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(54) Title: A LUBRICATING OIL COMPOSITION

(57) Abstract: A lubricating oil composition that is free of organic friction modifiers, comprising (A) an oil of lubricating viscosity in a major proportion; (B) as an additive component in a minor proportion, a separately-prepared oil-soluble zinc salt of a dithiophosphoric acid, the dithiophosphoric acid being the reaction product of phosphorus pentasulphide with one or more alcohols, at least 50 mole % of the alcohol(s) having formula ROH where R is linear C18 to C26 saturated or double-bond unsaturated hydrocarbyl group; and (C) as an additive component in a minor proportion, a separately-prepared oil-soluble zinc salt of a dithiophosphoric acid, the dithiophosphoric acid being the reaction product of a phosphorus pentasulphide with one or more aliphatic alcohols consisting of an alcohol or alcohols each having from three to eight carbon atoms.



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A LUBRICATING OIL COMPOSITION

FIELD OF THE INVENTION

The present invention relates to automotive lubricating oil compositions, more especially to automotive lubricating oil compositions for use in piston engines, especially gasoline (spark-ignited) and diesel (compression-ignited), crankcase lubrication, such compositions being referred to as crankcase lubricants. In particular, the present invention relates to use of additives with friction modification properties in automotive lubricating oil compositions.

BACKGROUND OF THE INVENTION

A crankcase lubricant is an oil used for general lubrication in an internal combustion engine where an oil sump is situated generally 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. Further, phosphorus in the form of dihydrocarbyl dithiophosphate metal salts have been used as extreme pressure, antiwear and antioxidant additives in lubricating oil compositions for internal combustion engines. The metal may be zinc, an alkali or alkaline earth metal, or aluminium, lead, tin, molybdenum, manganese, nickel or copper. Of these, zinc salts of dihydrocarbyl dithiophosphate (ZDDPs) are most commonly used.

Organic friction modifiers may have a limited treat rate in lubricants because of their tendency to become incompatible with metal detergent colloids, used in the lubricant, at higher treat rates. US-A-5,013,465 ('465) discusses the problem of using ZDDP's in combination with friction modifiers (column 1, lines 24 – 39). It proposes a

solution, namely using a mixture of simple C₄-C₁₀ alcohols and certain more polar substituted alcohols, in appropriate proportions, to make friction-modified ZDDP's with excellent handling properties. '465 states that, usually, there is more of the simple alcohol than the polar substituted alcohol, on a molar basis, to produce a mobile liquid oil-soluble product (column 2, lines 57 – 59). EP-A-2 161 326 describes use of similar additives in combination with molybdenum additives.

DE 941 218 C describes the zinc salt of the oleyl alcohol/P₂S₅ reaction product, but nowhere describes or suggests that it has lubricant friction modification properties.

SUMMARY OF THE INVENTION

As noted above, '465's disclosure is limited in the amount of friction modifying entity that can be incorporated into ZDDP.

The present invention meets the above problem by manufacturing ZDDP's from certain alcohols that have been found to confer friction modification properties on a lubricant without the need for substantial, separate additions of organic friction modifiers. In contrast to '465's solution, the present invention uses an alcohol that is less polar than the simple alcohol and in a molar proportion greater than that of the simple alcohol. Thus, a much higher proportion of friction modifier may be incorporated, and the simple alcohol may not need to be used.

In accordance with a first aspect, the present invention provides a lubricating oil composition that is free of organic friction modifiers, comprising, or made by admixing:

- (A) an oil of lubricating viscosity in a major proportion;
- (B) as an additive component in a minor proportion, a separately prepared oil-soluble zinc salt of a dithiophosphoric acid, the dithiophosphoric acid being the reaction product of phosphorus pentasulphide with one or more alcohols, at least 50 mole % of the alcohol or alcohols having

the formula ROH where R is a linear C18 to C26 saturated or double-bond unsaturated hydrocarbyl group; and

- (C) as an additive component in a minor proportion, a separately-prepared oil-soluble zinc salt of a dithiophosphoric acid, the dithiophosphoric acid being the reaction product of phosphorus pentasulphide with one or more aliphatic alcohols consisting of an alcohol or alcohols each having from three to eight carbon atoms.

According to a second aspect, the present invention provides a method of improving the friction modification properties of a lubricating oil composition, which method comprises incorporating into the composition in a minor amount an additive component (B) as defined in the first aspect of the invention.

According to a third aspect, the present invention provides a method of lubricating surfaces of the combustion chamber of an internal combustion chamber during its operation comprising:

- (i) providing, in respective minor amounts, zinc salts (B) and (C) as defined in the first aspect of the invention in a major amount of an oil of lubricating viscosity to make a lubricating oil composition, to improve the friction modification properties of the composition;
- (ii) providing the lubricating oil composition in the combustion chamber;
- (iii) providing a hydrocarbon fuel in the combustion chamber; and
- (iv) combusting the fuel in the combustion chamber.

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 only hydrogen and carbon atoms and that is bonded to the remainder of the compound directly via a carbon atom.

“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;

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

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

“TBN” means total base number as measured by ASTM D2896;

“phosphorus content” is measured by ASTM D5185;

“sulfur content” is measured by ASTM D2622; and

“sulfated ash content” is measured by ASTM D874.

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.

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

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)

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).

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.

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.

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.

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, dicicosyl 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.

Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols, and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

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.

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 H₂ 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.

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

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 of the invention, 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.

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 additives, such as described hereinafter, in a single concentrate.

The oil of lubricating viscosity may be provided in a major amount, in combination with minor amounts of additive components, (B) and (C) as defined herein 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.

Preferably, the oil of lubricating viscosity is present in an amount of greater than 55 mass %, more preferably greater than 60 mass %, even more preferably greater than 65 mass %, based on the total mass of the lubricating oil composition. Preferably, the oil of lubricating viscosity is present in an amount of less than 98 mass %, more preferably less than 95 mass %, even more preferably less than 90 mass %, based on the total mass of the lubricating oil composition.

In the present invention, the oil of lubricating viscosity may be provided in a major amount, in combination with respective minor amounts 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.

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.

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.

The lubricating oil compositions of the invention 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.

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.

The lubricating oil composition of the present invention may contain low levels of phosphorus, namely not greater than 0.09 mass %, preferably up to 0.08 mass %, more preferably up to 0.06 mass % of phosphorus, expressed as atoms of phosphorus, based on the total mass of the composition.

Typically, the lubricating oil composition may contain low levels of sulfur. Preferably, the lubricating oil composition contains up to 0.4, more preferably up to 0.3, most preferably up to 0.2, mass % sulfur, expressed as atoms of sulfur, based on the total mass of the composition.

Typically, the lubricating oil composition may contain low levels of sulfated ash. Preferably, the lubricating oil composition contains up to 1.0, preferably up to 0.8, mass % sulfated ash, based on the total mass of the composition.

Suitably, the lubricating oil composition may have a total base number (TBN) of between 4 to 15, preferably 5 to 11.

ADDITIVE COMPONENT (B)

In (B), R is, as stated, a linear C18 to C26 saturated or a double-bond unsaturated hydrocarbyl group. Preferably, R is a C18 to C22, more preferably a C18 group.

A saturated hydrocarbyl group is an alkyl group. An unsaturated hydrocarbyl group has one or more sources of double-bond unsaturation; thus it may, for example, be an alkenyl group or an alkadienyl group.

A stearyl group and an oleyl group, particularly oleyl, are noteworthy examples of R.

(B) is obtainable by reacting a basic zinc compound with a dithiophosphoric acid obtainable by reacting phosphorus pentasulfide with one or more alcohols, at least 50 mole % of which have the formula ROH. For example, from 60 to 100, such as 70 to 100, such as 75 to 100, such as 90 to 100, mole % of the alcohol or alcohols may have the formula ROH. In particular, all of the alcohol(s) may have the formula ROH.

R may be a mixture, i.e. derived from a mixture of alcohols ROH as defined herein.

Any alcohol or alcohols, other than those of the formula ROH, may have the formula R^1OH where R^1 is an alkyl or alkenyl, preferably alkyl, group and has 3 to 12, such as 3 to 10, such as 5 to 8, carbon atoms.

Thus, 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 50 up to 100 mole % of the alcohol(s) of the formula ROH, and alcohol(s) of the formula R^1OH as the balance, if any.

The dithiophosphoric acid obtainable from ROH may have the formula $(RO)_2P(S)SH$ and the zinc salt obtainable therefrom may have the formula $[(RO)_2P(S)S]_2Zn$.

ADDITIVE COMPONENT (C)

Additive component (C) is made exclusively from aliphatic alcohol(s) having 3-8 carbon atoms and therefore contains correspondingly small aliphatic groups. It is present to enhance properties such as the anti-wear properties of the lubricating oil composition. Examples of additive component (C) are known in the art and are used commercially. The aliphatic, preferably alkyl, groups may all be secondary or all

primary or both secondary and primary; they may, for example, contain 4 to 8 carbon atoms; they may be the same or different.

Preferably, at least a proportion of the aliphatic groups comprises secondary aliphatic groups. For example, greater than 60 mole %, preferably greater than 70 mole %, more preferably greater than 80 mole %, even more preferably greater than 90 mole %, such as all, of the aliphatic groups may be secondary aliphatic groups. As examples, of secondary aliphatic groups there may be mentioned sec-butyl and 4-methyl-2-pentyl. Any balance may be primary aliphatic groups.

Suitably, the lubricating oil composition contains an amount of additive components (B) and (C) that introduce 0.02 to 0.09 wt.%, preferably 0.02 to 0.08 wt.%, more preferably 0.02 to 0.06 wt.% of phosphorus into the composition.

Suitably, the additive components (B) and (C) are present in an amount of 0.1 to 10 mass %, preferably 0.1 to 5 mass %, more preferably 0.1 to 2 mass %, of the lubricating oil composition, based on the total mass of the lubricating oil composition.

Suitably, (B) constitutes more than 50 mole % of the total number of moles of (B) and (C), such as 70 to 95, for example 75 to 90, mole %.

In accordance with a preferred embodiment of the present invention, the additive components (B) and (C) represent the sole phosphorus-containing additive components in the lubricating oil composition.

One or more of each of additive components (B) and (C) may be present.

Organic friction modifiers are excluded. Examples of excluded organic friction modifiers are glyceryl monoesters of higher fatty acids, for example, glyceryl mono-oleate; esters of long chain polycarboxylic acids with diols, for example, the butane diol ester of a dimerized unsaturated fatty acid; oxazoline compounds; and alkoxyated alkyl-substituted mono-amines, diamines and alkyl ether amines, for example, ethoxyated tallow amine and ethoxyated tallow ether amine.

CO-ADDITIVES

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

<u>Additive</u>	<u>Mass %</u> (Broad)	<u>Mass %</u> (Preferred)
Ashless Dispersant	0.1 – 20	1 – 8
Metal Detergents	0.1 – 15	0.2 – 9
Friction modifier	0 – 5	0 – 1.5
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.

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 co-additives, the remainder being oil of lubricating viscosity.

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.

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.

Dispersants are usually “ashless”, as mentioned above, being 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.

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 C₄ refinery stream.

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.

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.

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 reaction of 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.

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 preferred metal detergents are neutral and overbased alkali or alkaline earth metal salicylates having a TBN of from 50 to 450, preferably a TBN of 50 to 250. Highly preferred salicylate detergents include alkaline earth metal salicylates, particularly magnesium and calcium, especially, calcium salicylates. Preferably, the alkali or alkaline earth metal salicylate detergent is the sole detergent in the lubricating oil composition. Unexpectedly, it has been found that the use of a salicylate detergent improves the phosphorus retention of a lubricating oil composition containing a ZDDP additive, particularly additive component (B) in the lubricating oil composition of the present invention.

Metal-containing (or ash-generating) friction modifiers may be included. Examples include oil-soluble organo-molybdenum compounds. Such organo-molybdenum

friction modifiers also provide antioxidant and antiwear credits to a lubricating oil composition. Suitable oil-soluble organo-molybdenum compounds have 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. The molybdenum compound is dinuclear or trinuclear.

One class of preferred organo-molybdenum compounds useful in all aspects of the present invention is tri-nuclear molybdenum compounds of the formula $\text{Mo}_3\text{S}_k\text{L}_n\text{Q}_z$ 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.

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.

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.

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.

They may be classified as radical scavengers (e.g. sterically hindered phenols, secondary aromatic amines, and organo-copper salts); hydroperoxide decomposers (e.g., organosulfur 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).

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

Dihydrocarbyl dithiophosphate metals salts other than (B) and (C) may be used. They 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 prepared 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.

Anti-wear agents reduce friction and excessive wear and are usually based on compounds containing sulfur 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.

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

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.

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 C₈ to C₁₈ dialkyl fumarate/vinyl acetate copolymers and polyalkylmethacrylates.

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

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 reaction of 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.

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 ethylene-propylene post grafted with an active monomer such as maleic anhydride) which are then derivatised with, for example, an alcohol or amine.

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

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

The following ZDDP's were tested. All were oil-soluble zinc salts of a dithiophosphoric acid, the salts being made substantially as described in US-A-5,013,465.

Z1: the acid was the reaction product of P_2S_5 with oleyl alcohol (100 mole %).

Z2†: the acid was the reaction product of P_2S_5 with sec-C₆ alcohol (100 mole %).

Z3: the acid was the reaction product of P_2S_5 with a mixture of sec-C₆ alcohol (47 mole %) and oleyl alcohol (53 mole %).

Z4†: the acid was the reaction product of P_2S_5 with a mixture of sec-C₆ alcohol (89 mole %) and oleyl alcohol (11 mole %).

Z5: the acid was the reaction product of P_2S_5 with stearyl alcohol (100 mole %).

Z6: the acid was the reaction product of P_2S_5 with a mixture of sec-C₆ alcohol (47 mole %) and stearyl alcohol (53 mole %).

Z7: the acid was the reaction product of P_2S_5 with a mixture of 90 mole % sec-C₄ alcohol and 10 mole % prim-C₈ alcohol.

* the sec-C₆ alcohol is 4-methylpentan-2-ol.

† indicates ZDDP's used in comparative examples.

All other ZDDP's were used in examples of the invention, though Z7 is also used in a comparative example.

The preparation of Z1 is given below in detail as an illustration of the preparative methods used.

DDPA Synthesis

A 1 litre baffled flange flask was charged with 310.45g (1.156 mol) of oleyl alcohol (ex Aldrich; MW = 268.48). The flask was fitted with a coiled water cooled condenser, mechanical stirrer using glass rod with PTFE paddle, nitrogen inlet, glass pocket containing oil for thermocouple and nitrogen outlet at top of condenser. The outlet led to two traps containing sodium hydroxide 32g (2.9 eq) dissolved in 1 litre of water (800 ml and 200 ml) and one of potassium permanganate (13.6g) dissolved in 150 ml of water. The stirrer was set at 400 rpm and the nitrogen flow at 40-50 ml/min. The mixture was heated to 65°C over 20 mins using a WEST controlled mantle. Approximately 61.56g (0.2753 mol) of phosphorus pentasulphide (ex Phosphorus Derivatives Inc) having a phosphorus content of 27.70 % (= MW of 223.61) was added to the reactor by screwfeed over 40 mins allowing a mild exotherm to take place with external heating after 35 mins. The actual amount added = 62.33 – 0.30 g (in screwfeed) = 62.03 g. The mixture was then heat-soaked at 85°C for 5 hrs 24 mins during which most of the solid dissolved, and cooled with compressed air to 50°C. The weighed solution was finally filtered under vacuum through a sintered glass funnel into a 1 litre three-necked round-bottomed flask for subsequent nitrogen sparging. The solid remaining in the pot was filtered, washing out with toluene to determine the unreacted weight of P₂S₅. Solids adhering to parts of the apparatus were washed with heptane, dried and weighed before and after removal with a wipall. This operation determined the exact weight of P₂S₅ consumed in the synthesis. P₂S₅ in pot = 0.22g, P₂S₅ in apparatus = 0.08g.

Extra wt in trap 1 = 9.56g (Theo = 9.41g). No extra wt in trap 2.

Yield of DDPA = 361.54g – 0.22g = 361.32g (=99.6%) (Theo = 362.77g).

The Wt % of Phosphorus in the DDPA product was calculated using the following formula;

$$\begin{aligned} \text{Wt \% of Phosphorus} &= \frac{\text{Wt \% of P}_2\text{S}_5 \text{ consumed} \times \text{\% of P in P}_2\text{S}_5}{\text{Wt of DDPA produced}} = 61.73 \times 27.70 / 361.32 \\ &= 4.7324 \% \text{ P} \end{aligned}$$

355.95g of product was isolated as a clear green liquid.

ZDDP Synthesis

The DDPA in a 1 litre three-necked round-bottomed flask was sparged with nitrogen at 300 ml min with magnetic stirring for 1 hour to remove any residual H₂S. The outlet led to the same trap system as that used in the DDPA preparation.

A 1 litre baffled flange flask was charged with 28.00g (0.34408 mol) of zinc oxide (ex GH Chemicals), 0.763 g (0.0034756 mol) of zinc acetate dihydrate (ex Aldrich) and 34.51 g of SN150(FAW). The flask was fitted with a coiled water-cooled condenser, mechanical stirrer using glass rod with PTFE paddle, nitrogen inlet, glass pocket containing oil for thermocouple and nitrogen outlet at top of condenser. The outlet led to the same trap system as that used in the DDPA preparation. The stirrer was set at 400 rpm and the nitrogen flow at 300 ml/min. 348 g of Prim C18(oleyl) DDPA (E00007-010) was added to the slurry through a 500 ml pressure equalizing dropping funnel with no external heating. One quarter of the charge was added over 18 mins causing a temperature rise to 28.2°C. A WEST controlled mantle was then used to raise the temperature of the mixture to 85°C over 20 mins maintaining the DDPA addition rate. The total addition time was 73 mins. The mixture was heat-soaked for 73 mins at 85°C and the weighed product rotary evaporated in a 2 litre flask under vacuum at 85°C for 2 hrs.

Crude yield = 407.96g (=99.2%) prior to rotary evaporation. (theo = 411.27g)

Wt loss after rotary evaporation = 2.40g (from 399.35g of product)

Estimated Wt loss from total product = 1.43g (theo for water = 6.26g, for alcohol = 14.24g C18)

No increase in trap weights was observed for whole of experimental procedure.

2% by weight of celite 521 filter aid (7.96 g) was added to the product and rotated on a rotary evaporator at 85°C for a few minutes at atmospheric pressure. 10g of celite 521 slurried in 150 ml SN150(FAW) was then added to a filter press preheated to 80°C and filtered to provide a pad. The product was added to this and filtered at 80 psi for 13 mins.

365.75g of clear pale yellow/green oil was obtained which became slight hazy on cooling.

Each of the above ZDDP's was blended into a lubricating oil composition at a treat rate to allow 0.077 wt % of phosphorus to be delivered to the formulation. Apart from the identity of the ZDDP, each composition was the same and comprised an adpack consisting of detergents, antifoam, dispersants, antioxidant and diluent blended with a viscosity modifier, pour point depressant, base stock and the ZDDP. The formulations contained no organic friction modifiers.

TESTING AND RESULTS

First Set

A high frequency reciprocating rig was used to evaluate the coefficient of friction of each of the above compositions. Experimentation was carried out using a step ramp profile: coefficient of friction was measured for 5 minutes at each temperature as the temperature was increased from 40°C to 140°C at 20°C intervals. A 4 N load was applied via a 400 g weight and the upper specimen reciprocated over a distance of 1 mm at a frequency of 40 Hz.

Sample results are set out in the table below in which a representative coefficient of friction value at each temperature is given.

TABLE 1

Composition (identified by ZDDP)	21s; 40°C	571s; 60°C	866s; 80°C	1181s; 100°C	1466s; 120°C	1776s; 140°C
Z1	0.130	0.136	0.132	0.124	0.106	0.096
Z2†	0.140	0.140	0.155	0.149	0.149	0.141
Z3	0.129	0.129	0.124	0.117	0.109	0.096
Z4†	0.142	0.137	0.145	0.148	0.143	0.146
Z5	0.115	0.113	0.111	0.111	0.107	0.112
Z6	0.116	0.119	0.125	0.125	0.119	0.107

It is seen that the ZDDP's of the invention generally gave rise to better (i.e. smaller) coefficient of friction values than the comparison ZDDP's.

Second Set

The same high frequency reciprocating rig was used to evaluate the coefficient of friction of a second set of lubricating oil compositions. Each such composition contained one or both of Z1 (oleyl alcohol) and Z7 (mainly secondary) together with components known in the art. They did not contain organic friction modifiers. The compositions were identical other than in respect of the presence and amounts of Z1 and Z7.

Six compositions were tested:

mass % Z1:	1.883	1.600	1.412	0.941	0.471	-
mass % Z7:	-	0.144	0.241	0.481	0.722	0.963

Sample results, being an average of two runs, are set out in the table below in which a representative coefficient of friction value at each temperature is given.

TABLE 2

Composition Z1/Z7 (mole %)	21s; 40°C	571s; 60°C	866s; 80°C	1181s; 100°C	1466s; 120°C	1776s; 140°C
100 /0	0.131	0.132	0.122	0.114	0.105	0.094
85/15 *	0.127	0.127	0.123	0.115	0.105	0.094
75/25 *	0.127	0.129	0.123	0.115	0.106	0.095
50/50	0.128	0.124	0.128	0.136	0.136	0.136
25/75	0.115	0.130	0.143	0.144	0.149	0.150
0/100	0.111	0.136	0.146	0.154	0.157	0.157

Lower values in the table indicate superior performance and most significance should be given to the values obtained at the higher temperatures, i.e. 100°C, 120°C and 140°C, because they more closely represent working temperatures, e.g. in the valve train. It is seen that all Z1-containing compositions performed better than the composition (0/100) that lacked Z1. This illustrates the friction modification effect of Z1 in the absence of an organic friction modifier. The asterisked compositions performed better than the compositions with higher proportions of Z7 and the 50/50 combination gives an improvement over the 25/75 and 0/100 combinations. The 100/0 composition performed well in the tests but the addition of Z7, as is known in the art, would improve the anti-wear properties of the formulation.

CLAIMS

1. A lubricating oil composition that is free of organic friction modifiers comprising, or made by admixing:
 - (A) an oil of lubricating viscosity in a major proportion;
 - (B) as an additive component in a minor proportion, a separately prepared oil-soluble zinc salt of a dithiophosphoric acid, the dithiophosphoric acid being the reaction product of phosphorus pentasulphide with one or more alcohols, at least 50 mole % of the alcohol or alcohols having the formula ROH where R is a linear C18 to C26 saturated or double-bond unsaturated hydrocarbyl group; and
 - (C) as an additive component in a minor proportion, a separately-prepared oil-soluble zinc salt of a dithiophosphoric acid, the dithiophosphoric acid being the reaction product of phosphorus pentasulphide with one or more aliphatic alcohols consisting of an alcohol or alcohols each having from three to eight carbon atoms.
2. A composition as claimed in claim 1 wherein in (B) 70 to 100 mole % of the alcohol or alcohols have said formula ROH.
3. A composition as claimed in claim 1 or 2 wherein in (B) any alcohol or alcohols, other than those of formula ROH, have the formula R¹OH where R¹ has 3 to 12, such as 3 to 10, such as 5 to 8, carbon atoms and is an alkyl or alkenyl, preferably alkyl, group.
4. A composition as claimed in any of claims 1 to 3 wherein in (B) R is a linear C18 to C22 saturated or unsaturated hydrocarbyl group.
5. A composition as claimed in claim 4 where R is a linear C18 saturated or unsaturated hydrocarbyl group.

6. A composition as claimed in claim 5 where R is an oleyl group.
7. A composition as claimed in any of claims 1 to 5 where, in (C), the one or more aliphatic alcohols comprise one or more secondary aliphatic alcohols such as greater than 60, such as greater than 70, such as greater than 80, such as greater than 90, such as 100, mole %.
8. A composition as claimed in any of claims 1 to 7 where, in (C), the one or more secondary aliphatic alcohols have 4 to 8 carbon atoms.
9. A composition as claimed in any of claims 1 to 8 wherein other additive components, different from (B) and from (C), are present and are selected from one or more of ashless dispersants, metal detergents, corrosion inhibitors, antioxidants, pour point depressants, antiwear agents, friction modifiers, demulsifiers, antifoam agents and viscosity modifiers.
10. A composition as claimed in any of claims 1 to 9 wherein (B) and (C) together introduce 0.02 to 0.09, such as 0.02 to 0.09, such as 0.02 to 0.08, such as 0.02 to 0.06, mass % of phosphorus, expressed as phosphorus atoms, into the composition.
11. A method of improving the friction modification properties of a lubricating oil composition, which method comprises incorporating into the composition in a minor amount an additive component (B) as defined in any of claims 1 to 6.
12. A method of lubricating surfaces of the combustion chamber of an internal combustion chamber during its operation comprising:
 - (i) providing, in respective minor amounts, zinc salts (B) and (C) as defined in any of claims 1 to 8 in a major amount of an oil of lubricating viscosity to make a lubricating oil composition, to improve the friction modification properties of the composition;

- (ii) providing the lubricating oil composition in the combustion chamber;
- (iii) providing a hydrocarbon fuel in the combustion chamber; and
- (iv) combusting the fuel in the combustion chamber.

AMENDED CLAIMS
received by the International Bureau on
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CLAIMS

1. A lubricating oil composition that is free of organic friction modifiers comprising, or made by admixing:
 - (A) an oil of lubricating viscosity in a major proportion;
 - (B) as an additive component in a minor proportion, a separately prepared oil-soluble zinc salt of a dithiophosphoric acid, the dithiophosphoric acid being the reaction product of phosphorus pentasulphide with one or more alcohols, at least 50 mole % of the alcohol or alcohols having the formula ROH where R is a linear C18 to C26 double-bond unsaturated hydrocarbyl group; and
 - (C) as an additive component in a minor proportion, a separately-prepared oil-soluble zinc salt of a dithiophosphoric acid, the dithiophosphoric acid being the reaction product of phosphorus pentasulphide with one or more aliphatic alcohols consisting of an alcohol or alcohols each being a secondary aliphatic alcohol having from three to eight carbon atoms.
2. A composition as claimed in claim 1 wherein in (B) 70 to 100 mole % of the alcohol or alcohols have said formula ROH.
3. A composition as claimed in claim 1 or 2 wherein in (B) any alcohol or alcohols, other than those of formula ROH, have the formula R¹OH where R¹ has 3 to 12, such as 3 to 10, such as 5 to 8, carbon atoms and is an alkyl or alkenyl, preferably alkyl, group.
4. A composition as claimed in any of claims 1 to 3 wherein in (B) R is a linear C18 to C22 unsaturated hydrocarbyl group.
5. A composition as claimed in claim 4 where R is a linear C18 unsaturated hydrocarbyl group.

6. A composition as claimed in claim 5 where R is an oleyl group.
7. A composition as claimed in any of claims 1 to 6 where, in (C), the one or more secondary aliphatic alcohols have 4 to 8 carbon atoms.
8. A composition as claimed in any of claims 1 to 7 wherein other additive components, different from (B) and from (C), are present and are selected from one or more of ashless dispersants, metal detergents, corrosion inhibitors, antioxidants, pour point depressants, antiwear agents, friction modifiers, demulsifiers, antifoam agents and viscosity modifiers.
9. A composition as claimed in any of claims 1 to 8 wherein (B) and (C) together introduce 0.02 to 0.09, such as 0.02 to 0.09, such as 0.02 to 0.08, such as 0.02 to 0.06, mass % of phosphorus, expressed as phosphorus atoms, into the composition.
10. A method of improving the friction modification properties of a lubricating oil composition, which method comprises incorporating into the composition in a minor amount an additive component (B) as defined in any of claims 1 to 6.
11. A method of lubricating surfaces of the combustion chamber of an internal combustion chamber during its operation comprising:
 - (i) providing, in respective minor amounts, zinc salts (B) and (C) as defined in any of claims 1 to 7 in a major amount of an oil of lubricating viscosity to make a lubricating oil composition, to improve the friction modification properties of the composition;
 - (ii) providing the lubricating oil composition in the combustion chamber;
 - (iii) providing a hydrocarbon fuel in the combustion chamber; and

- (iv) combusting the fuel in the combustion chamber.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2010/058085

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10M159/12 C10M141/10
ADD. C10N10/04 C10N30/06 C10N40/25 C10N70/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 026 364 A (LUBRIZOL CORP) 20 April 1966 (1966-04-20) the whole document	1-10, 12
X	EP 0 768 366 A1 (TONEN CORP [JP]) 16 April 1997 (1997-04-16)	11
A	the whole document	1-10, 12
X	US 5 672 572 A (ARAI KATSUYA [JP] ET AL) 30 September 1997 (1997-09-30) the whole document	1-12
A	US 5 384 054 A (KADKHODAYAN ABBAS [US]) 24 January 1995 (1995-01-24) claims 1-4, 8 column 1, lines 22-27 column 3, line 35 - column 4, line 6	1-12
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2010/058085

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 941 218 C (BASF AG) 5 April 1956 (1956-04-05) cited in the application page 3, lines 35-39, 72-92 page 4, lines 115-122; example 3 page 5; example 6; table 1 -----	1-12
A	GB 855 005 A (EXXON RESEARCH ENGINEERING CO) 23 November 1960 (1960-11-23) the whole document -----	1-12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2010/058085

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