compounds, especially those of the formula $Mo_3S_kL_nQ_z$ and mixtures thereof wherein the L are independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compound soluble in the oil, n is from 1 to 4, k varies from 4 to 7, Q is selected from the group of neutral electron donating compounds such as water, amines, alcohols, phosphines, and ethers, and z ranges from 0 to 5 and includes non-stoichiometric values. At least 21 total carbon atoms should be present among all the ligands' organo groups, such as at least 25, at least 30, or at least 35 carbon atoms.
The ligands are selected from the group consisting of

-X- R 1,



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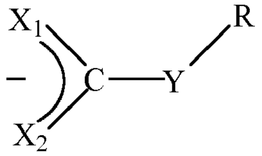

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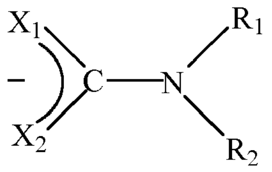

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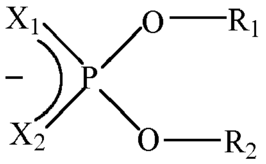

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and mixtures thereof, wherein X, X_1, X_2, and Y are independently selected from the group of oxygen and sulfur, and wherein R_1, R_2, and R are independently selected from hydrogen and organo groups that may be the same or different. Preferably, the organo groups are hydrocarbyl groups such as alkyl (e.g., in which the carbon atom attached to the remainder of the ligand is primary or secondary), aryl, substituted aryl and ether groups. More preferably, each ligand has the same hydrocarbyl group.

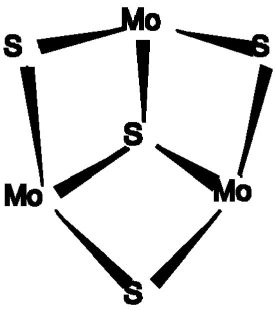
[0048] The term "hydrocarbyl" denotes a substituent having carbon atoms directly attached to the remainder of the ligand and is predominantly hydrocarbyl in character within the context of this invention. Such substituents include the following:

1. Hydrocarbon substituents, that is, aliphatic (for example alkyl or alkenyl), alicyclic (for example cycloalkyl or cycloalkenyl) substituents, aromatic-, aliphatic- and alicyclic-substituted aromatic nuclei and the like, as well as cyclic substituents wherein the ring is completed through another portion of the ligand (that is, any two indicated substituents may together form an alicyclic group).

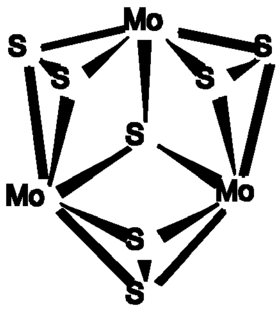
2. Substituted hydrocarbon substituents, that is, those containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbyl character of the substituent. Those skilled in the art will be aware of suitable groups (e.g., halo, especially chloro and fluoro, amino, alkoxyl, mercapto, alkylmercapto, nitro, nitroso, sulfoxy, etc.).

[0049] Importantly, the organo groups of the ligands should have a sufficient number of carbon atoms to render the compound soluble in the oil. For example, the number of carbon atoms in each group will generally range between about 1 to about 100, preferably from about 1 to about 30, and more preferably between about 4 to about 20. Preferred ligands include dialkyldithiophosphate, alkylxanthate, carboxylates, dialkyldithiocarbamate, and mixtures thereof. Most preferred are the dialkyldithiocarbamates. Those skilled in the art will realize that formation of the compounds requires selection of ligands having the appropriate charge to balance the core's charge (as discussed below).

[0050] Compounds having the formula $Mo_3S_kLQ_z$ have cationic cores surrounded by anionic ligands, wherein the cationic cores are represented by structures such as



6, and



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which have net charges of +4. Consequently, in order to solubilize these cores the total charge among all the ligands must be -4. Four monoanionic ligands are preferred. Without wishing to be bound by any theory, it is believed that two or more trinuclear cores may be bound or interconnected by means of one or more ligands and the ligands may be multidentate, i.e., having multiple connections to one or more cores. It is believed that oxygen and/or selenium may be substituted for sulfur in the core(s).

[0051] Oil-soluble trinuclear molybdenum compounds are preferred and can be prepared by reacting in the appropriate liquid(s)/solvent(s) a molybdenum source such as $(NH_4)_2Mo_3S_{13}$-$n(H_2O)$, where n varies between 0 and 2 and includes non-stoichiometric values, with a suitable ligand source such as a tetralkylthiuram disulfide. Other oil-soluble trinuclear molybdenum compounds can be formed during a reaction in the appropriate solvent(s) of a molybdenum source such as $(NH_4)_2Mo_3S_{13}\cdot n(H_2O)$, a ligand source such as tetralkylthiuram disulfide, dialkyldithiocarbamate, or dialkyldithiophosphate, and a sulfur abstracting agent such cyanide ions, sulfite ions, or substituted phosphines. Alternatively, a trinuclear molybdenum-sulfur halide salt such as $[M']_2[Mo_3S_7A_6]$, where M' is a counter ion, and A is a halogen such as Cl, Br, or I, may be reacted with a ligand source such as a dialkyldithiocarbamate or dialkyldithiophosphate in the appropriate liquid(s)/solvent(s) to form an oil-soluble trinuclear molybdenum compound. The appropriate liquid/solvent may be, for example, aqueous or organic.

[0052] The ligand chosen must have a sufficient number of carbon atoms to render the compound soluble in the lubricating composition. The term "oil-soluble" as used herein does not necessarily indicate that the compounds or additives are soluble in the oil in all proportions. It does mean that they are soluble in use, transportation, and storage.

[0053] A sulfurized molybdenum containing composition prepared by (i) reacting an acidic molybdenum compound and a basic nitrogen compound selected from the group consisting of succinimide, a carboxylic acid amide, a hydrocarbyl monoamine, a phosphoramide, a thiophosphoramide, a Mannich base, a dispersant-viscosity index improver, or a mixture thereof, in the presence of a polar promoter, to form a molybdenum complex (ii) reacting the molybdenum complex with a sulfur containing compound, to thereby form a sulfur and molybdenum containing composition is useful within the context of this invention. The sulfurized molybdenum containing compositions may be generally characterized as a molybdenum/sulfur complex of a basic nitrogen compound. The precise molecular formula of these molybdenum compositions is not known with certainty. However, they are believed to be compounds in which molybdenum, whose valences are satisfied with atoms of oxygen or sulfur, is either complexed by, or the salt of one or more nitrogen atoms of the basic nitrogen containing compound used in the preparation of these compositions.

[0054] The lubricating compositions of the present invention may contain a minor amount of an oil soluble molybdenum compound. If present an amount of at least 10 ppm up to about 600 ppm of molybdenum from a molybdenum compound may be present in the lubricating oil composition. Preferably, about 10 ppm to 300 ppm of molybdenum from a molybdenum compound is used. More preferably, no more than 100 ppm of molybdenum from a molybdenum compound is used. These values are based upon the weight of the lubricating composition.

Friction Modifiers

[0055] The lubricating oil composition may contain an organic oil-soluble friction modifier. Typically, the friction modifier may make up about 0.02 to 2.0 wt.% of the lubricating oil composition.

[0056] Friction modifiers include such compounds as aliphatic amines or ethoxylated aliphatic amines, aliphatic fatty acid amides, aliphatic carboxylic acids, aliphatic carboxylic esters of polyols such as glycerol esters of fatty acids as exemplified by glycerol oleate, which is preferred, aliphatic carboxylic ester-amides, aliphatic phosphonates, aliphatic thiophosphates, etc., wherein the aliphatic group usually contains above about eight carbon atoms so as to render the compound suitably oil soluble. Also suitable are aliphatic substituted succinimides formed by reacting one or more aliphatic succinic acids or anhydrides with ammonia.

[0057] 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. These may be used in amounts of from 0.01 to 5.0 wt.%, preferably about 0.1 to 3.0 wt.%. They are preferably used when mineral oil base stocks are employed but are not generally required when the base stock is a PAO or synthetic ester.

[0058] Foam control can be provided by many compounds including an antifoamant of the polysiloxane type, for example, silicone oil or polydimethyl siloxane.

[0059] Some of the above-mentioned additives can provide a multiplicity of effects; thus for example, a single additive may act as a dispersant-oxidation inhibitor. This approach is well known and does not require further elaboration.

[0060] 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. The invention comprising the product results from the admixture of the additive components to form a lubricating oil composition.

[0061] Preferably, the additives are blended together to form a concentrate or additive package that is subsequently blended into base stock to make the finished lubricant. The concentrate or additive package may contain the viscosity modifier, or the viscosity modifier may be added separately from the concentrate or additive package to form the lubricating oil composition. 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.

[0062] The final crankcase lubricating oil formulation may employ from 10 to 50 mass %, preferably 15 to 40 mass% of the concentrate or additive package, with the remainder being base stock.

[0063] The present invention will now be further described with references to the following illustrative examples; in which all quantities are given on a 100% active matter basis (i.e. excluding any diluent oil).

Example 1

[0064] Lubricating oil composition Oil A, was prepared by mixing an additive package comprising 4.8 mass% of a polyisobutenyl succinimide dispersant made from a polyisobutenyl with a number average molecular weight (Mn) of 2225, 1.08 mass% of polyisobutenyl succinimide dispersants made from a polyisobutenyl with a number average molecular weight (Mn) of 950, 0.74 mass% of a 321 TBN overbased calcium salicylate detergent and 0.34 mass% of a 565 TBN overbased calcium salicylate detergent, 0.43 mass% of 709 TBN overbased magnesium sulfonate detergent, 0.84 mass% of HiTec 5777 dispersant-viscosity modifier, and additional zinc dialkyl dithiophosphate, organic molybdenum dithiocarbamate and antioxidant into a base stock comprising a mixture of Group I and Group III base oils. Oil A comprised 0.96 wt% sulphated ash, 0.08 wt% phosphorous, 0.21 wt% sulfur, 130 ppm of atomic boron, 50 ppm molybdenum, 0.153 mass % calcium and 0.069 mass% magnesium. The salicylate soap content of Oil A was 8.8mmol and the total soap content of the Oil was 0.85 mass% soap. The calcium salicylate detergents provide the lubricating oil composition with 0.5 mass% calcium as sulphated ash. The dispersants provide the lubricating oil composition with 0.135 mass% nitrogen, with 0.096 mass% N being provided by the high molecular weigh dispersant and 0.039 mass% being provided by low molecular weight dispersant.

[0065] Oil A was then run in the ASTM D7422 engine test, more commonly known as the Mack T-12. The Mack T-12 test is designed to evaluate the ability of an oil to minimize wear in an engine equipped with an EGR system. The Mack T-12 engine test is part of the API CJ-4 and ACEA E6 performance categories.

[0066] The engine used is a modified Mack E7 E-Tech 460 rated at 460 bhp and 1,800 rpm, with EGR system. The test runs over 300 hours and at the end of the test piston ring wear, cylinder liner wear, lead bearing corrosion, oil consumption and oxidation are evaluated.

[0067] The pass fail limits and the results for Oil A are set out in Table 1 below:

Table 1

Criteria	Pass/Fail Limit	Oil A
Top ring weight loss	<105	73
Cylinder wear	≤21	5.9
Lead corrosion	≤30	23
Oil Consumption	≤80	56.8
Merits	1000	1342

[0068] Oil A clearly passed the Mack T-12 test at the required API CJ-4 and ACEA E6 performance levels.

Example 2

[0069] Lubricating oil composition Oil B, was prepared by mixing an additive package comprising 4.8 mass% of a polyisobutenyl succinimide dispersant made from a polyisobutenyl with a number average molecular weight (Mn) of 2225, 1.08 mass% of polyisobutenyl succinimide dispersants made from a polyisobutenyl with a number average molecular weight (Mn) of 950, 0.84 mass% of a 321 TBN overbased calcium salicylate detergent and 0.34 mass% of a 565 TBN overbased calcium salicylate detergent, 0.43 mass% a 709 TBN of overbased magnesium sulfonate detergent, 0.84 mass% of HiTec 5777 dispersant-viscosity modifier, and zinc dialkyl dithiophosphate, molybdenum dithiocarbamate and antioxidant, into a base stock comprising a mixture of Group I and Group III base oils. Oil B comprised 1.0 wt% sulphated ash, 0.08 wt% phosphorous, 0.21 wt% sulfur, 130 ppm of atomic boron 50 ppm molybdenum, 0.165 mass% calcium and 0.069 mass% magnesium. The salicylate soap content of Oil B was 9.8mmol and the total soap content of the Oil was 0.92mass% soap. The calcium salicylate detergents providing the lubricating oil composition with 0.54 mass% calcium as sulphated ash. The dispersants provide the lubricating oil composition with 0.135 mass% nitrogen, with 0.096 mass% nitrogen being provided by high molecular weight dispersant and 0.039 mass% being provided by low molecular weight dispersant.

[0070] Oil B was then run in the Mercedes-Benz OM646 LA (CEC L-99-08) engine test, which is part of the ACEA and Daimler specifications . This 300-hour test uses the 2.2L common rail diesel OM646 DE 22 LA engine to evaluate engine lubricant performance with respect to engine wear and overall cleanliness, as well as piston cleanliness and ring sticking.

[0071] The pass fail limits and the results for Oil B are set out in Table 2 below:

Table 2

Criteria	Pass/Fail Limit (ACEA E6)	Oil B
Cam outlet wear	≤140	87.3

[0072] It can be seen from the results in Table 2 that Oil B passes the OM646LA engine test at the required performance level for ACEA E6. The test also achieves all of the necessary parameters for the more stringent MB 228.51 specification level.

Claims

1. A lubricating oil composition having a phosphorus content of up to 0.12 wt%, a sulfated ash content of up to 1.2 wt% comprising:

    (a) a major amount of an oil of lubricating viscosity;
    (b) an alkali metal or alkaline earth metal alkyl salicylate lubricating oil detergent providing from 7-15 mmol salicylate soap per kilogram of lubricating oil composition;
    (c) one or more ashless, nitrogen-containing dispersants providing the lubricating oil composition with from at least 0.12 wt% to 0.20 wt% atomic nitrogen, based on the weight of the lubricating oil composition, and
    (d) a dispersant-viscosity modifier.

2. A lubricating oil composition according to claim 1, wherein the phosphorous content is no more than 0.08 wt%.

3. A lubricating oil composition according to claim 1 or 2, wherein the sulfated ash content is no more than 1.0 wt%.

4. A lubricating oil composition according to claim 1, 2 or 3, wherein the alkali metal or alkaline earth metal alkyl salicylate lubricating oil detergent providing from 8-11 mmol salicylate soap per kilogram of lubricating oil composition.

5. A lubricating oil composition according to any one of the preceding claims, wherein the one or more dispersants provide the lubricating oil composition with from at least 0.12 wt% to 0.17 wt% atomic nitrogen, based on the weight of the lubricating oil composition.

6. A lubricating oil composition according to any one of the preceding claims, wherein the alkali metal or alkaline earth metal alkyl salicylate is calcium or magnesium salicylate or a combination thereof.

7. A lubricating oil composition according to any one of the preceding claims, further comprising an alkaline earth metal alkyl sulphonate lubricating oil detergent.

8. A lubricating oil composition according to any one of the preceding claims, wherein the dispersant is a polyisobutenyl succinimide dispersant.

9. A lubricating oil composition according to any one of the preceding claims which meets the requirements of both the API-CJ4 specification and the ACEA E6 specification.

10. A method of lubricating a vehicle engine comprising an exhaust gas recirculation (EGR) system comprising use in that engine of a lubricating oil composition according to any one of claims 1 to 9.

11. A method according to claim 10, wherein the engine is a compression ignition engine.

12. A method according to claim 11, wherein the engine is a heavy duty diesel engine.

13. A method according to any one of claims 10 -12, wherein the engine further comprises a selective catalytic reduction device.

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EUROPEAN SEARCH REPORT

Application Number
EP 11 15 9502

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X	US 2008/153722 A1 (VAN LEEUWEN JEROEN [NL] ET AL) 26 June 2008 (2008-06-26) * paragraphs [0062], [0063], [0077]; claims 1,6,9; table 2 * -----	1-13	INV. C10M163/00 C10M167/00 ADD. C10N30/06 C10N40/25
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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	9 June 2011	Bertrand, Samuel

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