(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 952 563 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
09.12.2015 Bulletin 2015/50

(21) Application number: **15170236.2**

(22) Date of filing: **02.06.2015**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA

(30) Priority: **02.06.2014 EP 14170782**

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(51) Int Cl.:
C10M 161/00 *(2006.01)*
C10N 10/04 *(2006.01)*
C10N 30/12 *(2006.01)*
C10N 40/25 *(2006.01)*

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(54) LUBRICATING OIL COMPOSITIONS

(57) A lubricating oil composition having a sulphated ash content of less than or equal to 1.2 mass % as determined by ASTM D874 and a phosphorous content of less than or equal to 0.12 mass % as determined by ASTM D5185, which lubricating oil composition comprises or is made by admixing: an oil of lubricating viscosity, in a major amount; an oil-soluble or oil-dispersible polymeric friction modifier as an additive in an effective minor amount; and, an oil-soluble or oil-dispersible dihydrocarbyl dithiophosphate metal salt as an additive in an effective minor amount.

Printed by Jouve, 75001 PARIS (FR)

Description

FIELD OF THE INVENTION

[0001] The present invention relates to automotive lubricating oil compositions. More specifically, although not exclusively, the present invention relates to automotive crankcase lubricating oil compositions for use in gasoline (spark-ignited) and diesel (compression-ignited) internal combustion engines, such compositions being referred to as crankcase lubricants; and to the use of additives in such lubricating oil compositions for improving the anti-corrosion performance properties in respect of the non-ferrous metallic engine components (i.e. suppressing the corrosion of the non-ferrous metallic engine components), particularly the engine components containing copper and/or lead (e.g. bearings).

BACKGROUND OF THE INVENTION

[0002] 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.

[0003] Anti-wear agents are typically used as additives in a crankcase lubricant to reduce excessive wear of the metallic engine components. Such anti-wear agents are usually based on compounds containing sulphur or phosphorus or both, for example compounds that are capable of depositing polysulfide films on the surfaces of the metallic engine components. Common anti-wear agents which are routinely employed in a crankcase lubricant are dihydrocarbyl dithiophosphate metal salts.

[0004] It is also desirable to reduce the energy and fuel consumption requirements of the engine and there is, therefore, also a need for crankcase lubricants which reduce the overall friction of the engine. Reducing friction losses in an engine typically contributes significantly to improving fuel economy performance and fuel economy retention properties of the engine. Accordingly, it has long been known to use ashless organic friction modifiers, for example ashless nitrogen-free organic friction modifiers (e.g. esters formed from carboxylic acids and alkanols, such as glycerol monooleate (GMO)), as additives in a crankcase lubricant to obtain improved friction properties and improved fuel economy performance.

[0005] Accordingly, in order to provide a crankcase lubricant having the desired anti-wear performance and the desired friction properties, lubricating oil formulators have typically employed a dihydrocarbyl dithiophosphate metal salt anti-wear additive in combination with an ashless organic friction modifier additive, such as GMO, in the lubricating oil composition.

[0006] It has now been found that the use of an ashless organic friction modifier additive, such as GMO, in the lubricant typically produces a significant amount of lead and copper corrosion. Moreover, when the ashless organic friction modifier additive, such as GMO, is used in combination with a dihydrocarbyl dithiophosphate metal salt anti-wear additive the amount of lead corrosion typically further increases. The corrosive nature of the ashless organic friction modifier additive, such as GMO, and the increase in lead corrosion attributable to the combination of the ashless organic friction modifier additive and the dihydrocarbyl dithiophosphate metal salt presents problems for the lubricant oil formulator. For example, the corrosive nature of the additive components, particularly when used in combination, may necessitate reduced treat rates of the additive(s) thereby impacting on the anti-wear performance and/or fuel economy performance of the lubricant; alternatively, or additionally, it may be necessary to include further relatively expensive anti-corrosion additives in the lubricant to counteract the corrosive nature of the dihydrocarbyl dithiophosphate metal salts and ashless organic friction modifier additives.

[0007] Accordingly, there is a need for lubricating oil compositions that include dihydrocarbyl dithiophosphate metal salt anti-wear agents and ashless organic friction modifier additives which exhibit improved anti-corrosion performance properties in respect of the non-ferrous metallic engine components, particularly those components which contain copper and/or lead, or alloys thereof.

SUMMARY OF THE INVENTION

[0008] In accordance with a first aspect, the present invention provides a lubricating oil composition having a sulphated ash content of less than or equal to 1.2 mass % as determined by ASTM D874 and a phosphorous content of less than or equal to 0.12 mass % as determined by ASTM D5185, which lubricating oil composition comprises or is made by admixing:

(A) an oil of lubricating viscosity, in a major amount;

(B) an oil-soluble or oil-dispersible polymeric friction modifier as an additive in an effective minor amount, the polymeric friction modifier being the reaction product of solely:

  (i) a functionalised polyolefin;

(ii) a polyalkylene glycol;
(iii) a polyol; and,
(iv) a polycarboxylic acid

and,
(C) at least one oil-soluble or oil-dispersible dihydrocarbyl dithiophosphate metal salt as an additive in an effective minor amount.

[0009] Preferably, the lubricating oil composition of the present invention is a crankcase lubricant.

[0010] Unexpectedly, it has been found that the use of the polymeric friction modifier (B), as defined in accordance with the first aspect of the invention, as an additive in an effective minor amount in a lubricating oil composition comprising an oil of lubricating viscosity in a major amount, may suppress the corrosion of the non-ferrous metal (e.g. copper and/or lead) containing engine components compared with a comparable lubricant which does not include the polymeric friction modifier (B). In other words, the polymeric friction modifier (B) may function as an anti-corrosion agent in respect of the non-ferrous metal containing engine components, especially the engine components which include copper and/or lead, or an alloy containing such metals.

[0011] Furthermore, it has also been found that the use of the oil-soluble or oil-dispersible polymeric friction modifier (B) as defined in the first aspect of the present invention, as an additive in an effective minor amount, in combination with the oil-soluble or oil-dispersible dihydrocarbyl dithiophosphate metal salt as defined in the first aspect of the present invention, as an additive in an effective minor amount, in a lubricating oil composition comprising an oil of lubricating viscosity in a major amount, typically provides a lubricant that exhibits an improved inhibition and/or reduction in the corrosion (i.e. suppresses the corrosion) of the non-ferrous metal (e.g. copper and/or lead) containing engine components compared with a comparable lubricant which includes an ashless organic friction modifier, such as GMO, in combination with an oil-soluble or oil-dispersible dihydrocarbyl dithiophosphate metal salt as defined in the first aspect of the present invention.

[0012] Still further, it has been found that the use of the oil-soluble or oil-dispersible polymeric friction modifier (B) as defined in the first aspect of the present invention, as an additive in an effective minor amount, in combination with the oil-soluble or oil-dispersible dihydrocarbyl dithiophosphate metal salt as defined in the first aspect of the present invention, as an additive in an effective minor amount, in a lubricating oil composition comprising an oil of lubricating viscosity in a major amount, typically provides a lubricant that exhibits an improved inhibition and/or reduction in the corrosion (i.e. suppresses the corrosion) of the copper containing metallic engine components compared with: (i) a comparable lubricant which includes the dihydrocarbyl dithiophosphate metal salt but not the polymeric friction modifier (B); and, (ii) a comparable lubricant which does not include both the dihydrocarbyl dithiophosphate metal salt and the polymeric friction modifier (B).

[0013] Accordingly, such reduced levels of non-ferrous metal corrosion (e.g. reduced levels of copper and/or lead corrosion) associated with the use of the polymeric friction modifier (B) compared with an ashless organic friction modifier such as GMO, particularly when used in combination with a dihydrocarbyl dithiophosphate metal salt, may permit increased treat rates of the combination of such additives in a lubricant. Additionally, or alternatively, such reduced levels of non-ferrous metal corrosion may reduce the need for the use of relatively expensive supplemental anti-corrosion additives. Accordingly, the use of the polymeric friction modifier (B) in combination with a dihydrocarbyl dithiophosphate metal salt typically provides the formulator with a higher degree of flexibility when formulating lubricating oil compositions which must meet strict anti-wear performance and fuel economy performance criteria as specified in industry lubricating oil specifications and in original equipment manufacturer's specifications.

[0014] In accordance with a second aspect, the present invention provides a method of lubricating a spark-ignited or compression-ignited internal combustion engine comprising lubricating the engine with a lubricating oil composition as defined in accordance with the first aspect of the present invention.

[0015] In accordance with a third aspect, the present invention provides the use, in the lubrication of a spark-ignited or compression-ignited internal combustion engine, of an oil-soluble or oil-dispersible polymeric friction modifier (B) as defined in the first aspect of the invention, as an additive in an effective minor amount, in a lubricating oil composition comprising an oil of lubricating viscosity in a major amount to reduce and/or inhibit corrosion (i.e. suppress the corrosion) of the non-ferrous metal containing engine components during operation of the engine. Suitably, the non-ferrous metal containing engine components include copper, lead, or an alloy of such metals.

[0016] Suitably, the lubricating oil composition as defined in the third aspect of the invention further includes a dihydrocarbyl dithiophosphate metal salt as defined in the first aspect of the present invention, as an additive in an effective minor amount.

[0017] In accordance with a fourth aspect, the present invention provides the use, in the lubrication of a spark-ignited or compression-ignited internal combustion engine, of an oil-soluble or oil-dispersible polymeric friction modifier (B) as defined in the first aspect of the invention, as an additive in an effective minor amount, in combination with an oil-soluble or oil-dispersible dihydrocarbyl dithiophosphate metal salt (C) as defined in the first aspect of the present invention, as an additive in an effective minor amount, in a lubricating oil composition comprising an oil of lubricating viscosity in a major amount, to reduce and/or inhibit corrosion (i.e. suppress the corrosion) of the non-ferrous metal containing engine components during operation of the engine. Suitably, the non-ferrous metal containing engine components include copper, lead or an alloy of such metals, especially copper or an alloy thereof.

[0018] In accordance with a fifth aspect, the present invention provides the use, in the lubrication of a spark-ignited or compression-ignited internal combustion engine, of a lubricating oil composition in accordance with the first aspect of the present invention to reduce and/or inhibit corrosion (i.e. suppress the corrosion) of the non-ferrous containing metallic engine components during operation of the engine. Suitably, the non-ferrous metal containing engine components include copper, lead or an alloy of such metals, especially copper or an alloy thereof.

[0019] In accordance with a sixth aspect, the present invention provides a method of inhibiting and/or reducing the corrosion (i.e. suppressing the corrosion) of the non-ferrous metal containing engine components of an engine, which method comprises lubricating the engine with a lubricating oil composition which comprises an oil of lubricating viscosity in a major amount and an oil-soluble or oil-dispersible polymeric friction modifier (B) as defined in the first aspect of the invention, as an additive in an effective minor amount, and operating the engine. Suitably, the non-ferrous metal containing engine components include copper, lead or an alloy of such metals. Suitably, the engine as defined in the sixth aspect of the present invention is a spark-ignited or compression-ignited internal combustion engine.

[0020] In accordance with a seventh aspect, the present invention provides a method of inhibiting and/or reducing the corrosion (i.e. suppressing the corrosion) of the non-ferrous metal containing engine components of an engine, which method comprises lubricating the engine with a lubricating oil composition of the first aspect of the present invention and operating the engine. Suitably, the non-ferrous metal containing engine components include copper, lead or an alloy of such metals, especially copper or an alloy thereof. Suitably, the engine as defined in the seventh aspect of the present invention is a spark-ignited or compression-ignited internal combustion engine.

[0021] Preferably, the oil-soluble or oil-dispersible dihydrocarbyl dithiophosphate metal salt (C) is an oil-soluble or oil-dispersible dihydrocarbyl dithiophosphate zinc salt (i.e. a zinc dihydrocarbyl dithiophosphate (ZDDP)), more preferably an oil-soluble or oil-dispersible zinc dialkyl dithiophosphate.

[0022] Preferably, the lubricating oil composition of the first aspect of the present invention and as defined in the second, third, fourth, fifth, sixth and seventh aspects of the present invention further includes one or more co-additives in an effective minor amount (0.1 to 30 mass %), other than additive components (B) and (C), selected from ashless dispersants, metal detergents, corrosion inhibitors, antioxidants, pour point depressants, antiwear agents, friction modifiers, demulsifiers, antifoam agents and viscosity modifiers.

[0023] The lubricating oil composition of the present invention has a sulphated ash content of less than or equal to 1.2, preferably less than or equal to 1.1, more preferably less than or equal to 1.0, mass % (ASTM D874) based on the total mass of the composition.

[0024] Preferably, the lubricating oil composition of the present invention contains low levels of phosphorus. The lubricating oil composition contains phosphorus in an amount of less than or equal to 0.12 mass %, preferably up to 0.11 mass %, more preferably less than or equal to 0.10 mass %, even more preferably less than or equal to 0.09 mass %, even more preferably less than or equal to 0.08 mass %, most preferably less than or equal to 0.06, mass % of phosphorus (ASTM D5185) based on the total mass of the composition. Suitably, the lubricating oil composition contains phosphorus in an amount of greater than or equal to 0.01, preferably greater than or equal to 0.02, more preferably greater than or equal to 0.03, even more preferably greater than or equal to 0.05, mass % of phosphorus (ASTM D5185) based on the total mass of the composition.

[0025] Typically, the lubricating oil composition of the present invention may contain low levels of sulfur. Preferably, the lubricating oil composition contains sulphur in an amount of up to 0.4, more preferably up to 0.3, even more preferably up to 0.2, mass % sulphur (ASTM D2622) based on the total mass of the composition.

[0026] Typically, a lubricating oil composition according to the present invention contains up to 0.30, more preferably up to 0.20, most preferably up to 0.15, mass % nitrogen, based on the total mass of the composition and as measured according to ASTM method D5291.

[0027] Suitably, the lubricating oil composition may have a total base number (TBN), as measured in accordance with ASTM D2896, of 4 to 15, preferably 5 to 12, mg KOH/g.

[0028] In this specification, the following words and expressions, if and when used, have the meanings given 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 provided they do not affect the essentially hydrocarbyl nature of the group. Those skilled in the art will be aware of suitable groups (e.g., halo, especially chloro and fluoro, amino, alkoxyl, mercapto, alkylmercapto, nitro, nitroso, sulfoxy, etc.). Preferably, the group consists essentially of hydrogen and carbon atoms, unless specified otherwise. Preferably, the hydrocarbyl group comprises an aliphatic hydrocarbyl group. The term "hydrocarbyl" includes "alkyl", "alkenyl", "allyl" and "aryl" as defined herein;

"alkylene" is synonymous with "alkanediyl" and means a C_2 to C_{20}, preferably a C_2 to C_{10}, more preferably a C_2 to C_6 bivalent saturated acyclic aliphatic hydrocarbon radical derived from an alkane by removal of a hydrogen atom from two different carbon atoms; it may be linear or branched. Representative examples of alkylene include ethylene (ethanediyl), propylene (propanediyl), butylene (butanediyl), isobutylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, 1-methyl ethylene, 1-ethyl ethylene, 1-ethyl-2-methyl ethylene, 1,1-dimethyl ethylene and 1-ethyl propylene;

"poly(alkylene)" means a polymer containing the appropriate alkanediyl repeating group. Such polymers may be formed by polymerisation of the appropriate alkene (e.g. polyisobutylene may be formed by polymerising isobutene);

"alkyl" means a C_1 to C_{30} alkyl group which is bonded to the remainder of the compound directly via a single carbon atom. Unless otherwise specified, alkyl groups may, when there are a sufficient number of carbon atoms, be linear (i.e. unbranched) or branched, be cyclic, acyclic or part cyclic/acyclic. Preferably, the alkyl group comprises a linear or branched acyclic alkyl group. Representative examples of alkyl groups include, but are not limited to, methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, neo-pentyl, hexyl, heptyl, octyl, dimethyl hexyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, icosyl and triacontyl;

"alkynyl" means a C_2 to C_{30}, preferably a C_2 to C_{12}, group which includes at least one carbon to carbon triple bond and is bonded to the remainder of the compound directly via a single carbon atom, and is otherwise defined as "alkyl";

"aryl" means a C_6 to C_{18}, preferably C_6 to C_{10}, aromatic group, optionally substituted by one or more alkyl groups, halo, hydroxyl, alkoxy and amino groups, which is bonded to the remainder of the compound directly via a single carbon atom. Preferred aryl groups include phenyl and naphthyl groups and substituted derivatives thereof, especially phenyl and alkyl substituted derivatives thereof;

"alkenyl" means a C_2 to C_{30}, preferably a C_2 to C_{12}, group which includes at least one carbon to carbon double bond and is bonded to the remainder of the compound directly via a single carbon atom, and is otherwise defined as "alkyl";

"polyol" means an alcohol which includes two or more hydroxyl functional groups (i.e. a polyhydric alcohol) but excludes a "polyalkylene glycol" (component B(ii)) which is used to form the oil-soluble or oil-dispersible polymeric friction modifier. More specifically, the term "polyol" embraces a diol, triol, tetrol, and/or related dimers or chain extended polymers of such compounds. Even more specifically, the term "polyol" embraces glycerol, neopentyl glycol, trimethylolethane, trimethylolpropane, trimethylolbutane, pentaerythritol, dipentaerythritol, tripentaerythritol and sorbitol;

"polycarboxylic acid" means an organic acid, preferably a hydrocarbyl acid, more preferably an aliphatic hydrocarbyl acid, which includes 2 or more carboxylic acid functional groups. The term "polycarboxylic acid" embraces di-, tri- and tetra- carboxylic acids;

"halo" or "halogen" includes fluoro, chloro, bromo and iodo;

"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;

"ashless" in relation to an additive means the additive does not include a metal;

"ash-containing" in relation to an additive means the additive includes a metal;

"major amount" means in excess of 50 mass % of a composition expressed in respect of the stated component and in respect of the total mass of the composition, reckoned as active ingredient of the component;

"minor amount" means less than 50 mass % of a composition, expressed in respect of the stated additive and in respect of the total mass of the composition, reckoned as active ingredient of the additive;

"effective minor amount" in respect of an additive means a minor amount of such an additive in a lubricating oil composition so that the additive provides the desired technical effect;

"non-ferrous metal" includes a metal or an alloy thereof comprising lead, copper, tin, or an alloy thereof of such metals, preferably a metal of copper or lead, or an alloy thereof of such metals, especially copper or an alloy thereof;

non-ferrous metal corrosion (e.g. corrosion of copper and lead) is measured by the High Temperature Corrosion Bench Test in accordance with ASTM D6594;

"ppm" means parts per million by mass, based on the total mass of the lubricating oil composition;

"metal content" of the lubricating oil composition or of an additive component, for example molybdenum content or total metal content of the lubricating oil composition (i.e. the sum of all individual metal contents), is measured by ASTM D5185;

"TBN" in relation to an additive component or of a lubricating oil composition of the present invention, means total base number (mg KOH/g) as measured by ASTM D2896;

"KV_{100}" means kinematic viscosity at 100°C as measured by ASTM D445;

"phosphorus content" is measured by ASTM D5185;

"sulfur content" is measured by ASTM D2622; and,

"sulfated ash content" is measured by ASTM D874.

[0029] All percentages reported are mass % on an active ingredient basis, i.e. without regard to carrier or diluent oil, unless otherwise stated.

[0030] 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.

[0031] Further, it is understood that any upper and lower quantity, range and ratio limits set forth herein may be independently combined. Accordingly, any upper and lower quantity, range and ratio limits set forth herein associated with a particular technical feature of the present invention may be independently combined with any upper and lower quantity, range and ratio limits set forth herein associated with one or more other particular technical feature(s) of the present invention. Furthermore, any particular technical feature of the present invention, and all preferred variants thereof, may be independently combined with any other particular technical feature(s), and all preferred variants thereof.

[0032] Also, it will be understood that the preferred features of each aspect of the present invention are regarded as preferred features of every other aspect of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0033] 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)

[0034] 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.

[0035] The base stock groups are defined in the American Petroleum Institute (API) publication "Engine Oil Licensing and Certification System", Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998. Typically, the base stock will have a viscosity preferably of 3-12, more preferably 4-10, most preferably 4.5-8, mm^2/s (cSt) at 100°C.

[0036] Definitions for the base stocks and base oils in this invention are the same as those found in the American Petroleum Institute (API) publication "Engine Oil Licensing and Certification System", Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998. Said publication categorizes base stocks as follows:

a) Group I base stocks contain less than 90 percent saturates and/or greater than 0.03 percent sulphur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table E-1.

b) Group II base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulphur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table E-1.

c) Group III base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulphur and have a viscosity index greater than or equal to 120 using the test methods specified in Table E-1.

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

e) Group V base stocks include all other base stocks not included in Group I, II, III, or IV.

Table E-1: Analytical Methods for Base Stock

Property	Test Method
Saturates	ASTM D 2007
Viscosity Index	ASTM D 2270
Sulphur	ASTM D 2622
	ASTM D 4294
	ASTM D 4927
	ASTM D 3120

[0037] Other oils of lubricating viscosity which may be included in the lubricating oil composition are detailed as follows:

> 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.

[0038] 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.

[0039] 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, sebasic 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 oftetraethylene glycol and two moles of 2-ethylhexanoic acid.

[0040] 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.

[0041] 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.

[0042] 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. Whilst the composition of the base oil will depend upon the particular application of the lubricating oil composition and the oil formulator will chose the base oil to achieve desired performance characteristics at reasonable cost, the base oil of a lubricating oil composition according to the present invention typically comprises no more than 85 mass % Group IV base oil, the base oil may comprise no more than 70 mass % Group IV base oil, or even no more than 50 mass % Group IV base oil. The base oil of a lubricating oil composition according to the present invention may comprise 0 mass % Group IV base oil. Alternatively, the base oil of a lubricating oil composition according to the present invention may comprise at least 5 mass %, at least 10 mass % or at least 20 mass % Group IV base oil. The base oil of a lubricating oil composition according to the present invention may comprise from 0 to 85 mass%, or from 5-85 mass %, alternatively from 10-85 mass % Group IV base oil.

[0043] Preferably, the volatility of the oil of lubricating viscosity or oil blend, as measured by the NOACK test (ASTM D5800), is less than or equal to 20 %, preferably less than or equal to 16 %, preferably less than or equal to 12 %, more preferably less than or equal to 10 %. Preferably, the viscosity index (VI) of the oil of lubricating viscosity is at least 95, preferably at least 110, more preferably up to 120, even more preferably at least 120, even more preferably at least 125, most preferably from about 130 to 140.

[0044] The oil of lubricating viscosity is provided in a major amount, in combination with a minor amount 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 additives directly to the oil or by adding them 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.

[0045] 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.

[0046] 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.

[0047] Preferably, the lubricating oil composition is a multigrade oil identified by the viscometric descriptor SAE 20WX, SAE 15WX, SAE 10WX, SAE 5WX or SAE 0WX, where X represents any one of 20, 30, 40 and 50; the characteristics of the different viscometric grades can be found in the SAE J300 classification. In an embodiment of each aspect of the invention, independently of the other embodiments, the lubricating oil composition is in the form of an SAE 10WX, SAE 5WX or SAE 0WX, preferably in the form of a SAE 5WX or SAE 0WX, wherein X represents any one of 20, 30, 40 and 50. Preferably X is 20 or 30.

POLYMERIC FRICTION MODIFIER (B)

[0048] The oil-soluble or oil-dispersible polymeric friction modifier (B) is the reaction product of solely:

(i) a functionalised polyolefin, as defined herein;
(ii) a polyalkylene glycol;
(iii) a polyol; and,
(iv) a polycarboxylic acid, as defined herein.

[0049] By the word "solely", we mean the oil-soluble or oil-dispersible polymeric friction modifier (B), as defined in each aspect of the present invention, is a copolymer derived from the reaction of only a functionalised polyolefin, a polyalkylene glycol, a polyol and a polycarboxylic acid (i.e. a copolymer which is the reaction product of only one or more functionalised polyolefins, one or more polyalkylene glycols, one or more polyols and one or more polycarboxylic acids).

The Functionalised Polyolefin (B(i))

[0050] The one or more functionalised polyolefins is a polyalkylene which includes at least one diacid or anhydride functional group. The one or more functionalised polyolefins is preferably derived from polymerisation of an olefin, especially a mono-olefin, having from 2 to 6 carbon atoms, such as ethene, propene, but-1-ene and isobutene (i.e. 2-methyl propene) and the resulting polyolefin functionalised with a diacid or anhydride functional group. Preferably, the one or more functionalised polyolefins is a poly(C_2 to C_6 alkylene) functionalised with a diacid or anhydride functional group. Even more preferably, the one or more functionalised polyolefins is derived from polymerisation of isobutene and the resulting polyisobutylene functionalised with a diacid or anhydride functional group (i.e. the functionalised polyolefin is functionalised polyisobutylene).

[0051] The polyalkylene part (e.g. the poly(C_2 to C_6 alkylene)) of the one or more functionalised polyolefins suitably includes a carbon chain of 15 to 500 (e.g. 35 to 500, 40 to 500, 50 to 500), preferably 50 to 200, carbon atoms. Suitably, the polyalkylene part of the one or more functionalised polyolefins has a number average molecular weight (Mn) of from 300 to 5000, preferably 500 to 1500, especially 800 to 1200 daltons.

[0052] The functionalised polyolefin(s) includes at least one diacid or anhydride functional group which is capable of reacting with a hydroxyl functional group of the polyalkylene glycol (B(ii)) or a hydroxyl group of the polyol (B(iii)). Accordingly, the functionalised polyolefin(s) may be formed by reaction of the polyolefin (i.e. poly(alkylene)) with an unsaturated diacid or anhydride. Preferably, the functionalised polyolefin(s) includes an anhydride functional group. Suitably the anhydride functionalised polyalkylene(s) is derived from the reaction of the polyalkylene (e.g. the poly(C_2 to C_6 alkylene)) with an anhydride, especially maleic anhydride which forms a succinic anhydride functional group. Accordingly, the functionalised polyolefin(s) includes an anhydride functional group, especially a succinic anhydride functional group.

[0053] Accordingly, preferred one or more functionalised polyolefins is a polyalkylene which includes an anhydride functional group, more preferably a poly(C_2 to C_6 alkylene) which includes an anhydride functional group, even more preferably a poly(C_2 to C_6 alkylene) which includes a succinic anhydride functional group, especially polyisobutylene(s) (PIB(s)) which includes a succinic anhydride functional group - namely polyisobutylene succinic anhydride(s) (PIBSA(s)). Suitably, the polyisobutylene of the PIBSA has a number average molecular weight (Mn) of from 300 to 5000, preferably 500 to 1500, especially 800 to 1200 daltons. PIB is a commercially available compound and sold under the trade name of Glissopal by BASF and this product can be reacted to give a functionalised polyolefin (B(i)).

[0054] Suitably, the functionalised polyolefin(s) which includes a diacid or anhydride functional group as defined herein (e.g. a poly(C_2 to C_6 alkylene) which includes a diacid or anhydride functional group, even more preferably a poly(C_2 to C_6 alkylene) which includes a succinic anhydride functional group, especially a polyisobutylene (PIB) which includes a succinic anhydride functional group - namely polyisobutylene succinic anhydride (PIBSA)) is formed by a direct thermal condensation reaction (i.e. thermal ene reaction) between the appropriate unsaturated diacid or anhydride (e.g. maleic anhydride) and the polyolefin (e.g. poly(C_2 to C_6 alkylene), preferably polyisobutylene (PIB)). This process is known as the thermal ene reaction and is usually conducted at a temperature of greater than 150°C for 1 to 48 hours. The functionalised polyolefin formed by the thermal ene reaction is chemically distinct and has different physical and chemical properties than a comparable functionalised polyolefin which is formed by a chlorination process (i.e. chlorination of the polyolefin followed by reaction with the appropriate diacid or anhydride).

The Polyalkylene Glycol (B(ii))

[0055] Suitably, the one or more polyalkylene glycols is a poly(C_2 to C_{20} alkylene) glycol, preferably a poly(C_2 to C_{10} alkylene) glycol, more preferably a poly(C_2 to C_6 alkylene) glycol. Preferred one or more polyalkylene glycols are one or more polyethylene glycols or one or more polypropylene glycols or one or more mixed poly(ethylene-propylene) glycols, or combinations thereof. The most preferred one or more polyalkylene glycols are one or more polyethylene glycols (PEGs), especially a water soluble PEG.

[0056] The polyalkylene glycol includes two hydroxyl groups which are capable of reacting with the functional group of the functionalised polyolefin (B(i)), thereby forming an essentially polyolefin-polyalkylene glycol copolymer, and/or reacting with the polycarboxylic acid (B(iv)), thereby forming an essentially polyolefin-polyalkylene glycol-carboxylic acid compound or a polyalkylene glycol-carboxylic acid compound. It will be appreciated that such compounds may react further with the functionalised polyolefin (B(i)), the polyalkylene glycol (B(ii)), the polyol (B(iii)) and/or the polycarboxylic acid (B(iv)).

[0057] Suitably, the polyalkylene glycol(s) (e.g. PEG) has a number average molecular weight (Mn) of from 300 to 5000, preferably 400 to 1000, especially 400 to 800, daltons. Accordingly, in a preferred embodiment the polyalkylene glycol (B(ii)) is PEG_{400}, PEG_{600} or PEG_{1000}. Suitably, PEG_{400}, PEG_{600} and PEG_{1000} are commercially available from Croda International.

The Polyol (B(iii))

[0058] The polyol reactant is capable of reacting with the functionalised polyolefin thereby providing a backbone moiety which links together separate blocks of functionalised polyolefin. Suitably, when the functionalised polyolefin is functionalised with an anhydride or diacid functional group, the polyol provides a backbone moiety which links together, via ester bonds, separate blocks of the polyolefin.

[0059] Suitably, the polyol reactant is also capable of reacting with the polycarboxylic acid thereby providing a polyol-carboxylic acid compound, wherein such compound may react further with the functionalised polyolefin (B(i)) and/or the polyalkylene glycol (B(ii)).

[0060] The polyol is an alcohol which includes two or more hydroxyl functional groups (i.e. a polyhydric alcohol) but excludes a "polyalkylene glycol" (component B(ii)) which is used to form the oil-soluble or oil-dispersible polymeric friction modifier. Preferably, the polyol includes three or more hydroxyl functional groups. Accordingly, the polyol may be a diol, triol, tetrol, and/or related dimers or chain extended polymers of such compounds. Suitably, the one or more polyols is a C_2 to C_{20} hydrocarbyl polyol, more preferably a C_2 to C_{20} aliphatic hydrocarbyl polyol, even more preferably a saturated C_2 to C_{20} aliphatic hydrocarbyl polyol, even more preferably a saturated C_2 to C_{15} aliphatic hydrocarbyl polyol. Suitably, the polyol has a molecular weight (Mw) of less than or equal to 400, preferably less than or equal to 350, more preferably less than or equal to 300, most preferably less than or equal to 280, daltons. Examples of suitable polyols include glycerol, neopentyl glycol, trimethylolethane, trimethylolpropane, trimethylolbutane, pentaerythritol, dipentaerythritol, tripentaerythritol and sorbitol. A highly preferred polyol is glycerol.

The Polycarboxylic Acid (B(iv))

[0061] The polycarboxylic acid reactant is capable of reacting with the hydroxyl group of the polyalkylene glycol (B(ii)) thereby providing a back bone moiety which links together, via ester bonds, separate blocks of polyalkylene glycol.

[0062] Suitably, the polycarboxylic acid is also capable of reacting with the polyol (B(iii)), thereby providing a polyol-carboxylic acid compound, wherein such compound may react further with the functionalised polyolefin (B(i)) and/or the polyalkylene glycol (B(ii)).

[0063] The polycarboxylic acid is an organic acid which has two or more carboxylic acid groups. The polycarboxylic acid may be a di-, tri- and tetra- carboxylic acid; dicarboxylic acids are preferred. Suitably, the one or more polycarboxylic acids is a C_2 to C_{30} hydrocarbyl polycarboxylic acid, preferably a C_2 to C_{20} hydrocarbyl polycarboxylic acid, even more preferably a C_2 to C_{30} hydrocarbyl dicarboxylic acid, even more preferably a C_2 to C_{20} hydrocarbyl dicarboxylic acid, even more preferably a C_2 to C_{20} aliphatic hydrocarbyl dicarboxylic acid. Still even more preferably, the one or more polycarboxylic acids is an acyclic C_2 to C_{30} aliphatic hydrocarbyl dicarboxylic acids, even more preferably an acyclic C_2 to C_{20} aliphatic hydrocarbyl dicarboxylic acids. Linear polycarboxylic acids are preferred to branched chain polycarboxylic acids. Saturated polycarboxylic acids are preferred to unsaturated polycarboxylic acids, such as maleic acid.

[0064] Accordingly, the one or more preferred polycarboxylic acids is a C_2 to C_{30} hydrocarbyl polycarboxylic acid, such as a saturated C_2 to C_{30} hydrocarbyl polycarboxylic acid (e.g. a saturated C_2 to C_{30} hydrocarbyl dicarboxylic acid), more preferably a C_2 to C_{30} aliphatic hydrocarbyl polycarboxylic acid, such as a saturated C_2 to C_{30} aliphatic hydrocarbyl polycarboxylic acid (e.g. a saturated C_2 to C_{30} aliphatic hydrocarbyl dicarboxylic acid), more preferably a C_2 to C_{20} aliphatic hydrocarbyl polycarboxylic acid, such as a saturated C_2 to C_{20} aliphatic hydrocarbyl polycarboxylic acid (e.g. a saturated C_2 to C_{20} aliphatic hydrocarbyl dicarboxylic acid), even more preferably a C_6 to C_{20} aliphatic hydrocarbyl polycarboxylic acid, such as a saturated C_6 to C_{20} aliphatic hydrocarbyl polycarboxylic acid (e.g. a saturated C_6 to C_{20} aliphatic hydrocarbyl dicarboxylic acid), even more preferably a C_8 to C_{20} aliphatic hydrocarbyl polycarboxylic acid, such as a saturated C_8 to C_{20} aliphatic hydrocarbyl polycarboxylic acid (e.g. a saturated C_8 to C_{20} aliphatic hydrocarbyl dicarboxylic acid - especially sebacic acid).

[0065] Suitable polycarboxylic acids include oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid and sebacic acid. The most preferred polycarboxylic acid is sebacic acid.

[0066] Thus according to a highly preferred embodiment the oil-soluble or oil-dispersible polymeric friction modifier (B) is the reaction product of solely:

(i) PIBSA, as defined herein;
(ii) polyethylene glycol, as defined herein;
(iii) a polyol, preferably glycerol; and
(iv) a polycarboxylic acid, preferably sebacic acid.

[0067] Suitably, during formation of the polymeric friction modifier multiple reactions between the functionalised polyolefin (B(i)), polyalkylene glycol (B(ii)), polyol (B(iii)) and polycarboxylic acid (B(iv)) may occur. For example, the functionalised polyolefin and the polyalkylene glycol may react so that the polyolefin is linked directly to the polyalkylene glycol (e.g. via an ester bond) and subsequent reactions may occur between the resulting polymer with either the functionalised polyolefin, polyalkylene glycol, polyol and/or polycarboxylic acid. Alternatively, or additionally, the polyalkylene glycol may react with the polycarboxylic acid to form blocks of polyalkylene glycol linked together by the esterified polycarboxylic acid and subsequent reactions may occur between the resulting blocks of polyalkylene glycol with the functionalised polyolefin and/or blocks of the functionalised polyolefin. Still further, the functionalised polyolefin may react with the polyol to form blocks of the functionalised polyolefin linked together (typically via an ester linkage) by the polyol and subsequent reactions may occur between the resulting blocks of functionalised polyolefin with the polyalkylene glycol and/or blocks of the polyalkylene glycol.

[0068] Accordingly, the functionalised polyolefin, polyalkylene glycol, polyol and polycarboxylic acid may react to form a block copolymer. When present the number of block copolymer units in the organic friction modifier additive typically ranges from 2 to 20, preferably 2 to 15, more preferably 2 to 10, units.

[0069] As with all polymers, the polymeric friction modifier will typically comprise a mixture of molecules of various sizes. The polymeric friction modifier (B) suitably has a number average molecular weight of from 1,000 to 30,000, preferably from 1,500 to 25,000, more preferably from 2,000 to 20,000, daltons.

[0070] The polymeric friction modifier (B) suitably has an acid value of less than 20, preferably less than 15 and more preferably less than 10 mg KOH/g (ASTM D974). The polymeric friction modifier (B) suitably has an acid value of greater than 1, preferably greater than 1.5 mg KOH/g. In a preferred embodiment, the polymeric friction modifier (B) has an acid value in the range of 1.5 to 9.

[0071] The polymeric friction modifier (B) may be prepared by techniques well known to those skilled in the art, such as described in US patent application no. 13/582,589. Typically, the functionalised polyolefin, polyalkylene glycol, polyol, and polycarboxylic acid are heated at 100 to 250°C in the presence of a catalyst (e.g. tetrabutyl titanate) and water removed.

[0072] In a preferred embodiment the polymeric friction modifier (B) is a reaction product of maleinised polyisobutylene (PIBSA), PEG, glycerol and sebacic acid, wherein the polyisobutylene of the maleinised polyisobutylene (PIBSA) has a number average molecular weight of around 950 daltons, the PIBSA has an approximate saponification value of 98mg KOH/g and the PEG has a number average molecular weight of around 600 daltons and a hydroxyl value of 190 mg KOH/g. A suitable additive may be made by charging 158.4 g (0.128 mol) of PIBSA, 101 g (0.168 mol) of PEG_{600}, 10.4 g (0.0514 mol) of sebacic acid and 7.7 g (0.0835 mol) of glycerol into a glass round bottomed flask equipped with a nitrogen purge, mechanical stirrer, isomantle heater and distillation arm. The reaction takes place in the presence of 0.5 ml of esterification catalyst tetrabutyl titanate at 180-230°C, with removal of water to a final acid value of 1.7 mg/KOH/g. Accordingly, alternative polymeric friction modifiers (B) may be prepared by analogous synthetic methods.

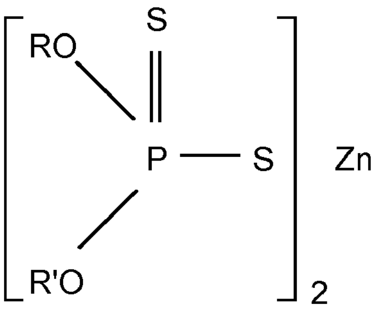
[0073] The polymeric friction modifier (B) is suitably present in the lubricating oil composition of the present invention, on an active matter basis, in an amount of at least 0.1, preferably at least 0.2, mass % based on the total mass of the lubricating oil composition. The polymeric friction modifier of the present invention is suitably present in the lubricating oil composition, on an active matter basis, in an amount of less than or equal to 5, preferably less than or equal to 3, more preferably less than or equal to 1.5, mass %, based on the total mass of the lubricating oil composition.

DIHYDROCARBYL DITHIOPHOSPHATE METAL SALT (C)

[0074] For the lubricating oil compositions of the present invention, any suitable oil-soluble or oil-dispersible dihydrocarbyl dithiophosphate metal salt having anti-wear properties in lubricating oil compositions may be employed. Noteworthy are dihydrocarbyl dithiophosphate metal salts wherein the metal may be an alkali or alkaline earth metal, or aluminium, lead, tin, molybdenum, manganese, nickel, copper, or preferably, zinc. Accordingly, a preferred dihydrocarbyl dithiophosphate metal salt is zinc dihydrocarbyl dithiophosphate (ZDDP), more preferably zinc dialkyl dithiophosphate, especially zinc di(C_2 to C_8 alkyl) dithiophosphate wherein the C_2 to C_8 alkyl groups of the zinc di(C_2 to C_8 alkyl) dithiophosphate may be the same or different.

[0075] Dihydrocarbyl dithiophosphate metal salts may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohols or a phenol with P_2S_5 and then neutralizing the formed DDPA with a metal compound. For example, a dithiophosphoric acid may be made by reacting mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared where the hydrocarbyl groups on one are entirely secondary in character and the hydrocarbyl groups on the others are entirely primary in character. To make the metal salt, any basic or neutral metal compound could be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of metal due to the use of an excess of the basic metal compound in the neutralization reaction.

[0076] The preferred zinc dihydrocarbyl dithiophosphates (ZDDP) are oil-soluble salts of dihydrocarbyl dithiophosphoric acids and may be represented by the following formula:



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

[0077] The dihydrocarbyl dithiophosphate metal salt, such as ZDDP, is added to the lubricating oil compositions in amounts sufficient to provide no greater than 1200ppm, preferably no greater than 1000ppm, more preferably no greater than 900ppm, most preferably no greater than 850ppm by mass of phosphorous to the lubricating oil, based upon the total mass of the lubricating oil composition, and as measured in accordance with ASTM D5185. The dihydrocarbyl dithiophosphate metal salt, such as ZDDP, is suitably added to the lubricating oil compositions in amounts sufficient to provide at least 100ppm, preferably at least 350ppm, more preferably at least 500ppm by mass of phosphorous to the lubricating oil, based upon the total mass of the lubricating oil composition, and as measured in accordance with ASTM D5185.

[0078] Suitably, the dihydrocarbyl dithiophosphate metal salt, such as ZDDP, is present in an amount of greater than or equal to 0.1, preferably greater than or equal to 0.25, more preferably greater than or equal to 0.5, mass % based on the total mass of the lubricating oil composition. Suitably, the dihydrocarbyl dithiophosphate metal salt, such as ZDDP, is present in an amount of less than or equal to 10, preferably less than or equal to 5.0, more preferably less than or equal to 3.0, mass % based on the total mass of the lubricating oil composition.

ENGINES

[0079] 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 internal combustion engines, particularly spark-ignited or compression-ignited two- or four- stroke reciprocating engines, by adding the composition thereto. The engines may be conventional gasoline or diesel engines designed to be powered by gasoline or petroleum diesel, respectively; alternatively, the engines may be specifically modified to be powered by an alcohol based fuel or biodiesel fuel.

CO-ADDITIVES

[0080] 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 in a fully formulated lubricant.

Additive	**Mass %**	**Mass %**
	(Broad)	(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

(continued)

Additive	Mass %	Mass %
	(Broad)	(Preferred)
Anti-Foaming Agent	0 - 5	0.001 - 0.15
Supplement Anti-Wear Agents	0 - 5	0 - 2
Viscosity Modifier (1)	0 - 10	0.01 - 4
Mineral or Synthetic Base Oil	Balance	Balance

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

[0081] 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.

[0082] Suitably, the lubricating oil composition includes one or more co-additives in a minor amount, other than additive components (B) and (C), selected from ashless dispersants, metal detergents, corrosion inhibitors, antioxidants, pour point depressants, antiwear agents, friction modifiers, demulsifiers, antifoam agents and viscosity modifiers.

[0083] 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.

[0084] Metal detergents function both as detergents to reduce or remove deposits and as acid neutralizers or rust inhibitors, thereby reducing wear and corrosion and extending engine life. Detergents generally comprise a polar head with a long hydrophobic tail, with the polar head comprising a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal in which case they are usually described as normal or neutral salts, and would typically have a total base number or TBN (as can be measured by ASTM D2896) of from 0 to 80 mg KOH/g. A large amount of a metal base may be incorporated by reacting excess metal compound (e.g., an oxide or hydroxide) with an acidic gas (e.g., carbon dioxide). The resulting overbased detergent comprises neutralized detergent as the outer layer of a metal base (e.g. carbonate) micelle. Such overbased detergents may have a TBN of 150 mg KOH/g or greater, and typically will have a TBN of from 250 to 450 mg KOH/g or more. In the presence of the compounds of Formula I, the amount of overbased detergent can be reduced, or detergents having reduced levels of overbasing (e.g., detergents having a TBN of 100 to 200 mg KOH/g), or neutral detergents can be employed, resulting in a corresponding reduction in the SASH content of the lubricating oil composition without a reduction in the performance thereof.

[0085] 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. Combinations of detergents, whether overbased or neutral or both, may be used.

[0086] In one embodiment of the present invention, the lubricating oil composition includes metal detergents that are chosen from neutral or overbased calcium sulfonates having TBN of from 20 to 450 mg KOH/g, and neutral and overbased calcium phenates and sulfurized phenates having TBN of from 50 to 450 mg KOH/g, and mixtures thereof.

[0087] Sulfonates may be prepared from sulfonic acids which are typically obtained by the sulfonation of alkyl substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum or by the alkylation of aromatic hydrocarbons. Examples included those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl or their halogen derivatives such as chlorobenzene, chlorotoluene and chloronaphthalene. The alkylation may be carried out in the presence of a catalyst with alkylating agents having from about 3 to more than 70 carbon atoms. The alkaryl sulfonates usually contain from about 9 to about 80 or more carbon atoms, preferably from about 16 to about 60 carbon atoms per alkyl substituted aromatic moiety. The oil soluble sulfonates or alkaryl sulfonic acids may be neutralized with oxides, hydroxides, alkoxides, carbonates, carboxylate, sulfides, hydrosulfides, nitrates, borates and ethers of the metal. The amount of metal compound is chosen having regard to the desired TBN of the final product but typically ranges from about 100 to 220 mass % (preferably at least 125 mass %) of that stoichiometrically required.

[0088] Metal salts of phenols and sulfurized phenols are prepared by reaction with an appropriate metal compound such as an oxide or hydroxide and neutral or overbased products may be obtained by methods well known in the art. Sulfurized phenols may be prepared by reacting a phenol with sulfur or a sulfur containing compound such as hydrogen sulfide, sulfur monohalide or sulfur dihalide, to form products which are generally mixtures of compounds in which 2 or more phenols are bridged by sulfur containing bridges.

[0089] In another embodiment of the present invention, the lubricating oil composition comprises metal detergents that are neutral or overbased alkali or alkaline earth metal salicylates having a TBN of from 50 to 450 mg KOH/g, preferably a TBN of 50 to 250 mg KOH/g, or mixtures thereof. Highly preferred salicylate detergents include alkaline earth metal salicylates, particularly magnesium and calcium, especially, calcium salicylates. In one embodiment of the present invention, alkali or alkaline earth metal salicylate detergents are the sole metal-containing detergent in the lubricating oil composition.

[0090] Supplemental anti-wear agents, other than dihydrocarbyl dithiophosphate metal salts (additive component (C)), which may be included in the lubricating oil composition comprise 1,2,3-triazoles, benzotriazoles, sulfurised fatty acid esters, and dithiocarbamate derivatives.

[0091] Ashless dispersants comprise an oil-soluble polymeric hydrocarbon backbone having functional groups that are capable of associating with particles to be dispersed. Typically, the dispersants comprise amine, alcohol, amide, or ester polar moieties attached to the polymer backbone often via a bridging group. The ashless dispersants may be, for example, selected from oil-soluble salts, esters, amino-esters, amides, imides, and oxazolines of long chain hydrocarbon substituted mono and dicarboxylic acids or their anhydrides; thiocarboxylate derivatives of long chain hydrocarbons; long chain aliphatic hydrocarbons having a polyamine attached directly thereto; and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and a polyalkylene polyamine.

[0092] Friction modifiers include glycerol monoesters of higher fatty acids, for example, glycerol mono-oleate (GMO); esters of long chain polycarboxylic acids with diols, for example, the butane diol ester of a dimerized unsaturated fatty acid; oxazoline compounds; and alkoxylated alkyl-substituted mono-amines, diamines and alkyl ether amines, for example, ethoxylated tallow amine and ethoxylated tallow ether amine.

[0093] Typically, the total amount of additional organic ashless friction modifier in a lubricant according to the present invention does not exceed 5 mass %, based on the total mass of the lubricating oil composition and preferably does not exceed 2 mass % and more preferably does not exceed 0.5 mass %. In an embodiment of the present invention, the lubricating oil composition contains no additional organic ashless friction modifier.

[0094] Other known friction modifiers comprise 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.

[0095] One class of preferred organo-molybdenum compounds useful in all aspects of the present invention is trinuclear 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.

[0096] 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.

[0097] 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.

[0098] Viscosity modifiers (VM) function to impart high and low temperature operability to a lubricating oil. The VM used may have that sole function, or may be multifunctional. Multifunctional viscosity modifiers that also function as dispersants are also known. Suitable viscosity modifiers are polyisobutylene, copolymers of ethylene and propylene and higher alpha-olefins, polymethacrylates, polyalkylmethacrylates, methacrylate copolymers, copolymers of an unsaturated dicarboxylic acid and a vinyl compound, inter polymers of styrene and acrylic esters, and partially hydrogenated copolymers of styrene/ isoprene, styrene/butadiene, and isoprene/butadiene, as well as the partially hydrogenated homopolymers of butadiene and isoprene and isoprene/divinylbenzene.

[0099] Anti-oxidants, sometimes referred to as oxidation inhibitors, 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 oxidation catalysts inert. Oxidative deterioration can be evidenced by sludge in the lubricant, varnish-like deposits on the metal surfaces, and by viscosity growth. Examples of suitable antioxidants are selected from copper-containing antioxidants, sulfur-containing antioxidants, aromatic amine-containing antioxidants, hindered phenolic antioxidants, dithiophosphates derivatives, and metal thiocarbamates. Preferred anti-oxidants are aromatic amine-containing antioxidants, hindered phenolic antioxidants and mixtures thereof. In a preferred embodiment, an antioxidant is present in a lubricating oil composition of the present invention.

[0100] Rust inhibitors selected from the group consisting of nonionic polyoxyalkylene polyols and esters thereof, polyoxyalkylene phenols, and anionic alkyl sulfonic acids may be used.

[0101] Copper and lead bearing corrosion inhibitors may be used, but are typically not required with the formulation of the present invention. Typically such compounds are the thiadiazole polysulfides containing from 5 to 50 carbon atoms, their derivatives and polymers thereof. Derivatives of 1, 3, 4 thiadiazoles such as those described in U.S. Patent Nos. 2,719,125; 2,719,126; and 3,087,932; are typical. Other similar materials are described in U.S. Patent Nos. 3,821,236; 3,904,537; 4,097,387; 4,107,059; 4,136,043; 4,188,299; and 4,193,882. Other additives are the thio and polythio sulfenamides of thiadiazoles such as those described in UK Patent Specification No. 1,560,830. Benzotriazoles derivatives also fall within this class of additives. When these compounds are included in the lubricating composition, they are preferably present in an amount not exceeding 0.2 wt. % active ingredient.

[0102] A small amount of a demulsifying component may be used. A preferred demulsifying component is described in EP 330522. 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.

[0103] Pour point depressants, otherwise known as lube oil flow improvers, lower the minimum temperature at which the fluid will flow or can be poured. Such additives are well known. Typical of those additives which improve the low temperature fluidity of the fluid are C_8 to C_{18} dialkyl fumarate/vinyl acetate copolymers, polyalkylmethacrylates and the like.

[0104] Foam control can be provided by many compounds including an antifoamant of the polysiloxane type, for example, silicone oil or polydimethyl siloxane.

[0105] The individual additives may be incorporated into a base stock in any convenient way. Thus, each of the components can be added directly to the base stock or base oil blend by dispersing or dissolving it in the base stock or base oil blend at the desired level of concentration. Such blending may occur at ambient or elevated temperatures.

[0106] Preferably, all the additives except for the viscosity modifier and the pour point depressant are blended into a concentrate or additive package described herein as the additive package that is subsequently blended into base stock to make the finished lubricant. The concentrate will typically be formulated to contain the additive(s) in proper amounts to provide the desired concentration in the final formulation when the concentrate is combined with a predetermined amount of a base lubricant.

[0107] The concentrate is preferably made in accordance with the method described in US 4,938,880. That patent describes making a pre-mix of ashless dispersant and metal detergents that is pre-blended at a temperature of at least about 100°C. Thereafter, the pre-mix is cooled to at least 85°C and the additional components are added.

[0108] Typically, the additive package used to formulate the lubricating oil composition according to the present invention has a total base number (TBN) as measured by ASTM D2896 of 25 to 100, preferably 45 to 80, and the lubricating oil composition according to the present invention has a total base number (TBN) as measured by ASTM D2896 of 4 to 15, preferably 5 to 12. In an embodiment of the present invention, the additive package does not have a total base number (TBN) as measured by ASTM D2896 of between 62 and 63.5 and the lubricating oil composition does not have a total base number (TBN) as measured by ASTM D2896 of between 9.05 and 9.27.

[0109] The final crankcase lubricating oil formulation may employ from 2 to 20, preferably 4 to 18, and most preferably 5 to 17, mass % of the concentrate or additive package with the remainder being base stock.

[0110] In an embodiment of the present invention, a lubricating oil composition according to the first aspect of the invention does not comprise 0.2-0.25 mass% of sulphur as measured according to ASTM method D4927.

[0111] In an embodiment of the present invention, a lubricating oil composition according to the first aspect of the invention does not comprise 0.08-0.11 mass% of nitrogen as measured according to ASTM method D5291.

EXAMPLES

[0112] The invention will now be described in the following examples which are not intended to limit the scope of the claims hereof.

[0113] Unless otherwise specified, all of the additives described in the Examples are available as standard additives from lubricant additive companies such as Infineum UK Ltd, Lubrizol Corporation and Afton Chemical Corporation.

Example 1 Preparation of Polymeric Friction Modifier (B)

[0114] A 500 cm^3 5-necked round-bottomed flask equipped with a nitrogen purge, stirrer with a gas-tight stirrer bearing, temperature probe and distillation arm attached to an exit bubbler was charged with PIBSA (158.4 g, 0.128 mol), PEG_{600} (101.0 g, 0.168 mol), sebacic acid (10.4 g, 0.0514 mol) and glycerol (7.7 g, 0.0835 mol) and the mixture heated at 180 °C with stirring for 1 hour. The reaction mixture was then heated to a temperature of 230°C for 1 hour and then tetrabutyl titanate (0.5 ml) added thereto and heating and stirring continued for 2 hours at a temperature of 230°C and a reduced pressure of between 50 to 150 mbar. The reaction mixture was cooled to below 100°C and the polymeric friction modifier (B) poured from the round bottom flask. The polymeric friction modifier (B) had an acid value of 1.7 mg KOH/g.

Example 2 Anti-Corrosion Performance

[0115] Six lubricating oil compositions (referred to as the base lubricant and Oils 1 to 5) were prepared. Each of the base lubricant and Oils 1 to 5 contained an identical Group II base stock and equal amounts of the following identical additives: an overbased calcium sulphonate detergent (TBN 300 mg KOH/g); a dispersant; anti-oxidants; a molybdenum friction modifier; and a viscosity modifier. Oils 1 to 5 also included the additional additive(s), on an active ingredient basis, as detailed in Table 1. Those oils which included ZDDP (i.e. Oils 3 to 5) had a phosphorus content of 880ppm as measured by ASTM D5185. Oil 5 represents a lubricating oil composition of the present invention.

Table 1

Component	Base lubricant	Oil 1 Mass%	Oil 2 Mass%	Oil 3 Mass%	Oil 4 Mass%	Oil 5 Mass%
ZDDP	-	-	-	1.10	1.10	1.10
Polymeric friction modifier (B)[1]	-	0.50	-	-	-	0.50
Glycerol monooleate	-	-	0.50	-	0.50	-

[0116] The polymeric friction modifier was the compound of Example 1.

TESTING AND RESULTS

[0117] Corrosion control is measured using the High Temperature Corrosion Bench Test (HTCBT) in accordance with ASTM D6594-06. This test method simulates the corrosion of non-ferrous metals, such as copper and lead found in cam followers and bearings, in lubricants; the corrosion process under investigation being induced by lubricant chemistry rather than lubricant degradation or contamination.

[0118] Four metal specimens of copper, lead, tin and phosphor bronze are immersed in a measured amount of a test lubricating oil (100 ml) within a sample tube. The sample tube is immersed in a heated oil bath so that the temperature of the test lubricating oil is heated to 135°C. The test lubricating oil is heated at 135°C for 168 hours and during this time dry air is blown through the heated oil at a rate of 5 litres per hour. After which, the test lubricating oil is cooled and the metal specimens removed and examined for corrosion. The concentration of copper, tin and lead in the test lubricating oil composition and a reference sample of the lubricating oil composition (i.e. a new sample of the test lubricating oil) is then determined in accordance with ASTM D5185. The difference between the concentration of each of the metal contaminants in the test lubricating oil composition and those of the reference sample lubricating oil composition provides a value for the change in the various metal concentrations before and after the test. The industry standard limits to meet the requirements of API CJ-4 are 20 ppm maximum for copper and 120 ppm maximum for lead. The results for the base lubricant and Oils 1 to 5 are set out in Table 2.

Table 2

Corrosion	Base lubricant	Oil 1	Oil 2	Oil 3	Oil 4	Oil 5
Lead (ppm)	23	13	403	63	420	108
Copper (ppm)	33	29	49	27	22	9

[0119] It can be seen from the results in Table 2 that the base lubricant which does not include ZDDP, an ashless organic friction modifier or the polymeric friction modifier (B) produces 23 ppm of lead corrosion and 33 ppm of copper corrosion. A comparison of the results of Oil 1, which is equivalent to the base lubricant that includes the polymeric friction modifier (B), with those of the base lubricant demonstrate that the inclusion of the polymeric friction modifier (B) in Oil 1 inhibits corrosion of both copper (29 ppm versus 33 ppm) and lead (13 ppm versus 23 ppm). In contrast, the inclusion of an ashless organic friction modifier (GMO) in the base lubricant (Oil 2) significantly enhances both lead (403 ppm versus 23 ppm) and copper (49 ppm versus 33 ppm) corrosion.

[0120] As can be seen by a comparison of the results of Oil 3 with those of the base lubricant, the inclusion of ZDDP in the base lubricant increases lead corrosion (63 ppm versus 23 ppm) but shows a marginal improvement in copper corrosion (27 ppm versus 33 ppm). As can be seen from a comparison of the results of Oil 4 with those of the base lubricant, the inclusion of both ZDDP and an ashless organic friction modifier (GMO) in the base lubricant (Oil 4) significantly increases lead corrosion (420ppm versus 23 ppm) but provides an improvement in copper corrosion (22 ppm versus 33 ppm). It is noticeable from a comparison of the results of Oil 5 (a lubricant of the invention which includes ZDDP and the polymeric friction modifier (B)) with those of Oil 4, that the polymeric friction modifier (B) provides significantly less lead corrosion than the ashless organic friction modifier present in Oil 4 (108 ppm versus 420 ppm) and the polymeric friction modifier is far superior than the ashless organic friction modifier at inhibiting copper corrosion (9 ppm versus 22 ppm). Moreover, a comparison of the results of Oil 5 with those of the base lubricant clearly demonstrate that the presence of both ZDDP and the polymeric friction modifier provides a significant decrease in copper corrosion (9 ppm versus 33 ppm).

Claims

1. A lubricating oil composition having a sulphated ash content of less than or equal to 1.2 mass % as determined by ASTM D874 and a phosphorous content of less than or equal to 0.12 mass % as determined by ASTM D5185, which lubricating oil composition comprises or is made by admixing:

(A) an oil of lubricating viscosity, in a major amount;
(B) an oil-soluble or oil-dispersible polymeric friction modifier as an additive in an effective minor amount, the polymeric friction modifier being the reaction product of solely:

(i) one or more functionalised polyolefins which is a poly(alkylene) functionalised with at least one diacid or anhydride functional group and wherein the poly(alkylene) of the functionalised polyolefin has a carbon chain length of from 50 to 500 carbon atoms;
(ii) one or more polyalkylene glycols;
(iii) one or more polyols; and,
(iv) one or more polycarboxylic acids which is a C_2 to C_{30} hydrocarbyl polycarboxylic acid;
and,

(C) at least one oil-soluble or oil-dispersible dihydrocarbyl dithiophosphate metal salt as an additive in an effective minor amount.

2. A composition as claimed in claim 1, wherein the one or more functionalised polyolefins is a poly(C_2 to C_6 alkylene) functionalised with at least one diacid or anhydride functional group and wherein the poly(C_2 to C_6 alkylene) part of the functionalised polyolefin has a carbon chain length of from 50 to 500 carbon atoms.

3. A composition as claimed in claim 1 or 2, wherein the one or more functionalised polyolefins (B (i)) is a polyisobutylene functionalised with at least one diacid or anhydride functional group.

4. A composition as claimed in any one of the preceding claims, wherein the one or more functionalised polyolefins (B (i)) is functionalised with a succinic anhydride functional group.

5. A composition as claimed in claim 1, wherein the one or more functionalised polyolefins (B (i)) is a polyisobutylene succinic anhydride (PIBSA).

6. A composition as claimed in any one of claims 1 to 5, wherein the one or more polyalkylene glycols (B(ii)) is a poly(C_2 to C_6 alkylene) glycol.

7. A composition as claimed in claim 6, wherein the one or more polyalkylene glycols is a polyethylene glycol (PEG).

8. A composition as claimed in any one of the preceding claims, wherein the one or more polyols (B(iii)) is a C_2 to C_{20} aliphatic hydrocarbyl polyol.

9. A composition as claimed in claim 8, wherein the one or more C_2 to C_{20} aliphatic hydrocarbyl polyols is glycerol.

10. A composition as claimed in any one of the preceding claims, wherein the one or more polycarboxylic acids (B(iv)) is a saturated C_2 to C_{20} aliphatic hydrocarbyl dicarboxylic acid.

11. The composition as claimed in claim 10, wherein the one or more saturated C_2 to C_{20} aliphatic hydrocarbyl dicarboxylic acids is sebacic acid.

12. The composition as claimed in any one of the preceding claims, wherein the oil-soluble or oil-dispersible dihydrocarbyl dithiophosphate metal salt is a zinc dihydrocarbyl dithiophosphate.

13. A method of lubricating a spark-ignited or compression-ignited internal combustion engine comprising lubricating the engine with a lubricating oil composition as claimed in any one of the preceding claims.

14. The use, in the lubrication of a spark-ignited or compression-ignited internal combustion engine, of an oil-soluble or oil-dispersible polymeric friction modifier (B) as defined in any one of claims 1 to 12, as an additive in an effective minor amount, in a lubricating oil composition comprising an oil of lubricating viscosity in a major amount to reduce and/or inhibit corrosion of the non-ferrous metal containing engine components during operation of the engine.

15. The use as claimed in claim 14, wherein the non-ferrous metal containing engine components comprises copper, lead, or an alloy of such metals.

16. The use as claimed in claim 14 or 15, wherein the lubricating oil composition further includes an oil-soluble or oil-dispersible dihydrocarbyl dithiophosphate metal salt (C) as defined in any one of claims 1 to 12, as an additive in an effective minor amount.

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EUROPEAN SEARCH REPORT

Application Number
EP 15 17 0236

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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C10M C10N

The present search report has been drawn up for all claims

2

Place of search	Date of completion of the search	Examiner
Munich	1 October 2015	Bertrand, Samuel

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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