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(54) **Lubricating oil compositions**

(57) A lubricant comprises (A) an oil of lubricating viscosity; (B) as an additive component, an oil-soluble zinc salt of a dithiophosphoric acid, the acid being obtainable by reacting phosphorus pentasulfide with a mixture of at least one first alcohol, and at least one second alcohol, the first alcohol having the formula ROH where R is an aliphatic hydrocarbyl group having at least four carbon atoms or is an aralkyl group, and the second alcohol being an ester of a polyhydric alcohol; and (C) as an additive component, an oil-soluble molybdenum compound having a di- or trinuclear molybdenum- and sulfur-containing core.

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Description

FIELD OF THE INVENTION

[0001] This invention relates to automotive lubricating oil compositions, more especially to compositions suitable for use in piston engine, especially gasoline (spark-ignited) and diesel (compression-ignited), crankcase lubrication, such compositions being referred to as crankcase lubricants; and to use of additives in friction modification. The invention also concerns use of friction modifiers in automotive lubrication.

BACKGROUND OF THE INVENTION

[0002] A crankcase lubricant is an oil used for general lubrication in an engine where there is an oil sump below the crankshaft of the engine and to which circulated oil returns. It is well known to include additives in crankcase lubricants for several purposes. Friction modifiers, also referred to as friction-reducing agents, may be boundary additives that operate by lowering friction coefficient and hence improve fuel economy; the use of glycerol monoesters as friction modifiers has been described in the art, for example in US-A-4,495,088; US-A-4,683,069; EP-A-0 092 946; and WO-A-01/72933. Glycerol monoester friction modifiers have been and are used commercially.

[0003] Other examples of friction modifiers are inorganic friction modifiers in the form of oil-soluble molybdenum-sulfur compounds such as described in US-B1-6,232,276. These too have been and are used commercially.

[0004] There may be advantages in using organic glycerol monoester friction modifiers in combination with inorganic molybdeunum-sulfur friction modifiers in crankcase lubricants. It has, however, been found that, in such use, glycerol monoesters may disrupt the beneficial formation of low friction molybdenum disulfide films (from the molybdenum-sulfur compounds) in boundary contacts and may appear to reduce the efficiency of phosphate glass wear-film formation at low temperatures. The art describes use of glycerol monoesters in combination with molybdenum-sulfur compounds in crankcase lubricants that also contain zinc dihydrocarbyl dithiophosphate compounds. See, for example, US-A1-2003/0199399 and US-A1-2006/0111253.

SUMMARY OF THE INVENTION

[0005] This invention meets the above-mentioned problem by chemically incorporating glycerol monoesters, and similar molecules, into zinc dihydrocarbyl dithiophosphate during preparation of the latter. It is then found that the problem is ameliorated as evidenced by the data in this specification. US-A-5,013,465 describes zinc dihydrocarbyl dithiophosphates having glycerol monoesters incorporated therein. It indicates their use in lubricating oil compositions with molybdenum friction modifiers. However, the friction modifiers are stated to be molybdenum complexes of polyisobutenyl succinic anhydride-amino alkenols rather than the molybdenum-sulfur compounds used in the present invention. Further, the application is indicated as being in automotive transmission fluids rather than crankcase lubrication.

[0006] In a first aspect, the invention comprises a lubricating oil composition comprising

(A) an oil of lubricating viscosity;

(B) as an additive component, an oil-soluble zinc salt of a dithiophosphoric acid, the dithiophosphoric acid being the reaction product of phosphorus pentasulphide with a mixture of at least one first alcohol and at least one second alcohol, the first alcohol having the formula ROH where R is an aliphatic hydrocarbyl group having at least four carbon atoms or is an alkaryl group, and the second alcohol being an ester of a polyhydric alchohol; and

(C) as an additive component, an oil-soluble molybdenum compound having a di-or trinuclear molybdenum- and sulphur-containing core.

[0007] In a second aspect, this invention provides a method of lubricating the crankcase of an internal combustion engine comprising operating the engine with the composition of the first aspect of the invention when the oil of lubricating viscosity is present in a major amount.

[0008] In a third aspect, this invention provides the use, in the lubrication of the crankcase of an internal combustion engine, of a combination of additive components (B) and (C), as defined in the first aspect of the invention, to improve their compatibility in a lubricating oil composition over the compatibility of (C) with an organic friction modifier in the form of said second alcohol in an analogous lubricating oil composition that contains the zinc salt in which an alcohol of formula ROH replaces the second alcohol, the improvement in compatability being determined by assessing sediment formation as a measure of additive package stability. To assess sediment formation, two additive packages are formulated, one with the additive component (B) and the other with a standard zinc dialkyldithiophosphate and an equivalent

amount of the ester of a polyhydric alcohol to that delivered to the package by the additive component (B) at the treat-rate used. The packages are stored at elevated temperature and the amount of sediment formed over a period of twelve weeks assessed.

[0009] In this specification, the following words and expressions, if and when used, have the meanings ascribed below:

"active ingredients" or "(a.i.)" refers to additive material that is not diluent or solvent;

"comprising" or any cognate word specifies the presence of stated features, steps, or integers or components, but does not preclude the presence or addition of one or more other features, steps, integers, components or groups thereof. The expressions "consists of" or "consists essentially of" or cognates may be embraced within "comprises" or cognates, wherein "consists essentially of" permits inclusion of substances not materially affecting the characteristics of the composition to which it applies;

"hydrocarbyl" means a chemical group of a compound that contains hydrogen and carbon atoms and that is bonded to the remainder of the compound directly via a carbon atom. The group may contain one or more atoms other than carbon and hydrogen ("hetero atoms") provided they do not affect the essentially hydrocarbyl nature of the group;

"major amount" means in excess of 50 mass % of a composition;

"minor amount" means less than 50 mass % of a composition;

phosphorus content is measured by ASTM D5185; and

molybdenum content is measured by ASTM D5185.

[0010] Also, it will be understood that various components used, essential as well as optimal and customary, may react under conditions of formulation, storage or use and that the invention also provides the product obtainable or obtained as a result of any such reaction.

[0011] Further, it is understood that any upper and lower quantity, range and ratio limits set forth herein may be independently combined.

DETAILED DESCRIPTION OF THE INVENTION

[0012] The features of the invention relating, where appropriate, to each and all aspects of the invention, will now be described in more detail as follows:

OIL OF LUBRICATING VISCOSITY (A)

[0013] The oil of lubricating viscosity (sometimes referred to as "base stock" or "base oil") is the primary liquid constituent of a lubricant, into which additives and possibly other oils are blended, for example to produce a final lubricant (or lubricant composition).

[0014] A base oil is useful for making concentrates as well as for making lubricating oil compositions therefrom, and may be selected from natural (vegetable, animal or mineral) and synthetic lubricating oils and mixtures thereof. It may range in viscosity from light distillate mineral oils to heavy lubricating oils such as gas engine oil, mineral lubricating oil, motor vehicle oil and heavy duty diesel oil. Generally the viscosity of the oil ranges from 2 to 30, especially 5 to 20, mm^2s^{-1} at 100°C.

[0015] Natural oils include animal and vegetable oils (e.g. castor and lard oil), liquid petroleum oils and hydrorefined, solvent-treated mineral lubricating oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils.

[0016] Synthetic lubricating oils include hydrocarbon oils such as polymerized and interpolymerized olefins (e.g. polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes)); alkylbenzenes (e.g. dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes); polyphenols (e.g. biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogues and homologues thereof.

[0017] Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g. phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) with a variety of alcohols (e.g. butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether,

propylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

[0018] Esters useful as synthetic oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols, and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

[0019] Unrefined, refined and re-refined oils can be used in the compositions of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from distillation or ester oil obtained directly from an esterification process and used without further treatment would be unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation are known to those skilled in the art. Re-refined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such re-refined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for approval of spent additive and oil breakdown products.

[0020] Other examples of base oil are gas-to-liquid ("GTL") base oils, i.e. the base oil may be an oil derived from Fischer-Tropsch synthesised hydrocarbons made from synthesis gas containing H_2 and CO using a Fischer-Tropsch catalyst. These hydrocarbons typically require further processing in order to be useful as a base oil. For example, they may, by methods known in the art, be hydroisomerized; hydrocracked and hydroisomerized; dewaxed; or hydroisomerized and dewaxed.

[0021] Base oil may be categorised in Groups I to V according to the API EOLCS 1509 definition.

[0022] When the oil of lubricating viscosity is used to make a concentrate, it is present in a concentrate-forming amount (e.g., from 30 to 70, such as 40 to 60, mass %) to give a concentrate containing for example 1 to 90, such as 10 to 80, preferably 20 to 80, more preferably 20 to 70, mass % active ingredient of an additive or additives, being components (B) and (C) above, optionally with one or more co-additives. The oil of lubricating viscosity used in a concentrate is a suitable oleaginous, typically hydrocarbon, carrier fluid, e.g. mineral lubricating oil, or other suitable solvent. Oils of lubricating viscosity such as described herein, as well as aliphatic, naphthenic, and aromatic hydrocarbons, are examples of suitable carrier fluids for concentrates.

[0023] Concentrates constitute a convenient means of handling additives before their use, as well as facilitating solution or dispersion of additives in lubricating oil compositions. When preparing a lubricating oil composition that contains more than one type of additive (sometime referred to as "additive components"), each additive may be incorporated separately, each in the form of a concentrate. In many instances, however, it is convenient to provide a so-called additive "package" (also referred to as an "adpack") comprising one or more co-additives, such as described hereinafter, in a single concentrate.

[0024] In the present invention, the oil of lubricating viscosity may be provided in a major amount, in combination with a minor amount of components (B) and (C) and, if necessary, one or more co-additives, such as described hereinafter, constituting a lubricating oil composition. This preparation may be accomplished by adding the additive directly to the oil or by adding it in the form of a concentrate thereof to disperse or dissolve the additive. Additives may be added to the oil by any method known to those skilled in the art, either before, at the same time as, or after addition of other additives.

[0025] The terms "oil-soluble" or "oil-dispersible", or cognate terms, used herein do not necessarily indicate that the compounds or additives are soluble, dissolvable, miscible, or are capable of being suspended in the oil in all proportions. These do mean, however, that they are, for example, soluble or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired.

[0026] The lubricating oil compositions of the invention may be used to lubricate mechanical engine components, particularly in internal combustion engines, e.g. spark-ignited or compression-ignited two- or four-stroke reciprocating engines, by adding the composition thereto. Preferably, they are crankcase lubricants.

[0027] The lubricating oil compositions of the invention (and also concentrates) comprise defined components that may or may not remain the same chemically before and after mixing with an oleaginous carrier. This invention encompasses compositions which comprise the defined components before mixing, or after mixing, or both before and after mixing.

[0028] When concentrates are used to make the lubricating oil compositions, they may for example be diluted with 3 to 100, e.g. 5 to 40, parts by mass of oil of lubricating viscosity per part by mass of the concentrate.

[0029] When the invention is a lubricating oil composition comprising a major amount of an oil of lubricating viscosity, the composition may have low levels of one or more of sulfated ash, phosphorus or sulfur. Thus, the composition may, for example, contain up to 1.2, preferably up to 1.0, mass % of sulfated ash, based on the total mass of the composition. It may, for example, contain up to 0.1, preferably up to 0.08, more preferably up to 0.06, mass % of phosphorus, expressed

as atoms of phosphorus, based on the total mass of the composition. It may, for example, contain up to 0.4, preferably up to 0.2, mass % of sulfur expressed as atoms of sulfur, based on the total mass of the composition.

ADDITIVE COMPONENT (B)

[0030] This is obtainable by reacting a basic zinc compound with a dithiophosphoric acid obtainable by reacting phosphorus pentasulfide with a mixture of at least one first alcohol of the formula ROH, where R is an aliphatic hydrocarbyl group having at least four carbon atoms, and at least one second alcohol which is an ester of a polyhydric alcohol.

[0031] The group R of the at least one first alcohol of the formula ROH has, for example, 4 to 12, preferably 4 to 10, more preferably 5 to 8, carbon atoms. The group R may be an alkyl or alkenyl group but it is preferably an alkyl group.

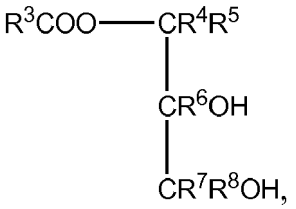
[0032] Suitable alkyl groups which R may represent include n-butyl, iso-butyl, sec-butyl, amyl, sec-hexyl, n-heptyl, n-octyl, iso-octyl or n-decyl, preferably sec-butyl, 4-methyl-2-pentyl or iso-octyl, more preferably 4-methyl-2-pentyl or iso-octyl, especially 4-methyl-2-pentyl.

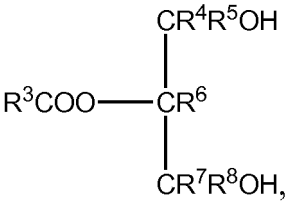
[0033] Preferably, when R represents an alkyl group, greater than 60, more preferably greater than 70, even more preferably greater than 80, even more preferably greater than 90, mole %, most preferably essentially all of the alkyl groups which R represents, are secondary alkyl groups, especially 4-methyl-2-pentyl groups.

[0034] Suitable alkenyl groups which R may represent include an alkyl phenyl group, especially a C_7 to C_{12} alkyl phenyl group, e.g. branched nonyl phenyl or branched dodecyl phenyl.

[0035] R may be a mixture, i.e. derived from a mixture of alcohols ROH as defined herein. In accordance with a preferred embodiment, R comprises a single aliphatic hydrocarbyl group, especially a single alkyl group as defined herein.

[0036] The second alcohol may have the formula $R^1(OH)_n$ where R^1 represents one or more ester-containing moieties, preferably monoester containing moieties, containing hydrogen and carbon atoms and having at least 12 carbon atoms and n is 1 or 2. Preferably, the second alcohol is a glyceryl derivative having the formula





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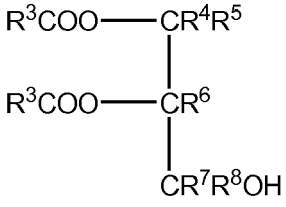

where R^3 is an aliphatic hydrogen- and carbon-containing group containing at least 9 carbon atoms and R^4, R^5, R^6, R^7 and R^8 are each independently hydrogen or alkyl groups. R^3 is preferably alkyl or alkenyl, usually with 9 to 30, preferably

12 to 26, more preferably 12 to 22, even more preferably 16 to 18, especially 18, carbon atoms. R^3 may for example be lauryl, myristyl, palmityl, stearyl, behenyl, oleyl, linoleyl or linolenyl, especially oleyl. R^4, R^5, R^6, R^7 and R^8 may be alkyl groups though they are all preferably hydrogen atoms.

[0037] Most preferably, the second alcohol comprises glycerol monooleate, glycerol dioleate or a mixture thereof, especially predominantly glycerol monooleate.

[0038] Suitably, the additive component (B) is formed by reacting a basic zinc compound with a dithiophosphoric acid obtainable by reacting phosphorus pentasulfide with a mixture comprising 75 to 95, preferably 75 to 90, mass % of the at least one first alcohol of the formula ROH and 5 to 25, preferably 10 to 25, mass % of the at least one second alcohol which is an ester of a polyhydric alcohol.

[0039] Suitably, the additive component (B) is present in an amount of 0.1 to 10, preferably 0.1 to 5, more preferably 0.1 to 2, mass % of the lubricating oil composition, based on the total mass of the lubricating oil composition.

[0040] In accordance with a preferred embodiment of the present invention, the additive component (B) represents the sole phosphorus-containing additive component in the lubricating oil composition.

ADDITIVE COMPONENT (C)

[0041] This may be any suitable oil-soluble organo-molybdenum compound, having a molybdenum-sulfur core. As examples there may be mentioned dithiocarbamates, dithiophosphates, dithiophosphinates, xanthates, thioxanthates, sulfides, and mixtures thereof. Particularly preferred are molybdenum dithiocarbamates, dialkyldithiophosphates, alkyl xanthates and alkylthioxanthates.

[0042] The molybdenum compound is, as stated above, dinuclear or trinuclear.

[0043] One class of preferred organo-molybdenum compounds useful in all aspects of the present invention is tri-nuclear molybdenum compounds of the formula $Mo_3S_kL_nQ_z$ and mixtures thereof wherein L are independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compounds soluble or dispersible in the oil, n is from 1 to 4, k varies from 4 through 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.

[0044] The molybdenum compounds may be present in a lubricating oil composition at a concentration in the range 0.1 to 2 mass %, or providing at least 10, such as 50 to 2,000, ppm by mass of molybdenum atoms.

[0045] Preferably, the molybdenum from the molybdenum compound is present in an amount of from 10 to 1500, such as 20 to 1000, more preferably 30 to 750, ppm based on the total weight of the lubricating oil composition. For some applications, the molybdenum is present in an amount of greater than 500 ppm.

CO-ADDITIVES

[0046] Co-additives, with representative effective amounts, that may also be present, different from (B) and (C), are listed below. All the values listed are stated as mass percent active ingredient.

Additive	Mass % (Broad)	Mass % (Preferred)
Ashless Dispersant	0.1 - 20	1 - 8
Metal Detergents	0.1 - 15	0.2 - 9
Corrosion Inhibitor	0 - 5	0 - 1.5
Metal Dihydrocarbyl Dithiophosphate	0 - 10	0 - 4
Anti-Oxidants	0 - 5	0.01 - 3
Pour Point Depressant	0.01 - 5	0.01 - 1.5
Anti-Foaming Agent	0 - 5	0.001 - 0.15
Supplement Anti-Wear Agents	0 - 5	0 - 2
Viscosity Modifier (1)	0 - 6	0.01 - 4
Mineral or Synthetic Base Oil	Balance	Balance

(1) Viscosity modifiers are used only in multi-graded oils.

[0047] The final lubricating oil composition, typically made by blending the or each additive into the base oil, may contain from 5 to 25, preferably 5 to 18, typically 7 to 15, mass % of the concentrate, the remainder being oil of lubricating

viscosity.

[0048] The above mentioned co-additives are discussed in further detail as follows; as is known in the art, some additives can provide a multiplicity of effects, for example, a single additive may act as a dispersant and as an oxidation inhibitor.

[0049] A dispersant is an additive whose primary function is to hold solid and liquid contaminations in suspension, thereby passivating them and reducing engine deposits at the same time as reducing sludge depositions. For example, a dispersant maintains in suspension oil-insoluble substances that result from oxidation during use of the lubricant, thus preventing sludge flocculation and precipitation or deposition on metal parts of the engine.

[0050] Dispersants are usually "ashless", that is non-metallic organic materials that form substantially no ash on combustion, in contrast to metal-containing, and hence ash-forming materials. They comprise a long hydrocarbon chain with a polar head, the polarity being derived from inclusion of e.g. an O, P, or N atom. The hydrocarbon is an oleophilic group that confers oil-solubility, having, for example 40 to 500 carbon atoms. Thus, ashless dispersants may comprise an oil-soluble polymeric backbone.

[0051] A preferred class of olefin polymers is constituted by polybutenes, specifically polyisobutenes (PIB) or poly-n-butenes, such as may be prepared by polymerization of a C_4 refinery stream.

[0052] Dispersants include, for example, derivatives of long chain hydrocarbon-substituted carboxylic acids, examples being derivatives of high molecular weight hydrocarbyl-substituted succinic acid. A noteworthy group of dispersants is constituted by hydrocarbon-substituted succinimides, made, for example, by reacting the above acids (or derivatives) with a nitrogen-containing compound, advantageously a polyalkylene polyamine, such as a polyethylene polyamine. Particularly preferred are the reaction products of polyalkylene polyamines with alkenyl succinic anhydrides, such as described in US-A-3,202,678; - 3,154,560; -3,172,892; -3,024,195; -3,024,237, -3,219,666; and -3,216,936, that may be post-treated to improve their properties, such as borated (as described in US-A-3,087,936 and - 3,254,025) fluorinated and oxylated. For example, boration may be accomplished by treating an acyl nitrogen-containing dispersant with a boron compound selected from boron oxide, boron halides, boron acids and esters of boron acids.

[0053] A detergent is an additive that reduces formation of piston deposits, for example high-temperature varnish and lacquer deposits, in engines; it normally has acid-neutralising properties and is capable of keeping finely divided solids in suspension. Most detergents are based on metal "soaps", that is metal salts of acidic organic compounds.

[0054] Detergents generally comprise a polar head with a long hydrophobic tail, the polar head comprising a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal when they are usually described as normal or neutral salts and would typically have a total base number or TBN (as may be measured by ASTM D2896) of from 0 to 80. Large amounts of a metal base can be included by reacting an excess of a metal compound, such as an oxide or hydroxide, with an acidic gas such as carbon dioxide. The resulting overbased detergent comprises neutralised detergent as an outer layer of a metal base (e.g. carbonate) micelle. Such overbased detergents may have a TBN of 150 or greater, and typically of from 250 to 500 or more.

[0055] Detergents that may be used include oil-soluble neutral and overbased sulfonates, 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 and sulfurized phenates having a TBN of from 50 to 450.

[0056] Anti-oxidants are sometimes referred to as oxidation inhibitors; they increase the resistance of the composition to oxidation and may work by combining with and modifying peroxides to render them harmless, by decomposing peroxides, or by rendering an oxidation catalyst inert. Oxidative deterioration can be evidenced by sludge in the lubricant, varnish-like deposits on the metal surfaces, and by viscosity growth.

[0057] They may be classified as radical scavengers (e.g. sterically-hindered phenols, secondary aromatic amines, and organo-copper salts); hydroperoxide decomposers (e.g., organosulphur and organophosphorus additives); and multifunctionals (e.g. zinc dihydrocarbyl dithiophosphates, which may also function as anti-wear additives, and organo-molybdenum compounds, which may also function as friction modifiers and anti-wear additives).

[0058] Examples of suitable antioxidants are selected from copper-containing antioxidants, sulphur-containing antioxidants, aromatic amine-containing antioxidants, hindered phenolic antioxidants, dithiophosphates derivatives, metal thiocarbamates, and molybdenum-containing compounds.

[0059] Dihydrocarbyl dithiophosphate metals salts are frequently used as antiwear and antioxidant agents. The metal may be an alkali or alkaline earth metal, or aluminium, lead, tin, zinc molybdenum, manganese, nickel or copper. Zinc salts are most commonly used in lubricating oil such as in amounts of 0.1 to 10, preferably 0.2 to 2, mass %, based upon the total mass of the lubricating oil compositions. They may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohols or a phenol with P_2S_5, and then neutralising the formed DDPA with a zinc compound. For example, a dithiophosphoric acid may be made by reaction with mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be pre-

pared where the hydrocarbyl groups on one acid are entirely secondary in character and the hydrocarbyl groups on the other acids 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 use of an excess of the basic zinc compound in the neutralisation reaction.

[0060] Anti-wear agents reduce friction and excessive wear and are usually based on compounds containing sulphur or phosphorous or both, for example that are capable of depositing polysulfide films on the surfaces involved. Noteworthy are the dihydrocarbyl dithiophosphates, such as the zinc dialkyl dithiophosphates (ZDDP's) discussed herein.

[0061] Examples of ashless anti-wear agents include 1,2,3-triazoles, benzotriazoles, thiadiazoles, sulfurised fatty acid esters, and dithiocarbamate derivatives.

[0062] Rust and corrosion inhibitors serve to protect surfaces against rust and/or corrosion. As rust inhibitors there may be mentioned non-ionic polyoxyalkylene polyols and esters thereof, polyoxyalkylene phenols, and anionic alkyl sulfonic acids.

[0063] Pour point depressants, otherwise known as lube oil flow improvers, lower the minimum temperature at which the oil will flow or can be poured. Such additives are well known. Typical of these additive are C_8 to C_{18} dialkyl fumarate/ vinyl acetate copolymers and polyalkylmethacrylates.

[0064] Additives of the polysiloxane type, for example silicone oil or polydimethyl siloxane, can provide foam control.

[0065] A small amount of a demulsifying component may be used. A preferred demulsifying component is described in EP-A-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.

[0066] Viscosity modifiers (or viscosity index improvers) impart high and low temperature operability to a lubricating oil. Viscosity modifiers that also function as dispersants are also known and may be prepared as described above for ashless dispersants. In general, these dispersant viscosity modifiers are functionalised polymers (e.g. interpolymers of ethylenepropylene post-grafted with an active monomer such as maleic anhydride) which are then derivatised with, for example, an alcohol or amine.

[0067] The lubricant may be formulated with or without a conventional viscosity modifier and with or without a dispersant viscosity modifier. Suitable compounds for use as viscosity modifiers are generally high molecular weight hydrocarbon polymers, including polyesters. Oil-soluble viscosity modifying polymers generally have weight average molecular weights of from 10,000 to 1,000,000, preferably 20,000 to 500,000, which may be determined by gel permeation chromatography or by light scattering.

EXAMPLES

[0068] The invention will now be particularly described in the following examples which are not intended to limit the scope of the claims hereof.

[0069] In the examples, the following additive components were used:

B: an oil-soluble zinc salt of a dithiophosphoric acid, the acid being the reaction product of P_2S_5 with a mixture of sec-C_6 alcohol and glycerol monooleate, the salt being made substantially as described in US-A-5,013,465;

C: an oil-soluble molybdenum dithiocarbamate having a trinuclear molybdenum- and sulfur-containing core and a dicocoamine-derived supporting ligand, and having the structure described in US 6232276, and being made as described in US 6569820;

X: an oil-soluble zinc salt of a dithiophosphoric acid, the acid being the reaction product of P_2S_5 with a sec-C_6 alcohol;

Y: glycerol monoleate as used in making additive component B above.

[0070] Using the same base oil, the above components were blended into lubricating oil compositions to provide an example of the invention (Example 1) and two reference examples (Examples 1^1 and 2^1) for comparison purposes. Each composition contained 0.08 mass % phosphorus and 75 ppm by mass of molybdenum. Further composition content is set forth below under the "Testing and Results" heading.

TESTING AND RESULTS

HFRR Tests

[0071] A high frequency reciprocating rig (HFRR), supplied by PCS Instruments, was used to evaluate the coefficient

of friction of each of the above compositions. The test was carried out at 20 HZ, 400g applied load, for 60 minutes at 120°C. Results were obtained as a trace of the average of three runs for each composition; a selection of the results is tabulated below where the values are coefficients of friction.

Example	Time (minutes)		
	1	25	40
1 (B+C)	0.174	0.097	0.089
1[1] (X + Y + C)	0.150	0.160	0.088
2[1] (X + C)	0.184	0.089	0.086

[0072] Each example had a comparable treat rate of 9 mass % of total additive package. Example 1 contained 1.187 mass % of B and Example 1[1] contained 1.000 mass % of X and 0.180 mass % of Y. Example 2[1], as a control, contained 1.000 mass % of X.

[0073] The results show that Example 1[1] is initially better than Example 1 but that Example 1 then gives rise to a significant drop in coefficient of friction which is not exhibited by Example 1[1]. Without wishing to be bound by any theory, an explanation is that free glycerol monooleate (Y) initially forms a surface film in Example 1[1]; a molybdenum sulfide film (from component C) forms after a few minutes in Example 1 to give rise to the observed drop in coefficient of friction; in Example 1[1], the free glycerol monooleate (Y) retards formation of the beneficial molybdenum disulfide film. Thus, incorporating glycerol monooleate into zinc dialkyl dithiophosphate, as in Example 1, eliminates the detrimental effect of free glycerol monooleate on molybdenum disulfide film formation.

MTM SLIM Tests (i.e. Mini-traction machine with spacer layer image mapping) (supplied by PCS Instruments)

[0074] MTM SLIM testing has been described in the literature - see Kapadia R, Glyde R, Wu Y L. Tribology Int., 40, (2007) 1667-1679.

[0075] Results were obtained in the form of traces. A selection of the results is tabulated below where the values are film thickness in nm.

Example	Time (minutes)						
	0	10	20	30	40	50	60
1 (B + C)	0.00	3.39	68.44	90.57	108.16	112.70	115.69
1[1] (X + Y + C)	0.01	0.01	0.02	0.02	0.04	0.63	11.41
2[1] (X + C)	0.00	19.18	67.47	89.54	95.57	109.81	114.08

[0076] The results demonstrate that the presence of free glycerol monooleate in Example 1[1] gives rise to much poorer film formation. Without wishing to be bound by any theory, it is believed that the free glycerol monooleate (Y) in Example 1[1] forms a surface film that prevents or inhibits phosphate glass or molybdenum disulfide film from forming. Thus, incorporating glycerol monooleate into the zinc dithiophosphate as in Example 1 eliminates the detrimental effect of free glycerol monooleate on phosphate glass or molybdenum disulfide film formation.

Claims

1. A lubricating oil composition comprising

(A) an oil of lubricating viscosity;
(B) as an additive component, an oil-soluble zinc salt of a dithiophosphoric acid, the dithiophosphoric acid being the reaction product of phosphorus pentasulphide with a mixture of at least one first alcohol and at least one second alcohol, the first alcohol having the formula ROH where R is an aliphatic hydrocarbyl group having at least four carbon atoms or is an alkaryl group, and the second alcohol being an ester of a polyhydric alchohol; and
(C) as an additive component, an oil-soluble molybdenum compound having a di-or trinuclear molybdenum- and sulphur-containing core.

2. The composition as claimed in claim 1, where the oil of lubricating viscosity is present in a concentrate-forming amount.

3. The composition as claimed in claim 1, where the oil of lubricating viscosity is present in a major amount.

4. The composition as claimed in any of claims 1 to 3 further comprising one or more co-additives, different form (B) and from (C), selected from ashless dispersants, metal detergents, corrosion inhibitors, antioxidants, pour point dispersants, friction modifiers, antifoam agents and viscosity modifiers.

5. A method of lubricating the crankcase of an internal combustion engine comprising operating the engine with the composition of claim 3 or of claim 4 when appendant to claim 3.

6. The use, in the lubrication of the crankcase of an internal combustion engine, of a combination of additive components (B) and (C), as defined in claim 1, to improve their compatibility in a lubricating oil composition over the compatibility of (C) with an organic friction modifier in the form of said second alcohol in an analogous lubricating oil composition that contains the zinc salt in which an alcohol of formula ROH replaces the second alcohol, the improvement in compatability being determined by assessing sediment formation as a measure of additive package stability.

7. The composition, method or use as claimed in any of claims 1 to 6 wherein R is a primary or secondary alkyl group having from 4 to 10 carbon atoms.

8. The composition, method or use as claimed in any of claims 1 to 7 where the second alcohol is an ester of glycerol and a mono-carboxylic acid containing 12 to 30 carbon atoms and 0 to 3 carbon-carbon double bonds.

9. The composition, method or use as claimed in claim 8 where the second alcohol is a mono-ester.

10. The composition, method or use as claimed in claim 8 or claim 9 where the carboxylic acid is a saturated or unsaturated C16 to C18 fatty acid, such as oleic acid.

11. The composition, method or use as claimed in any of claims 1 to 10 where the molybdenum compound is a molybdenum dithiocarbamate or a molybdenum dithiophosphate.

12. The composition, method or use as claimed in any of claims 1 to 11 where the molybdenum compound is trinuclear and has the formula $Mo_3S_kL_nQ_z$ in which L is a ligand having organo groups with a sufficient number of carbon atoms to render the compound oil soluble;

n is from 1 to 4;
k is from 4 to 7;
Q is a neutral electron-donating compound; and
z is from 0 to 5 and includes non-stoichiometric values.

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EUROPEAN SEARCH REPORT

Application Number
EP 08 10 5242

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
D,Y	US 5 013 465 A (COLCLOUGH TERENCE [GB]) 7 May 1991 (1991-05-07) * claims 1,2,9,11,13 * * column 12; example 4 * * column 8, line 61 - column 9, line 3 * * column 1, line 50 - line 53 * -----	1-12	INV. C10M159/12 C10M163/00 ADD. C10N10/04 C10N10/12
Y	WO 98/26030 A (EXXON RESEARCH ENGINEERING CO [US]; EXXON CHEMICAL PATENTS INC [US]) 18 June 1998 (1998-06-18) * claim 20 * * page 23; example 22 * * page 24; table 4 * -----	1-12	C10N40/25 C10N30/06

TECHNICAL FIELDS SEARCHED (IPC)

C10M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	28 November 2008	Greß, Tobias

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 08 10 5242

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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