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(54) **A lubricating oil composition comprising metal dialkyldithiophosphate and carbodiimide**

Schmierölzusammensetzung enthaltend ein Metaldialkyldithiophosphat und ein Carbodiimid

Composition d'huile de lubrification comprenant un métal dialkyldithiophosphate et un carbodiimide

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(56) References cited:
EP-A- 0 992 571 EP-A- 2 055 761
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EP 2 290 043 B1

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Description**FIELD OF THE INVENTION**

5 **[0001]** 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) internal combustion engines, crankcase lubrication, such compositions being referred to as crankcase lubricants.

10 **[0002]** In particular, although not exclusively, the present invention relates to automotive lubricating oil compositions for use in gasoline (spark-ignited) and diesel (compression-ignited) internal combustion engines fuelled at least in part with a biofuel, especially compression-ignited internal combustion engines fuelled at least in part with a biodiesel fuel and spark-ignited internal combustion engines fuelled at least in part with bioethanol fuel. In particular, although not exclusively, the present invention relates to automotive lubricating oil compositions, preferably having low levels of phosphorus and also low levels of sulfur and/or sulfated ash, which exhibit an improved inhibition and/or a reduction in the corrosion of the metallic engine parts; and to the use of additives in such compositions for improving the anti-corrosion properties of the lubricating oil composition.

BACKGROUND OF THE INVENTION

20 **[0003]** 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. The contamination or dilution of the crankcase lubricant in internal combustion engines, especially engines fuelled at least in part with a biofuel, is a concern.

25 **[0004]** Biodiesel fuels include components of low volatility which are slow to vaporize after injection of the fuel into the engine. Typically, an unburnt portion of the biodiesel and some of the resulting partially combusted decomposition products become mixed with the lubricant on the cylinder wall and are washed down into the oil sump, thereby contaminating the crankcase lubricant. The biodiesel fuel in the contaminated lubricant may form further decomposition products, due to the extreme conditions during lubrication of the engine. It has been found that the presence of biodiesel fuel and the decomposition products thereof in the crankcase lubricant promotes the corrosion of the metallic engine parts; particularly the softer metallic (i.e. non-ferrous) engine parts such as the lead and copper based bearing materials. 30 Moreover, it has been found that this problem is significantly worse in diesel engines which employ a late post-injection of fuel into the cylinder (e.g. light duty, medium duty and passenger car diesel engines) to regenerate an exhaust gas after-treatment device.

35 **[0005]** Exhaust gas after-treatment devices, such as a diesel particulate filter (DPF), require periodical regeneration to remove the build up of soot and to prevent them from having a detrimental effect on engine performance. One way to create conditions for initiating and sustaining regeneration of a DPF involves elevating the temperature of the exhaust gases entering the DPF to burn the soot. As a diesel engine runs relatively cool and lean, this may be achieved by adding fuel into the exhaust gases optionally in combination with the use of an oxidation catalyst located upstream of the DPF. Heavy duty diesel (HDD) engines, such as those in trucks, typically employ a late post-injection of fuel directly into the exhaust system outside of the cylinder, whilst light duty and medium duty diesel engines typically employ a late 40 post-injection of fuel directly into the cylinder during an expansion stroke. Surprisingly, it has been found that the corrosion of the softer metallic (i.e. non-ferrous) engine components increases significantly in a diesel engine fuelled at least in part with biodiesel when the engine employs a late post-injection of fuel directly into the cylinder. Although only theory, it is believed this increased engine corrosion is due to more biodiesel being absorbed by the lubricant on the more exposed cylinder wall, thereby increasing contamination of the lubricant in the sump.

45 **[0006]** A similar increase in the corrosion of the metallic engine parts, particularly the softer metallic (i.e. non-ferrous) engine components, has also been found to occur in spark-ignited internal combustion engines fuelled at least in part with an alcohol based fuel (e.g. bioethanol) due to the presence of the alcohol based fuel and the decomposition products thereof in the crankcase lubricant.

50 **[0007]** Accordingly, lubricating oil compositions which exhibit improved anti-corrosion properties in respect of the metallic engine components, particularly the softer metallic (i.e. non-ferrous) engine components such as those containing copper and/or lead (e.g. bearing materials), must be identified.

[0008] EP 2055761 discloses a Lubricating oil composition comprising zinc dialkyldithiophosphate and a metal phenate. This composition reduces copper and lead corrosion when the lubricant is contaminated with biofuel.

SUMMARY OF THE INVENTION

55 **[0009]** The present invention is based on the discovery that a lubricating oil can be formulated which exhibits significantly improved anti-corrosion properties, particularly in respect of the softer metallic (i.e. non-ferrous) engine components,

such as those containing lead and/or copper.

[0010] In accordance with a first aspect, the present invention provides a crankcase lubricating oil composition comprising:

- (A) an oil of lubricating viscosity in a major amount;
- (B) as an additive component in a minor amount, an oil-soluble metal salt of a dithiophosphoric acid in an amount that introduces 0.02 to 0.12 mass % of phosphorus into the lubricating oil composition;
- (C) as an additive component in a minor amount, an oil-soluble carbodiimide compound in an amount of 0.1 to 10 mass %, based on the total mass of the lubricating oil composition; and,

wherein the lubricating oil composition is contaminated with at least 0.3 mass %, based on the total mass of the lubricating oil composition, of a biofuel or a decomposition product thereof and mixtures thereof.

[0011] Preferably, the oil of lubricating viscosity comprises a Group II, Group III or Group IV base stock, especially a Group III base stock.

[0012] It has unexpectedly been found that a combination of the specific additive components (B) and (C) in a lubricating oil composition provides a significant improvement in the anti-corrosion properties of the lubricating oil composition with regard to the metallic engine components, particularly the softer metallic (i.e. non-ferrous) engine components. In particular, the inclusion of both of the additive components (B) and (C) in a lubricating oil composition, provides a lubricant that exhibits improved inhibition and/or reduction in the corrosion of the metallic engine components, particularly the softer metallic (i.e. non-ferrous) engine components, in use, in the lubrication of a spark-ignited or compression-ignited internal combustion engine, especially a spark-ignited or compression-ignited internal combustion engine which is fuelled at least in part with a biofuel.

[0013] According to a second aspect, the present invention provides a method of lubricating a compression-ignited or spark-ignited internal combustion engine which is fuelled at least in part with a biofuel, comprising operating the engine with a crankcase lubricating oil composition comprising (A) an oil of lubricating viscosity in a major amount; (B) as an additive component in a minor amount, an oil-soluble metal salt of a dithiophosphoric acid as defined in accordance with the first aspect of the invention in an amount that introduces 0.02 to 0.12 mass % of phosphorus into the lubricating oil composition; and, (C) as an additive component in a minor amount, an oil-soluble carbodiimide compound as defined in accordance with the first aspect of the invention in an amount of 0.1 to 10 mass %, based on the total mass of the lubricating oil composition.

[0014] Suitably, the method of the second aspect reduces and/or inhibits the corrosion of the metallic, especially the non-ferrous metallic, engine components. Preferably, the metallic engine components comprise lead, copper or mixtures thereof, especially lead.

[0015] According to a third aspect, the present invention provides the use of a minor amount of an additive component (B) comprising an oil-soluble metal salt of a dithiophosphoric acid as defined in accordance with the first aspect of the invention, in combination with a minor amount of an additive component (C) comprising an oil-soluble carbodiimide compound as defined in accordance with the first aspect of the invention, as a metal corrosion inhibitor, especially a soft metal (i.e. non-ferrous metal) corrosion inhibitor, in a crankcase lubricating oil composition which is contaminated with at least 0.3 mass %, based on the total mass of the lubricating oil composition, of a biofuel or a decomposition product thereof and mixtures thereof, wherein additive component (B) introduces 0.02 to 0.12 mass % of phosphorus into the lubricating oil composition and additive component (C) is present in an amount of 0.1 to 10 mass %, based on the total mass of the lubricating oil composition.

[0016] According to a fourth aspect, the present invention provides the use, in the lubrication of a spark-ignited or compression-ignited internal combustion engine which is fuelled at least in part with a biofuel, of a crankcase lubricating oil composition comprising (A) an oil of lubricating viscosity in a major amount; (B) as an additive component in a minor amount, an oil-soluble metal salt of a dithiophosphoric acid as defined in accordance with the first aspect of the invention in an amount that introduces 0.02 to 0.12 mass % of phosphorus into the lubricating oil composition; and, (C) as an additive component in a minor amount, an oil-soluble carbodiimide compound as defined in accordance with the first aspect of the invention in an amount of 0.1 to 10 mass %, based on the total mass of the lubricating oil composition, to reduce and/or inhibit the corrosion of the metallic engine components, especially the softer metallic (i.e. non-ferrous) engine components, during operation of the engine.

[0017] According to a fifth aspect, the present invention provides the use, in the lubrication of a spark-ignited or compression-ignited internal combustion engine which is fuelled at least in part with a biofuel, of a minor amount of an additive component (B), as defined in accordance with the first aspect of the invention in an amount that introduces 0.02 to 0.12 mass % of phosphorus into the lubricating oil composition, in combination with a minor amount of an additive component (C), as defined in accordance with the first aspect of the invention in an amount of 0.1 to 10 mass %, based on the total mass of the lubricating oil composition, to reduce and/or inhibit the corrosion of the metallic engine components, especially the softer metallic (i.e. non-ferrous) engine components, during operation of the engine.

[0018] According to an sixth aspect, the present invention provides a spark-ignited or compression-ignited internal combustion engine comprising a crankcase containing a lubricating oil composition comprising (A) an oil of lubricating viscosity in a major amount; (B) as an additive component in a minor amount, an oil-soluble metal salt of a dithiophosphoric acid as defined in accordance with the first aspect of the invention in an amount that introduces 0.02 to 0.12 mass % of phosphorus into the lubricating oil composition; and, (C) as an additive component in a minor amount, an oil-soluble carbodiimide compound as defined in accordance with the first aspect of the invention in an amount of 0.1 to 10 mass %, based on the total mass of the lubricating oil composition, wherein the engine is fuelled at least in part with a biofuel. Preferably, the engine is operating with a fuel comprising a biofuel and the engine is being lubricated with the lubricating oil composition.

[0019] In a preferred aspect of the second and fourth to sixth aspects of the present invention the engine comprises a spark-ignited internal combustion engine which is fuelled at least in part with an alcohol based fuel, preferably a bioalcohol based fuel, especially an ethanol based fuel such as bioethanol fuel.

[0020] In an alternative preferred aspect of the second and fourth to sixth aspects of the present invention the engine comprises a compression-ignited internal combustion engine which is fuelled at least in part with a biodiesel fuel.

[0021] Most preferably, the engine in accordance with the second and fourth to sixth aspects of the present invention comprises a compression-ignited internal combustion engine.

[0022] Preferably, the lubricating oil compositions as defined in the second and fourth to sixth aspects are each independently contaminated with at least 0.3 mass %, based on the total mass of the lubricating oil composition, of a biofuel or a decomposition product thereof and mixtures thereof.

[0023] Preferably, the additive components (B) and (C) form part of an additive package which also includes a diluent, preferably a base stock, and 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, antiwear agents, friction modifiers, demulsifiers and antifoam agents; the additive package being added to the oil of lubricating viscosity.

[0024] Preferably, the soft metal (i.e. non-ferrous metal) in accordance with the third aspect comprises copper or lead and mixtures thereof, especially lead. Similarly, the soft metallic (i.e. non-ferrous) engine components of the fourth and fifth aspects preferably comprise components which include copper or lead and mixtures thereof, especially lead, such as the lead and copper based bearing materials.

[0025] 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;

"alcohol based fuel" refers to a fuel including an alcohol, irrespective of the source of the alcohol, such as methanol, ethanol, propanol and butanol, especially ethanol. The term "alcohol based fuel" embraces pure alcohol based fuel (i.e. pure ethanol) and also alcohol based fuel blends comprising, for example, a mixture of an alcohol and petroleum gasoline;

"ethanol based fuel" refers to a fuel including ethanol and is otherwise defined in the same way as "alcohol based fuel";

"biofuel" refers to a biodiesel fuel, a bioalcohol fuel and an alcohol based fuel as defined herein (i.e. a fuel that does not consist of solely petroleum gasoline or petroleum diesel fuel). Preferably, the biofuel comprises biodiesel fuel, bioalcohol fuel and ethanol fuel as defined herein. More preferably, the term "biofuel" means a fuel derived at least in part from a renewable biological resource e.g. biodiesel fuel or bioalcohol fuel. Even more preferably the biofuel comprises biodiesel or bioethanol as defined herein, especially biodiesel;

"biodiesel fuel" refers to a fuel derived at least in part from a renewable biological resource (e.g. derivable from a natural oil/fat, such as vegetable oils or animal fats) comprising at least one alkyl ester, typically a mono-alkyl ester, of a long chain fatty acid. The term "biodiesel fuel" embraces pure biodiesel fuel (i.e. B100 as defined by ASTM D6751-08 (USA) and EN 14214 (Europe)) and also biodiesel fuel blends comprising a mixture of biodiesel fuel and another fuel, such as petroleum diesel fuel;

"bioalcohol fuel" refers to fuel including an alcohol derived from a renewable biological resource (e.g. fermented sugar) and is otherwise defined in the same way as "alcohol based fuel";

"bioethanol fuel" refers to fuel including ethanol derived from a renewable biological resource and is otherwise defined in the same way as "ethanol based fuel". The term "bioethanol fuel" embraces pure bioethanol fuel (i.e. pure bioethanol E100) and also bioethanol fuel blends comprising, for example, a mixture of bioethanol and petroleum gasoline;

"petroleum gasoline" refers to a gasoline fuel produced from petroleum;

"petroleum diesel fuel" refers to a diesel fuel produced from petroleum;

"bioethanol" refers to ethanol derived from a renewable biological resource;

"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. Preferably, the group consists essentially of hydrogen and carbon atoms, unless specified otherwise. The term "hydrocarbyl" includes "aliphatic", "aromatic", "alkyl", or "alkenyl" as defined herein;

"aliphatic" means a non-aromatic hydrocarbyl group. Unless otherwise specified, aliphatic groups may, when there are a sufficient number of carbon atoms, be linear or branched, be cyclic, acyclic or part cyclic/acyclic. Preferably, the aliphatic group comprises an acyclic aliphatic group, more preferably a linear aliphatic group;

"alkyl" means a C_1 to C_{40} 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 or branched, be cyclic, acyclic or part cyclic/acyclic. Preferably, the alkyl group comprises an acyclic alkyl group, more preferably a linear 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, triacontyl and tetracontyl. When specified, the alkyl group may be substituted or terminated by one or more substituents as defined herein, and/or be interrupted by one or more oxygen atoms and/or amino groups;

"alkenyl" means a C_1 to C_{40} group which includes at least one carbon-carbon double bond and is otherwise defined in the same way as "alkyl". Preferably, the alkenyl group comprises an acyclic alkenyl group, more preferably a linear alkenyl group. Representative examples of "alkenyl" include, but are not limited to ethenyl, propenyl, and isobutenyl;

"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;

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

"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 all the additives present in the composition, reckoned as active ingredient of the additive or additives;

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

"soft metal" means a non-ferrous metal or alloy thereof, preferably a metal or an alloy thereof comprising lead, copper, tin or aluminium and mixtures thereof, preferably lead or copper and mixtures thereof, especially lead;

"soft metallic engine component" means an engine component which includes a soft metal as defined herein;

"soft metal corrosion" is measured by the High Temperature Bench Corrosion Test (HTCBT) in accordance with

ASTM D6594 and, when appropriate, modified accordingly by the addition of a biofuel;

"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.

[0026] All percentages reported are mass % on an active ingredient basis, i.e., without regard to carrier or diluent oil, unless otherwise stated.

[0027] 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.

[0028] 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

[0029] 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)

[0030] 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).

[0031] A base oil is useful for making concentrates as well as for making lubricating oil compositions there from, 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 base stock will have a viscosity preferably of 3-12, more preferably 4-10, most preferably 4.5-8, mm²/s (cSt) at 100°C.

[0032] 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.

[0033] 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.

[0034] Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g. phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) with a variety of alcohols (e.g. butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

[0035] 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.

[0036] 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.

[0037] 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.

[0038] 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

[0039] Accordingly, the oil of lubricating viscosity comprises a Group I to Group V base stock. Preferably, the oil of lubricating viscosity comprises a Group II, Group III, Group IV or Group V base stock and mixtures thereof, more preferably a Group II, Group III or Group IV base stock and mixtures thereof, especially a Group III or Group IV base stock and mixtures thereof.

[0040] In preferred embodiment, the oil of lubricating viscosity consists essentially of a Group III base stock.

[0041] In an alternative embodiment, the oil of lubricating viscosity consists essentially of a mixture of a Group III and Group IV base stock.

[0042] Preferably, when the oil of lubricating viscosity includes a Group III base stock, the oil of lubricating viscosity comprises greater than or equal to 10 mass %, more preferably greater than or equal to 20 mass %, even more preferably greater than or equal to 25 mass %, even more preferably greater than or equal to 30 mass %, even more preferably greater than or equal to 40 mass %, even more preferably greater than or equal to 45 mass % of a Group III base stock, based on the total mass of the oil of lubricating viscosity. Even more preferably, the oil of lubricating viscosity comprises greater than 50 mass %, preferably greater than or equal to 60 mass %, more preferably greater than or equal to 70 mass %, even more preferably greater than or equal to 80 mass %, even more preferably greater than or equal to 90 mass % of a Group III base stock, based on the total mass of the oil of lubricating viscosity. Most preferably, the oil of lubricating viscosity consists essentially of a Group III base stock. The Group III base stock may be the sole oil of lubricating viscosity in the lubricating oil composition.

[0043] 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.

[0044] 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.

[0045] Preferably, the volatility of the oil of lubricating viscosity or oil blend, as measured by the NOACK test (ASTM D5880), is less than or equal to 16%, preferably less than or equal to 13.5%, preferably less than or equal to 12%, more preferably less than or equal to 10%, most preferably less than or equal to 8%. Preferably, the viscosity index (VI) of the oil of lubricating viscosity is at least 95, preferably at least 110, more preferably at least 120, even more preferably at least 125, most preferably from about 130 to 140.

[0046] 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.

[0047] Preferably, the lubricating oil composition of the present invention contains low levels of phosphorus, namely up to 0.12 mass %, preferably up to 0.11 mass %, more preferably not greater than 0.10 mass %, even more preferably up to 0.09 mass %, even more preferably up to 0.08 mass %, even more preferably up to 0.06 mass % of phosphorus, expressed as atoms of phosphorus, based on the total mass of the composition.

[0048] 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.

[0049] Typically, the lubricating oil composition may contain low levels of sulphated ash. Preferably, the lubricating oil composition contains up to and including 1.2, more preferably up to 1.1, even more preferably up to 1.0, even more preferably up to 0.8, mass % sulphated ash, based on the total mass of the composition.

[0050] Suitably, the lubricating oil composition may have a total base number (TBN) of 4 to 15, preferably 5 to 12. In heavy duty diesel (HDD) engine applications the TBN of the lubricating composition ranges from about 4 to 12, such as 6 to 12. In a passenger car diesel engine lubricating oil composition (PCDO) and a passenger car motor oil for a spark-ignited engine (PCMO), the TBN of the lubricating composition ranges from about 5.0 to about 12.0, such as from about 5.0 to about 11.0.

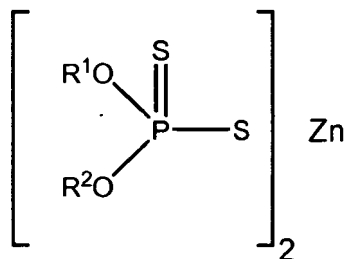
[0051] Preferably, the lubricating oil composition is a multigrade identified by the viscometric descriptor SAE 20WX, SAE 15WX, SAE 10WX, SAE 5WX or SAE 0WX, where X represents any one of 20, 30, 40 and 50; the characteristics of the different viscometric grades can be found in the SAE J300 classification. 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 an SAE 5WX or SAE 0WX, wherein X represents any one of 20, 30, 40 and 50. Preferably X is 20 or 30.

ADDITIVE COMPONENT (B)

[0052] Additive component (B) comprises a dihydrocarbyl dithiophosphate metal salt wherein the metal may be an alkali or alkaline earth metal, or aluminium, lead, tin, molybdenum, manganese, nickel, copper, or preferably, zinc. Dihydrocarbyl dithiophosphate metal salts are frequently used as antiwear and antioxidant agents.

[0053] 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.

[0054] The preferred dihydrocarbyl dithiophosphate metal salts are zinc dihydrocarbyl dithiophosphates (ZDDP) which are oil-soluble salts of dihydrocarbyl dithiophosphoric acids and may be represented by the following formula:



wherein R¹ and R² may be the same or different hydrocarbyl radicals containing from 1 to 18, preferably 2 to 12, carbon atoms and include radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R¹ and R² groups are alkyl groups of 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, n-propyl, i-propyl, n-butyl, iso-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. R¹ and R²) in the dithiophosphoric acid will generally be about 5 or greater. Preferably, the zinc dihydrocarbyl dithiophosphate comprises a zinc dialkyl dithiophosphate.

[0055] Preferably, the lubricating oil composition contains an amount of additive component (B) that introduces 0.02 to 0.12 mass%, 0.02 to 0.10 mass %, preferably 0.02 to 0.09 mass%, preferably 0.02 to 0.08 mass %, more preferably 0.02 to 0.06 mass % of phosphorus into the composition.

[0056] To limit the amount of phosphorus introduced into the lubricating oil composition by the additive component (B) to no more than 0.10 mass %, the dihydrocarbyl dithiophosphate metal salt should preferably be added to the lubricating oil compositions in amounts no greater than from 1.1 to 1.4 mass % (a.i.), based upon the total mass of the lubricating oil composition.

[0057] In accordance with a preferred embodiment of the present invention, the additive component (B) represents the sole phosphorus containing additive component in the lubricating oil composition.

ADDITIVE COMPONENT (C)

[0058] The oil-soluble carbodiimide compound may include a mono- or poly- carbodiimide containing compound. By the term mono-carbodiimide we mean a compound that includes a single carbodiimide group. Suitably, a poly-carbodiimide is a compound which includes two or more carbodiimide groups.

[0059] Suitable mono-carbodiimide containing compounds may be represented by a compound of general formula I:



wherein: R³ and R⁴ each independently represent hydrogen or a hydrocarbyl group, such as an aliphatic or aromatic hydrocarbyl group, which group is optionally terminated or substituted with one or more nitrogen and/or oxygen and/or halogen containing substituents and/or interrupted by one or more oxygen atoms and/or nitrogen atoms. Preferably, the hydrocarbyl group which R³ and R⁴ may each independently represent comprises a C₁ to C₄₀, preferably a C₁ to C₂₀, hydrocarbyl group.

[0060] Preferably, R³ and R⁴ each independently represent hydrogen, a C₁ to C₂₀ alkyl group, a C₁ to C₂₀ alkenyl group or a C₆ to C₁₈ aromatic group, each of which groups are optionally substituted or terminated with one or more substituents selected from C₁ to C₁₀ alkyl, a C₆ to C₁₈ aromatic group, halo, especially chloro, nitro or -OR⁵ where R⁵ represents hydrogen or C₁ to C₁₀ alkyl.

[0061] More preferably, R³ and R⁴ each independently represent a C₆ to C₁₈ aromatic group, especially a phenyl group, each of which groups are optionally substituted with one or more substituents selected from C₁ to C₁₀ alkyl, a C₆ to C₁₈ aromatic group, halo, especially chloro, nitro or -OR⁵ where R⁵ represents C₁ to C₁₀ alkyl.

[0062] Even more preferably, R³ and R⁴ in a compound of general formula I are both identical.

[0063] Representative examples of mono-carbodiimides include: di-isopropyl-carbodiimide, di-n-butyl-carbodiimide, methyl-tert-butyl-carbodiimide, dicyclohexyl-carbodiimide, diphenyl-carbodiimide, di-p-tolyl-carbodiimide and 4,4'-dido-decyl-diphenyl-carbodiimide.

[0064] In a highly preferred embodiment, R³ and R⁴ both represent a phenyl group, each of which phenyl groups are substituted in at least the 2-position or both the 2- and 6-positions with respect to the nitrogen atom of the carbodiimide bond with one or more substituents selected from C₁ to C₁₀ alkyl, halo, especially chloro, nitro or -OR⁵ where R⁵ represents C₁ to C₁₀ alkyl. Representative examples of such highly preferred mono-carbodiimides include: 2,2'-diethyl-diphenyl-carbodiimide, 2,2'-di-isopropyl-diphenyl-carbodiimide, 2,2'-diethoxy-diphenyl-carbodiimide, 2,6,2',6'-tetra-

ethyl-diphenyl-carbodiimide, 2,6,2',6'-tetra-isopropyl-diphenyl-carbodiimide, 2,6,2',6'-tetra-tert-butyl-diphenyl-carbodiimide, 2,6,2',6'-tetra-ethyl-3,3'-dichloro-diphenyl-carbodiimide, 2,2'-diethyl-6,6'-dichloro-diphenyl-carbodiimide, 2,6,2',6'-tetra-isobutyl-3,3'-dinitro-diphenyl-carbodiimide and 2,4,6,2',4',6'-hexa-isopropyl-diphenyl-carbodiimide.

[0065] Preferred mono-carbodiimides include 2,6,2',6'-tetra-tert-butyl-diphenyl-carbodiimide and 2,6,2',6'-tetra-isopropyl-diphenyl-carbodiimide, especially 2,6,2',6'-tetra-isopropyl-diphenyl-carbodiimide which is sold under the trade mark Additin RC8500™ by Rhein Chemie.

[0066] Representative examples of polycarbodiimides include: tetramethylene- ω,ω' -bis-(tert-butyl-carbodiimide), hexamethylene- ω,ω' -bis-(tert-butyl-carbodiimide) and tetramethylene- ω,ω' -bis-(phenyl-carbodiimide).

[0067] Most preferably, additive component (C) comprises a mono-carbodiimide.

[0068] Preferably, the additive component (C) is added to the lubricant composition in an amount of 0.05 to 10, more preferably 0.1 to 5, even more preferably 0.3 to 4, especially 0.5 to 3, mass % (a.i.), based on the total mass of the lubricating oil composition.

ADDITIVE COMPONENT (D)

[0069] In accordance with a preferred embodiment of the present invention, the lubricating oil composition further includes an oil-soluble metal deactivator (D) as an additive in a minor amount.

[0070] Metal deactivators which additive component (D) may represent include: compounds containing a triazole, thiadiazole or mercaptobenzimidazole ring. Such compounds are frequently used in lubricating oil compositions and may be prepared by known techniques as disclosed in US Patent 6,410,490 B.

[0071] Unexpectedly, it has been found that the inclusion of an additive component (D) in the lubricating oil composition may provide further inhibition and/or a reduction in the corrosion of the metallic engine components, particularly the softer metallic (i.e. non-ferrous) engine components. In particular, the inclusion of an additive component (D) in the lubricating oil composition may provide a marked improvement in the anti-corrosion properties of the lubricating oil composition with respect to the lead and copper containing engine components, especially the copper containing components.

[0072] Most preferably, the metal deactivator comprises a compound containing a triazole ring, which ring is optionally substituted with one or more substituents. Exemplary triazole ring containing compounds include triazole, benzotriazole and C_1 to C_{12} alkyl substituted benzotriazoles, such as tolutriazole. Preferred triazole ring containing compounds are benzotriazole and C_1 to C_{12} alkyl substituted benzotriazoles. An especially preferred triazole ring containing compound is tolutriazole.

[0073] Preferably, the nitrogen atom of the triazole ring in the triazole containing compound, as defined herein, is substituted with a C_1 to C_{10} hydrocarbyl group, such as an alkyl group, which group is optionally substituted with one or more nitrogen atoms and/or terminated with one or more $-NR^6R^7$ groups, where R^6 and R^7 each independently represent hydrogen or a C_1 to C_{20} hydrocarbyl group, such as a C_1 to C_{20} aliphatic hydrocarbyl group.

[0074] More preferably, the nitrogen atom of the triazole ring in the triazole containing compound as defined herein, is substituted with a $-CH_2(NR^6R^7)$ group, where R^6 and R^7 each independently represent hydrogen or C_1 to C_{20} aliphatic hydrocarbyl group.

[0075] Most preferably, the nitrogen atom of the triazole ring in the triazole containing compound as defined herein, is substituted with a $-CH_2(NR^6R^7)$ group, where R^6 and R^7 both represent a C_1 to C_{10} alkyl group.

[0076] An especially preferred triazole ring containing compound is 1-[bis(2-ethylhexyl)aminomethyl]-4-methylbenzotriazole which is sold under the trade name of IRGAMET 39 by Ciba.

[0077] Preferably, the additive component (D) is added to the lubricant composition in an amount of 0.01 to 0.5, more preferably 0.05 to 0.3, even more preferably 0.1 to 0.2, mass % (a.i.), based on the total mass of the lubricating oil composition.

ENGINES

[0078] The crankcase 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.

[0079] According to a preferred aspect of the invention, the lubricating oil composition is for use in the lubrication of a spark-ignited or compression ignited internal combustion engine which is fuelled at least in part with a biofuel; especially a spark-ignited internal combustion engine which is fuelled at least in part with a bioethanol fuel and a compression ignited internal combustion engine which is fuelled at least in part with a biodiesel fuel. Such 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.

[0080] Preferably, the lubricating oil composition is for use in the lubrication of a compression-ignited internal com-

bustion engine (diesel engine), especially a compression-ignited internal combustion engine which is fuelled at least in part with a biodiesel fuel. Such engines include passenger car diesel engines and heavy duty diesel engines, for example engines found in road trucks. More preferably, the lubricating oil composition is for use in the lubrication of a passenger car compression-ignited internal combustion engine (i.e. a light duty diesel engine), which is fuelled at least in part with a biodiesel fuel, especially such an engine which employs a late post-injection of fuel into the cylinder. Accordingly, the lubricating oil composition is for use in the lubrication of the crankcase of the aforementioned engines.

[0081] When the crankcase lubricating oil composition is used in the lubrication of a spark-ignited or compression-ignited internal combustion engine which is fuelled at least in part with a biofuel, the lubricant during operation of the engine becomes contaminated with biofuel and decomposition products thereof. Thus according to a preferred aspect of the present invention, the lubricating oil composition of the present invention comprises at least 0.3, preferably at least 0.5, more preferably at least 1, even more preferably at least 5, even more preferably at least 10, even more preferably at least 15, even more preferably at least 20, mass % of biofuel and/or a decomposition product thereof. Although the lubricating oil composition may comprise up to 50 mass % of biofuel and/or a decomposition product thereof, preferably it includes less than 35, more preferably less than 30, mass % of biofuel and/or a decomposition product thereof.

[0082] The biofuel comprises an alcohol based fuel in the case of spark-ignited internal combustion engines, preferably a bioalcohol fuel, especially bioethanol fuel.

[0083] The biofuel comprises biodiesel in the case of compression ignited internal combustion engines.

BIOFUELS

[0084] Biofuels include fuels that are produced from renewable biological resources and include biodiesel fuel as defined herein and bioethanol fuel which may be derived from fermented sugar. The term biofuel also embraces an "alcohol based fuel", such as "ethanol based fuel".

Alcohol Based Fuels

[0085] Alcohol based fuels are employed in spark-ignited internal combustion engines. The alcohol based fuel may include one or more alcohols selected from methanol, ethanol, propanol and butanol. The alcohol may be derived from a renewable biological source or a non-renewable source, such as petroleum. The alcohol based fuel may comprise 100 % by volume of one or more alcohols (i.e. pure alcohol). Alternatively the alcohol based fuel may comprise a blend of an alcohol and petroleum gasoline; suitable blends include 5, 10, 15, 20, 25, 30, 35, 40, 50, 60, 70, 80, 85, and 90, vol. % of the alcohol, based on the total volume of the alcohol and gasoline blend.

[0086] Preferably, the alcohol based fuel comprises an ethanol based fuel. More preferably, the alcohol based fuel comprises a bioalcohol fuel, especially a bioethanol fuel.

[0087] The bioethanol fuel comprises ethanol derived from a renewable biological source (i.e. bioethanol), preferably ethanol derived solely from a renewable biological source. The bioethanol may be derived from the sugar fermentation of crops such as corn, maize, wheat, cord grass and sorghum plants. The bioethanol fuel may comprise 100% by volume bioethanol (designated as E100); alternatively, the bioethanol fuel may comprise a blend of bioethanol and petroleum gasoline. The bioethanol fuel blend may have the designation "Exx" wherein xx refers to the amount of E100 bioethanol in vol. %, based on the total volume of the bioethanol fuel blend. For example, E10 refers to a bioethanol fuel blend which comprises 10 volume % E100 bioethanol fuel and 90 volume % of petroleum gasoline. For the avoidance of doubt, the term "bioethanol fuel" includes pure bioethanol fuel (i.e. E100) and bioethanol fuel blends comprising a mixture of bioethanol fuel and petroleum gasoline fuel.

[0088] Typically, the bioethanol fuel comprises E100, E95, E90, E85, E80, E75, E70, E65, E60, E55, E50, E45, E40, E35, E30, E25, E20, E15, E10, E8, E6 or E5. Highly preferred blends include E85 (ASTM D5798 (USA)), E10 (ASTM D4806 (USA)) and E5 (EN 228:2004 (Europe)).

Biodiesel Fuels

[0089] The biodiesel fuel comprises at least one alkyl ester, typically a mono-alkyl ester, of a long chain fatty acid derivable from vegetable oils or animal fats. Preferably, the biodiesel fuel comprises one or more methyl or ethyl esters of such long chain fatty acids, especially one or more methyl esters.

[0090] The long chain fatty acids typically comprise long chains which include carbon, hydrogen and oxygen atoms. Preferably, the long chain fatty acids include from 10 to 30, more preferably 14 to 26, most preferably 16 to 22, carbon atoms. Highly preferred fatty acids include palmitic acid, stearic acid, oleic acid and linoleic acid.

[0091] The biodiesel fuel may be derived from the esterification or transesterification of one or more vegetable oils and animal fats, such as corn oil, cashew oil, oat oil, lupine oil, kenaf oil, calendula oil, cotton oil, hemp oil, soybean oil, linseed oil, hazelnut oil, euphorbia oil, pumpkin seed oil, palm oil, rapeseed oil, olive oil, tallow oil, sunflower oil, rice oil,

sesame oil or algae oil. Preferred vegetable oils include palm oil, rapeseed oil and soybean oil.

[0092] Generally, a pure biodiesel fuel that meets the ASTM D6751-08 standard (USA) or EN 14214 standard (European) specifications is designated as B100. A pure biodiesel fuel may be mixed with a petroleum diesel fuel to form a biodiesel blend which may reduce emissions and improve engine performance. Such biodiesel blends are given a designation "Bxx" where xx refers to the amount of the B100 biodiesel in volume %, based on the total volume of the biodiesel blend. For example, B10 refers to a biodiesel blend which comprises 10 volume % B100 biodiesel fuel and 90 volume % of petroleum diesel fuel. For the avoidance of doubt, the term "biodiesel fuel" includes pure biodiesel fuel (i.e. B100) and biodiesel fuel blends comprising a mixture of biodiesel fuel and petroleum diesel fuel.

[0093] Typically, the biodiesel fuel comprises a B100, B95, B90, B85, B80, B75, B70, B65, B60, B55, B50, B45, B40, B35, B30, B25, B20, B15, B10, B8, B6, B5, B4, B3, B2 or B1. Preferably, the biodiesel fuel comprises a B50 designation or lower, more preferably a B5 to B40, even more preferably B5 to B40, most preferably B5 to B20.

CO-ADDITIVES

[0094] Co-additives, with representative effective amounts, that may also be present, different from additive components (B) and (C), and (D) if present, are listed below. All the values listed are stated as mass percent active ingredient.

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
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.		

[0095] 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.

[0096] 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.

[0097] 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.

[0098] 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.

[0099] 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.

[0100] 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.

[0101] 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 in mg KOH/g) 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.

[0102] 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.

[0103] 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.

[0104] Friction modifiers include 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. 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.

[0105] One class of preferred organo-molybdenum compounds useful in all aspects of the present invention is trinuclear 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.

[0106] 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.

[0107] 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.

[0108] 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.

[0109] 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).

[0110] 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.

[0111] 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. Examples of ashless anti-wear agents include 1,2,3-triazoles, benzotriazoles, sulfurised fatty acid esters, and dithiocarbamate derivatives.

[0112] 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, thiadiazoles and anionic alkyl sulfonic acids.

[0113] 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 fumerate/vinyl acetate copolymers and polyalkylmethacrylates.

[0114] Additives of the polysiloxane type, for example silicone oil or polydimethyl siloxane, can provide foam control.

[0115] 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.

[0116] 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.

[0117] 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.

[0118] The additives may be incorporated into an oil of lubricating viscosity (also known as a base oil) in any convenient way. Thus, each additive can be added directly to the oil by dispersing or dissolving it in the oil at the desired level of concentration. Such blending may occur at ambient temperature or at an elevated temperature. Typically an additive is available as an admixture with a base oil so that the handling thereof is easier.

[0119] When a plurality of additives are employed it may be desirable, although not essential, to prepare one or more additive packages (also known as additive compositions or concentrates) comprising additives and a diluent, which can be a base oil, whereby the additives, with the exception of viscosity modifiers, multifunctional viscosity modifiers and pour point depressants, can be added simultaneously to the base oil to form the lubricating oil composition. Dissolution of the additive package(s) into the oil of lubricating viscosity may be facilitated by diluent or solvents and by mixing accompanied with mild heating, but this is not essential. The additive package(s) will typically be formulated to contain the additive(s) in proper amounts to provide the desired concentration in the final formulation when the additive package(s) is/are combined with a predetermined amount of oil of lubricating viscosity. Thus, one or more detergents may be added to small amounts of base oil or other compatible solvents (such as a carrier oil or diluent oil) together with other desirable additives to form additive packages containing from 2.5 to 90, preferably from 5 to 75, most preferably from 8 to 60, mass %, based on the mass of the additive package, of additives on an active ingredient basis in the appropriate proportions. The final formulations may typically contain 5 to 40 mass % of the additive package(s), the remainder being oil of lubricating viscosity.

[0120] Preferably, the additive components (B) and (C), and (D) if present, form part of an additive package which also includes a diluent, preferably a base stock, and one or more co-additives in a minor amount, other than additive components (B), (C) and (D), selected from ashless dispersants, metal detergents, corrosion inhibitors, antioxidants, antiwear agents, friction modifiers, demulsifiers and antifoam agents; the additive package being added to the oil of lubricating viscosity.

EXAMPLES

[0121] The invention will now be particularly described in the following examples which are not intended to limit the scope of the claims hereof.

Corrosion Control: High Temperature Corrosion Bench Test (HTCBT)

[0122] 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.

[0123] 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.

[0124] The industry standard limits to meet the requirements of API CJ-4, which involves testing the lubricant in the absence of any added fuel, are 20 ppm maximum for copper and 120 ppm maximum for lead (i.e. these are the test limits for the pure lubricant only). Suitably, when the test is performed with a lubricating oil composition which includes a biofuel or a petroleum fuel, then the test has essentially been modified and such compositions are not required to meet the requirements of API CJ-4; the results of the test being used for comparative purposes to assess the effects of certain additives in the presence of a biofuel.

Example 1

[0125] A 5W-40 multigrade base crankcase lubricating oil formulation (Oil A) was prepared by admixing an oil of lubricating viscosity (a mixture of Group IV and Group III base stocks (67 mass %)) and a viscosity modifier concentrate (6.7 mass %) with a commercial additive package that contains an overbased detergent, an antioxidant, a dispersant and a ZDDP. Base Oil A has a phosphorus content of 0.11 mass % and a sulphated ash content of 0.99 mass %. All chemical additives described herein are available from standard suppliers of lubricant additives such as Infineum UK Ltd, Lubrizol Corporation, Afton Chemicals Corporation, for example.

[0126] The following 5W-40 multigrade lubricating oil formulations as detailed below were prepared by admixing Oil A with one or more of the specified components. Biodiesel fuel or petroleum diesel fuel was added to the lubricating oil compositions to simulate contamination of the oil during operation of a compression ignited internal combustion engine fuelled with biodiesel fuel or petroleum diesel fuel, respectively. Each lubricating oil formulation was evaluated for copper and lead corrosion control using the High Temperature Corrosion Bench Test; the results are displayed in Table 1.

- Reference Lubricant 1 comprising Oil A (90 mass %) and petroleum diesel fuel (10 mass %)
- Reference Lubricant 2 comprising Oil A (90 mass %) and B50¹ biodiesel fuel (10 mass %)
- Lubricant 1 comprising Oil A (88.5 mass %), B50¹ biodiesel fuel (10 mass %) and an oil-soluble carbodiimide compound (Additin RC8500[™], 1.5 mass %)
- Lubricant 2 comprising Oil A (87 mass %), B50¹ biodiesel fuel (10 mass %) and an oil-soluble carbodiimide compound (Additin RC8500[™], 3.0 mass %)

¹ B50 biodiesel fuel comprises a blend of B100 biodiesel fuel (50 mass %) and petroleum diesel fuel (50 mass %)

² Additin RC8500[™] is an oil soluble diaryl mono-carbodiimide compound available from Rhein Chemie.

Table 1.

	Reference Lubricant 1	Reference Lubricant 2	Lubricant 1	Lubricant 2
Copper corrosion (ppm)	6.5	172	73	72
Lead corrosion (ppm)	18.3	1703	500	22

[0127] The results demonstrate that for a lubricant comprising a lubricating oil of lubricating viscosity in a major amount and a ZDDP, as an additive component in a minor amount, the extent of copper and lead corrosion increases significantly in the presence of a biodiesel fuel compared with a petroleum diesel fuel (Compare Reference Lubricant 2 with Reference Lubricant 1). The inclusion of an oil-soluble carbodiimide (1.5 mass %) in Reference Lubricant 2 (i.e. Lubricant 1 of the present invention) reduces the level of biodiesel induced copper corrosion by 60% and the level of lead corrosion by 70% (Compare Lubricant 1 with Reference Lubricant 2). A further addition of the oil-soluble carbodiimide (1.5 mass %) to Lubricant 1 (i.e. Lubricant 2 of the present invention) essentially results in the complete suppression of the biodiesel induced lead corrosion (Compare Lubricant 2 with Reference Lubricants 1 and 2).

Example 2

[0128] Base lubricating oil formulation (Oil A) as detailed in Example 1 and Lubricant 3 of the invention comprising Oil A (98.5 mass %) and an oil-soluble carbodiimide compound (Additin RC8500[™], 1.5 mass %) were evaluated in the Mack T-12 Engine Test in accordance with ASTM D7427.

[0129] The Mack T-12 Engine Test is a standard test for evaluating wear performance in diesel engine lubricating oil formulations. The test is run over a 300 hour period employing a modified Mack E7 E-TECH V-MAC III diesel engine with exhaust gas recirculation (EGR). A warm up and a 1 hour break in are followed by a two phase test consisting of 100 hours at 1800 rpm and 200 hours at 1200rpm, both at constant speed and load.

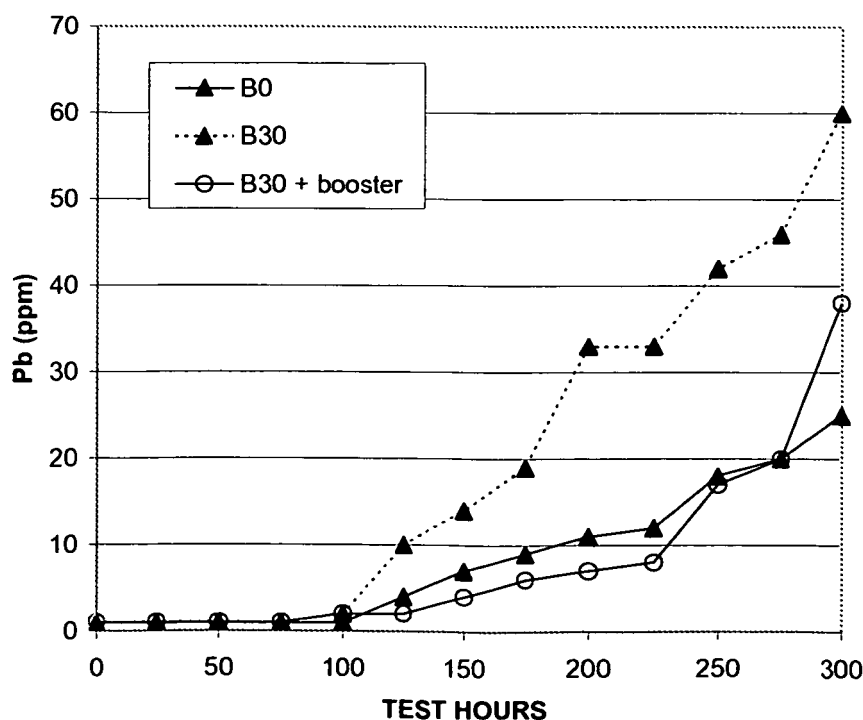


Figure 1

[0130] Figure 1 shows the extent of lead corrosion over the course of the tests. When Oil A is tested and the engine fuelled with petroleum diesel fuel (designated as B0), the level of lead corrosion increased gradually starting at 100 hours and was 25 ppm at the end of the test. When Oil A is tested and the engine fuelled with B30 biodiesel fuel (designated as B30), the lead level increased significantly after 100 hours with an end of test value of 60 ppm. However, when Lubricant 3 of the invention is tested and the engine fuelled with B30 biodiesel fuel (designated as B30 + booster), the lead level after 100 hours not only increases more slowly than the test using Oil A and fuelling the engine with B30 biodiesel but also the test employing Oil A and fuelling the engine with petroleum diesel. After approximately 275 hours the lead level of Lubricant 3 of the invention, when the engine is fuelled with B30 biodiesel fuel, is essentially identical to the run employing Oil A where the engine is fuelled with petroleum diesel.

[0131] The results indicate that the combination of an oil-soluble carbodiimide, as an additive component in a minor amount, and a ZDDP, as an additive component in a minor amount, in a lubricating oil composition including an oil of lubricating viscosity in a major amount suppresses biodiesel induced lead corrosion.

Example 3

[0132] A series of 5W-30 multigrade crankcase lubricating oil compositions, as detailed in Table 2, were prepared by admixing a Group III base stock and the various components as detailed in Table 2, namely: a calcium sulphonate detergent (TBN 300); a calcium phenate detergent; a dispersant, an antioxidant and a viscosity modifier concentrate. Reference Lubricants 3 and 4 did not include a ZDDP or an oil-soluble carbodiimide compound, Reference Lubricant 5 further included an oil-soluble carbodiimide compound (Additin RC8500™) but no ZDDP, and Lubricant 4 of the invention included both a ZDDP and an oil-soluble carbodiimide compound (Additin RC8500™). B50 biodiesel fuel (10 mass %) was added to Reference Lubricants 4 and 5 and Lubricant 4 of the invention to simulate contamination of the oil during operation of a diesel engine fuelled with biodiesel fuel; no biodiesel fuel was added to Reference Lubricant 3.

[0133] Each of the lubricants were evaluated for lead corrosion control using the High Temperature Corrosion Bench Test. The results are also detailed in Table 2.

[0134] As is evident from the results in Table 2, a lubricant of the present invention (Lubricant 4), containing a combination of both an oil-soluble carbodiimide compound and a ZDDP, suppresses biodiesel induced lead corrosion significantly compared with a comparable lubricant including only an oil-soluble carbodiimide compound and not a ZDDP (Reference Lubricant 5).

Table 2

	Reference Lubricant 3 (mass %)	Reference Lubricant 4 (mass %)	Reference Lubricant 5 (mass %)	Lubricant 4 (mass %)
Calcium sulfonate detergent	0.9	0.9	0.9	0.9
Calcium phenate detergent	2	2	2	2
Antioxidant	1	1	1	1
Dispersant	5.5	5.5	5.5	5.5
Viscosity modifier concentrate	5.5	5.5	5.5	5.5
ZDDP	0	0	0	1
RC8500	0	0	3	3
B50 Biodiesel	0	10	10	10
Base Stock	balance	balance	balance	balance
Sulfur (mass %)	0.12	0.12	0.12	0.28
Ash (mass %)	0.69	0/69	0.69	0.69
Phosphorus (mass %)	0	0	0	0.08
Lead Corrosion ppm	1897	6969	1489	253

Example 4

[0135] A 10W-40 multigrade base crankcase lubricating oil formulation (Oil B) was prepared by admixing a Group III base stock (69 mass %) and a viscosity modifier concentrate (10 mass %) with a commercial additive package containing an overbased detergent, a dispersant, an antioxidant and a ZDDP. Oil B has a phosphorus content of 0.08 mass % and a sulphated ash content of 1 mass %.

[0136] Reference Lubricant 6 comprises Oil B; Reference Lubricant 7 comprises Oil B plus an oil-soluble benzotriazole metal deactivator (IRGAMET 39™); Lubricants 5 to 7 of the invention are prepared by admixing Oil B with an oil-soluble carbodiimide compound (Additin RC8500™); and, Lubricant 8 of the invention is prepared by admixing Oil B with an oil-soluble carbodiimide compound (Additin RC8500™) and an oil-soluble benzotriazole metal deactivator (IRGAMET 39™). In addition, B50 biodiesel fuel (10 mass %) is added to each of the lubricants to simulate contamination of the oil during operation of a diesel engine fuelled with biodiesel fuel. The amount (mass % a.i.) of B50 biodiesel fuel, ZDDP, Additin RC8500™, and IRGAMET 39™ in each of the Lubricants is detailed in Table 3.

Table 3

Mass %	Reference Lubricant 6	Lubricant 5	Lubricant 6	Lubricant 7	Reference Lubricant 7	Lubricant 8
ZDDP	1	1	1	1	1	1
RC8500	0	0.5	1.0	1.5	0	1.5
IRGAMET 39	0	0	0	0	0.1	0.1
B50 Biodiesel	10	10	10	10	10	10

[0137] Each of the lubricants was evaluated for lead and copper corrosion control using the High Temperature Corrosion Bench Test. The results are detailed in Table 4.

Table 4

Pars per million (ppm)	Reference Lubricant 6	Lubricant 5	Lubricant 6	Lubricant 7	Reference Lubricant 7	Lubricant 8
Copper corrosion	161	76	70	64	49	29
Lead corrosion	2602	1399	646	330	1802	295

[0138] The results demonstrate that the combination of an oil-soluble carbodiimide, as an additive in a minor amount, and a ZDDP, as an additive in a minor amount, in a lubricating oil composition, comprising an oil of lubricating viscosity in a major amount, suppresses both biodiesel induced lead and copper corrosion (Compare Lubricants 5 to 7 with Reference Lubricant 6). The combination of an oil-soluble benzotriazole metal deactivator, as an additive in a minor amount, and a ZDDP, as an additive in a minor amount, in a lubricating oil composition, comprising an oil of lubricating viscosity in a major amount, also suppresses both biodiesel induced lead and copper corrosion; the level of copper corrosion being reduced by approximately 70 % and the level of lead corrosion being reduced by approximately 30 % (Compare Reference Lubricant 7 with Reference Lubricant 6). However, the combination of an oil-soluble benzotriazole metal deactivator, an oil-soluble carbodiimide and a ZDDP, as additives in a minor amount, in a lubricating oil composition, comprising an oil of lubricating viscosity in a major amount, results in a significant suppression of both biodiesel induced lead and copper corrosion; the level of copper corrosion being reduced by approximately 82 % and the level of lead corrosion being reduced by approximately 89 % (Compare Lubricant 8 with Reference Lubricant 6).

Example 6 Bioethanol Fuel

[0139] A 5W-30 multigrade base crankcase lubricating oil composition (Oil C) was prepared by admixing an oil of lubricating viscosity (a mixture of Group IV and Group III base stocks (70 mass %)) and a viscosity modifier concentrate (9.5 mass %) with a commercial additive package containing an overbased detergent, a dispersant, an antioxidant and a ZDDP. Oil C has a phosphorus content of 0.06 mass % and a sulphated ash content of 0.6 mass %.

[0140] Lubricants 9 and 10 of the invention are prepared by admixing Oil C with an oil-soluble carbodiimide compound (Additin RC8500™). Petroleum gasoline fuel (designated as E0) was added to Oil C to form Reference Lubricant 8 and also to Lubricant 9 of the invention to simulate contamination of the oil during operation of a spark-ignited internal combustion engine fuelled with petroleum gasoline fuel. Bioethanol fuel (E85 comprising a mixture of E100 bioethanol (85 mass %) and petroleum gasoline (15 mass %)) was added to Oil C to form Reference Lubricant 9 and also to Lubricant 10 of the invention to simulate contamination of the oil during operation of a spark-ignited internal combustion engine fuelled with bioethanol fuel. The amount (mass % a.i.) of E0 (petroleum gasoline fuel), E85 (bioethanol fuel), ZDDP and Additin RC8500™ in each of the Lubricants is detailed in Table 5.

Table 5

Mass %	Reference Lubricant 8	Lubricant 9	Reference Lubricant 9	Lubricant 10
ZDDP	0.6	0.6	0.6	0.6
RC8500	0	3	0	3
E0	10	10	0	0
E85	0	0	10	10

[0141] Each of the lubricants were evaluated for lead and copper corrosion control (in ppm) using the High Temperature Corrosion Bench Test. The results are detailed in Table 6.

Table 6

Parts per million (ppm)	Reference Lubricant 8	Lubricant 9	Reference Lubricant 9	Lubricant 10
Copper corrosion	8.4	4.8	15.3	10.6
Lead corrosion	23.4	4.2	88.1	23.5

[0142] The results demonstrate that the combination of an oil-soluble carbodiimide, as an additive in a minor amount, and a ZDDP, as an additive in a minor amount, in a lubricating oil composition, comprising an oil of lubricating viscosity in a major amount, suppresses both petroleum gasoline and bioethanol fuel induced lead and copper corrosion (Compare Lubricant 9 with Reference Lubricant 9 and Lubricant 10 with Reference Lubricant 9).

Claims

1. A crankcase lubricating oil composition comprising:

- (A) an oil of lubricating viscosity in a major amount;
- (B) as an additive component in a minor amount, an oil-soluble metal salt of a dithiophosphoric acid in an amount that introduces 0.02 to 0.12 mass % of phosphorus into the lubricating oil composition;
- (C) as an additive component in a minor amount, an oil-soluble carbodiimide compound in an amount of 0.1 to 10 mass %, based on the total mass of the lubricating oil composition; and,

wherein the lubricating oil composition is contaminated with at least 0.3 mass %, based on the total mass of the lubricating oil composition, of a biofuel or a decomposition product thereof and mixtures thereof.

2. The lubricating oil composition as claimed in claim 1, wherein the oil-soluble metal salt of a dithiophosphoric acid comprises a zinc salt of a dithiophosphoric acid, preferably a dihydrocarbyl dithiophosphate zinc salt, more preferably a zinc dialkyl dithiophosphate.
3. The lubricating oil composition as claimed in any one of the preceding claims, wherein the oil-soluble carbodiimide compound comprises a mono-carbodiimide of general formula I:



wherein:

R^3 and R^4 each independently represent hydrogen or a hydrocarbyl group, such as an aliphatic or aromatic hydrocarbyl group, which group is optionally terminated or substituted with one or more nitrogen and/or oxygen and/or halogen containing substituents and/or interrupted by one or more oxygen and/or nitrogen atoms.

4. The lubricating oil composition as claimed in claim 3, wherein each of R^3 and R^4 are identical.
5. The lubricating oil composition as claimed in any one of the preceding claims, further including (D) an oil-soluble metal deactivator as an additive in a minor amount.
6. The lubricating oil composition as claimed in claim 5, wherein the metal deactivator comprises a compound containing a triazole ring, a compound containing a thiadiazole ring or a compound containing a mercaptobenzimidazole ring.
7. The lubricating oil composition as claimed in any one of the preceding claims further comprising one or more co-additives in a minor amount, other than additive components (B) and (C), and (D) if present, selected from ashless dispersants, metal detergents, corrosion inhibitors, antioxidants, pour point depressants, antiwear agents, friction modifiers, demulsifiers, antifoam agents and viscosity modifiers.
8. A method of lubricating a compression-ignited or spark-ignited internal combustion engine which is fuelled at least in part with a biofuel, comprising operating the engine with a crankcase lubricating oil composition comprising (A) an oil of lubricating viscosity in a major amount; (B) as an additive component in a minor amount, an oil-soluble metal salt of a dithiophosphoric acid as defined in any one of claims 1 to 7 in an amount that introduces 0.02 to 0.12 mass % of phosphorus into the lubricating oil composition; and, (C) as an additive component in a minor amount, an oil-soluble carbodiimide compound as defined in any one of claims 1 to 7 in an amount of 0.1 to 10 mass %, based on the total mass of the lubricating oil composition.
9. The method as claimed in claim 8 for reducing and/or inhibiting the corrosion of the metallic engine components, preferably non-ferrous metallic engine components comprising lead, copper or mixtures thereof.

10. The use of a minor amount of an additive component (B) comprising an oil-soluble metal salt of a dithiophosphoric acid as defined in any one of claims 1 to 7, in combination with a minor amount of an additive component (C) comprising an oil-soluble carbodiimide compound as defined in any one of claims 1 to 7, as a metal corrosion inhibitor, especially a non-ferrous metal corrosion inhibitor, in a crankcase lubricating oil composition which is contaminated with at least 0.3 mass %, based on the total mass of the lubricating oil composition, of a biofuel or a decomposition product thereof and mixtures thereof, wherein additive component (B) introduces 0.02 to 0.12 mass % of phosphorus into the lubricating oil composition and additive component (C) is present in an amount of 0.1 to 10 mass %, based on the total mass of the lubricating oil composition.
11. The use, in the lubrication of a spark-ignited or compression-ignited internal combustion engine which is fuelled at least in part with a biofuel, of a crankcase lubricating oil composition comprising (A) an oil of lubricating viscosity in a major amount; (B) as an additive component in a minor amount, an oil-soluble metal salt of a dithiophosphoric acid as defined in any one of claims 1 to 7 in an amount that introduces 0.02 to 0.12 mass % of phosphorus into the lubricating oil composition; and, (C) as an additive component in a minor amount, an oil-soluble carbodiimide compound as defined in any one of claims 1 to 7 in an amount of 0.1 to 10 mass %, based on the total mass of the lubricating oil composition, to reduce and/or inhibit the corrosion of the metallic engine components, during operation of the engine.
12. The method as claimed in claim 9 or the use as claimed in claim 11, wherein the metallic engine components comprise non-ferrous metallic engine components, preferably engine components comprising lead, copper or mixtures thereof, especially lead.
13. The method as claimed in claim 8 or 9 or the use as claimed in claim 11, wherein the engine comprises a compression-ignited internal combustion engine which is fuelled at least in part with a biodiesel fuel.
14. A spark-ignited or compression-ignited internal combustion engine comprising a crankcase containing a lubricating oil composition comprising (A) an oil of lubricating viscosity in a major amount; (B) as an additive component in a minor amount, an oil-soluble metal salt of a dithiophosphoric acid as defined in any one of claims 1 to 7 in an amount that introduces 0.02 to 0.12 mass % of phosphorus into the lubricating oil composition; and, (C) as an additive component in a minor amount, an oil-soluble carbodiimide compound as defined in any one of claims 1 to 7 in an amount of 0.1 to 10 mass %, based on the total mass of the lubricating oil composition, wherein the engine is fuelled at least in part with a biofuel.
15. An engine as claimed in claim 14, wherein the engine is operating with the fuel comprising said biofuel and the engine is being lubricated with said lubricating oil composition.

Patentansprüche

1. Kurbelgehäuseschmierölszusammensetzung, die:

- (A) in einer größeren Menge Öl mit Schmierviskosität,
- (B) in einer geringeren Menge als Additivbestandteil öllösliches Metallsalz einer Dithiophosphorsäure in einer Menge, die 0,02 bis 0,12 Masse-% an Phosphor in die Schmierölszusammensetzung einbringt,
- (C) in einer geringeren Menge als Additivbestandteil öllösliche Carbodiimidverbindung in einer Menge von 0,1 bis 10 Masse-%, bezogen auf die gesamte Masse der Schmierölszusammensetzung, umfasst, und

wobei die Schmierölszusammensetzung mit mindestens 0,3 Masse-%, bezogen auf die gesamte Masse der Schmierölszusammensetzung, mit einem Biobrennstoff oder einem Zersetzungsprodukt davon und Mischungen davon kontaminiert ist.

2. Schmierölszusammensetzung wie in Anspruch 1 beansprucht, wobei das öllösliche Metallsalz einer Dithiophosphorsäure ein Zinksalz einer Dithiophosphorsäure umfasst, vorzugsweise ein Dikohlenwasserstoffdithiophosphatzinksalz, insbesondere ein Zinkdialkyldithiophosphat.
3. Schmierölszusammensetzung wie in einem der vorhergehenden Ansprüche beansprucht, wobei die öllösliche Carbodiimidverbindung ein Monocarbodiimid mit der allgemeinen Formel I:



umfasst, in der :

- 5 R^3 und R^4 jeweils unabhängig Wasserstoff oder eine Kohlenwasserstoffgruppe wiedergeben, wie eine aliphatische oder aromatische Kohlenwasserstoffgruppe, welche Gruppe ggfs. mit einem oder mehreren Substituenten, die Stickstoff und/oder Sauerstoff und/oder Halogen enthalten, terminiert oder substituiert ist, und/oder durch ein oder mehrere Sauerstoff und/oder Stickstoffatome unterbrochen ist.
- 10 **4.** Schmierölszusammensetzung wie in Anspruch 3 beansprucht, wobei jeder von R^3 und R^4 identisch sind.
- 5.** Schmierölszusammensetzung wie in einem der vorhergehenden Ansprüche beansprucht, die ferner als Additiv in einer geringeren Menge einen (D) öllöslichen Metalldesaktivator einschließt.
- 15 **6.** Schmierölszusammensetzung wie in Anspruch 5 beansprucht, wobei der Metalldesaktivator eine Verbindung umfasst, die einen Triazolring enthält, eine Verbindung, die einen Thiadiazolring enthält, oder eine Verbindung, die einen Mercaptobenzimidazolring enthält.
- 20 **7.** Schmierölszusammensetzung wie in einem der vorhergehenden Ansprüche beansprucht, die ferner in einer geringeren Menge ein oder mehrere Coadditive umfasst, die von den Additivbestandteilen (B) und (C), und (D), falls vorhanden, unterschiedlich sind, und die ausgewählt sind aus aschefreien Dispergiermitteln, Metaldetergenzien, Korrosionsinhibitoren, Antioxidanzien, Stockpunktsenkungsmitteln, Antiverschleißmitteln, Reibungsmodifizierungsmitteln, Demulgatoren, Antischaummitteln und Viskositätsmodifizierungsmitteln.
- 25 **8.** Verfahren zum Schmieren eines kompressionsgezündeten oder eines funkengezündeten internen Verbrennungsmotors, der zumindest teilweise mit Biobrennstoff angetrieben wird, bei welchem Verfahren der Motor mit einer Kurbelgehäuseschmierölszusammensetzung betrieben wird, die (A) in einer größeren Menge Öl mit Schmierviskosität, (B) in einer kleineren Menge als Additivbestandteil ein öllösliches Metallsalz einer Dithiophosphorsäure wie in einem der Ansprüche 1 bis 7 definiert in einer Menge, die 0,02 bis 0,12 Masse-% an Phosphor in die Schmierölszusammensetzung einbringt, und (C) in einer geringeren Menge als Additivbestandteil öllösliche Carbodiimidverbindung wie in einem der Ansprüche 1 bis 7 in einer Menge von 0,1 bis 10 Masse-%, bezogen auf die gesamte Masse der Schmierölszusammensetzung, umfasst.
- 30 **9.** Verfahren wie in Anspruch 8 beansprucht zum Verringern und/oder Inhibieren der Korrosion der metallischen Motorkomponenten, vorzugsweise metallischen Nicht-Eisenmotorkomponenten, die Blei, Kupfer oder Mischungen davon umfassen.
- 35 **10.** Verwendung einer geringeren Menge eines Additivbestandteils (B), der öllösliches Metallsalz einer Dithiophosphorsäure umfasst wie in einem der Ansprüche 1 bis 7 definiert, in Kombination mit einer geringeren Menge eines Additivbestandteils (C), der öllösliche Carbodiimidverbindung wie in einem der Ansprüche 1 bis 7 umfasst, als Metallkorrosionsinhibitor, insbesondere als Korrosionsinhibitor für Nicht-Eisenmetalle, in einer Kurbelgehäuseschmierölszusammensetzung, die bezogen auf die gesamte Masse der Schmierölszusammensetzung mit mindestens 0,3 Masse-% Biobrennstoff oder einem Zersetzungsprodukt davon und Mischungen davon kontaminiert ist, wobei Additivkomponente (B) 0,02 bis 0,12 Masse-% an Phosphor in die Schmierölszusammensetzung einbringt und Additivbestandteil (C) in einer Menge von 0,1 bis 10 Masse-% vorliegt, bezogen auf die gesamte Masse der Schmierölszusammensetzung.
- 40 **11.** Verwendung einer Kurbelgehäuseschmierölszusammensetzung, die (A) in einer größeren Menge Öl mit Schmierviskosität, (B) in einer geringeren Menge als Additivbestandteil öllösliches Metallsalz einer Dithiophosphorsäure wie in einem der Ansprüche 1 bis 7 definiert in einer Menge, die 0,02 bis 0,12 Masse-% an Phosphor in die Schmierölszusammensetzung einbringt, und (C) in einer geringeren Menge als Additivbestandteil öllösliche Carbodiimidverbindung wie in einem der Ansprüche 1 bis 7 definiert in einer Menge von 0,1 bis 10 Masse-%, bezogen auf die gesamte Masse der Schmierölszusammensetzung, umfasst, bei der Schmierung eines funkengezündeten oder kompressionsgezündeten internen Verbrennungsmotors, der zumindest teilweise mit Biobrennstoff angetrieben wird, zum Verringern und/oder Inhibieren der Korrosion der metallischen Motorkomponenten während des Betriebs des Motors.
- 55 **12.** Verfahren wie in Anspruch 9 beansprucht oder die Verwendung wie in Anspruch 11 beansprucht, wobei die metal-

lischen Motorkomponenten metallische Nicht-Eisen-Motorkomponenten umfassen, vorzugsweise Motorkomponenten, die Blei, Kupfer oder Mischungen davon, insbesondere Blei umfassen.

13. Verfahren wie in Anspruch 8 oder 9 beansprucht oder die Verwendung wie in Anspruch 11 beansprucht, wobei der Motor einen kompressionsgezündeten internen Verbrennungsmotor umfasst, der zumindest teilweise mit einem Biodieselsbrennstoff angetrieben wird.
14. Funkengezündeter oder kompressionsgezündeter interner Verbrennungsmotor, der ein Kurbelgehäuse umfasst, das eine Schmierölszusammensetzung enthält, die (A) in einer größeren Menge Öl mit Schmierviskosität, (B) in einer geringeren Menge als Additivbestandteil öllösliches Metallsalz einer Dithiophosphorsäure wie in einem der Ansprüche 1 bis 7 definiert in einer Menge, die 0,02 bis 0,12 Masse-% an Phosphor in die Schmierölszusammensetzung einbringt, und (C) in einer geringeren Menge als Additivbestandteil öllösliche Carbodiimidverbindung wie in einem der Ansprüche 1 bis 7 definiert in einer Menge von 0,1 bis 10 Masse-%, bezogen auf die gesamte Masse der Schmierölszusammensetzung, umfasst, wobei der Motor zumindest teilweise mit einem Biobrennstoff angetrieben wird.
15. Motor wie in Anspruch 14 beansprucht, wobei der Motor mit dem Brennstoff, der den Biobrennstoff umfasst, betrieben wird, und der Motor mit der Schmierölszusammensetzung geschmiert wird.

Revendications

1. Composition d'huile lubrifiante de carter, comprenant :

- (A) une huile de viscosité propre à la lubrification, en une quantité dominante ;
- (B) comme constituant servant d'additif en une petite quantité, un sel métallique, ou soluble dans l'huile, d'un acide dithiophosphorique en une quantité qui introduit 0,02 à 0,12 % en masse de phosphore dans la composition d'huile lubrifiante ;
- (C) comme constituant servant d'additif en une petite quantité, un composé du type carbodiimide soluble dans l'huile, en une quantité de 0,1 à 10 % en masse, sur la base de la masse totale de la composition d'huile lubrifiante ; et

ladite composition d'huile lubrifiante étant contaminée par au moins 0,3 % en masse, sur la base de la masse totale de la composition d'huile lubrifiante, d'un biocarburant ou d'un de ses produits de décomposition et leurs mélanges.

2. Composition d'huile lubrifiante suivant la revendication 1, dans laquelle le sel métallique, soluble dans l'huile, d'un acide dithiophosphorique comprend un sel de zinc d'un acide dithiophosphorique, avantageusement un dihydrocarbyl-dithiophosphate de zinc, plus avantageusement un dialkyl-dithiophosphate de zinc.
3. Composition d'huile lubrifiante suivant l'une quelconque des revendications précédentes, dans laquelle le composé du type carbodiimide, soluble dans l'huile, comprend un mono-carbodiimide de formule générale I :



dans laquelle :

R^3 et R^4 représentent chacun indépendamment un atome d'hydrogène ou un groupe hydrocarbyle, tel qu'un groupe hydrocarbyle aliphatique ou aromatique, groupe qui est facultativement terminé ou substitué avec un ou plusieurs substituants contenant de l'azote et/ou de l'oxygène et/ou un halogène et/ou interrompu par un ou plusieurs atomes d'oxygène et/ou d'azote.

4. Composition d'huile lubrifiante suivant la revendication 3, dans laquelle chaque groupe R^3 et chaque groupe R^4 sont identiques.
5. Composition d'huile lubrifiante suivant l'une quelconque des revendications précédentes, comprenant en outre (D) un désactivateur de métaux, soluble dans l'huile, comme additif en une petite quantité.
6. Composition d'huile lubrifiante suivant la revendication 5, dans laquelle le désactivateur de métaux comprend un

composé contenant un noyau triazole, un composé contenant un noyau thiadiazole ou un composé contenant un noyau mercaptobenzimidazole.

- 5 **7.** Composition d'huile lubrifiante suivant l'une quelconque des revendications précédentes, comprenant en outre un ou plusieurs co-additifs en une petite quantité, autres que les constituants servant d'additifs (B) et (C), et (D) s'il est présent, choisis entre des dispersants sans cendre, des détergents métalliques, des inhibiteurs de corrosion, des anti-oxydants, des agents abaissant le point d'écoulement, des agents anti-usure, des modificateurs de frottement, des désémulsionnants, des agents anti-mousse et des modificateurs de viscosité.
- 10 **8.** Procédé pour la lubrification d'un moteur à combustion interne à allumage par compression ou allumage par étincelle qui est alimenté au moins en partie avec un biocarburant, comprenant le fonctionnement du moteur avec une composition d'huile lubrifiante de carter comprenant (A) une huile de viscosité propre à la lubrification en une quantité dominante ; (B) comme constituant servant d'additif en une petite quantité, un sel métallique, soluble dans l'huile, d'un acide dithiophosphorique tel que défini dans l'une quelconque des revendications 1 à 7 en une quantité qui introduit 0,02 à 0,12 % en masse de phosphore dans la composition d'huile lubrifiante ; et (C), comme constituant servant d'additif en une petite quantité, un composé du type carbodiimide, soluble dans l'huile, tel que défini dans l'une quelconque des revendications 1 à 7 en une quantité de 0,1 à 10 % en masse, sur la base de la masse totale de la composition d'huile lubrifiante.
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- 20 **9.** Procédé suivant la revendication 8 pour la réduction et/ou l'inhibition de la corrosion des composants métalliques d'un moteur, de préférence des composants métalliques non ferreux d'un moteur comprenant le plomb, le cuivre ou leurs mélanges.
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- 30 **10.** Utilisation d'une petite quantité d'un constituant servant d'additif (B) comprenant un sel métallique, soluble dans l'huile, d'un acide dithiophosphorique tel que défini dans l'une quelconque des revendications 1 à 7, en association avec une petite quantité d'un constituant servant d'additif (C) comprenant un composé du type carbodiimide, soluble dans l'huile, tel que défini dans l'une quelconque des revendications 1 à 7, comme inhibiteur de corrosion des métaux, notamment inhibiteur de corrosion des métaux non ferreux, dans une composition d'huile lubrifiante de carter qui est contaminée par au moins 0,3 % en masse, sur la base de la masse totale de la composition d'huile lubrifiante, et un biocarburant ou d'un de ses produits de décomposition et leurs mélanges, dans lequel le constituant servant d'additif (B) introduit 0,02 à 0,12 % en masse de phosphore dans la composition d'huile lubrifiante et le constituant servant d'additif (C) est présent en une quantité de 0,1 à 10 % en masse, sur la base de la masse totale de la composition d'huile lubrifiante.
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- 40 **11.** Utilisation, dans la lubrification d'un moteur à combustion interne à allumage par étincelle ou allumage par compression qui est alimenté au moins en partie avec un biocarburant, d'une composition d'huile lubrifiante de carter comprenant (A) une huile de viscosité propre à la lubrification en une quantité dominante ; (B) comme constituant servant d'additif en une petite quantité, un sel métallique, soluble dans l'huile, d'un acide dithiophosphorique tel que défini dans l'une quelconque des revendications 1 à 7 en une quantité qui introduit 0,02 à 0,12 % en masse de phosphore dans la composition d'huile lubrifiante ; et (C), comme constituant servant d'additif en une petite quantité, un composé du type carbodiimide, soluble dans l'huile, tel que défini dans l'une quelconque des revendications 1 à 7 en une quantité de 0,1 à 10 % en masse, sur la base de la masse totale de la composition d'huile lubrifiante, pour réduire et/ou inhiber la corrosion des composants métalliques d'un moteur, au cours du fonctionnement du moteur.
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- 50 **12.** Procédé suivant la revendication 9 ou utilisation suivant la revendication 11, dans lequel les composants métalliques du moteur comprennent des composants métalliques non ferreux du moteur, de préférence des composants du moteur comprenant le plomb, le cuivre ou leurs mélanges, notamment le plomb.
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- 50 **13.** Procédé suivant la revendication 8 ou 9 ou utilisation suivant la revendication 11, dans lequel le moteur comprend un moteur à combustion interne à allumage par compression qui a été alimenté au moins en partie avec un carburant biodiesel.
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- 55 **14.** Moteur à combustion interne à allumage par étincelle ou allumage par compression comprenant un carter contenant une composition d'huile lubrifiante comprenant (A) une huile de viscosité propre à la lubrification en une quantité dominante ; (B) comme constituant servant d'additif en une petite quantité, un sel métallique, soluble dans l'huile, d'un acide dithiophosphorique tel que défini dans l'une quelconque des revendications 1 à 7 en une quantité qui introduit 0,02 à 0,12 % en masse de phosphore dans la composition d'huile lubrifiante ; et (C) comme constituant

EP 2 290 043 B1

servant d'additif en une petite quantité, un composé du type carbodiimide, soluble dans l'huile, tel que défini dans l'une quelconque des revendications 1 à 7 en une quantité de 0,1 à 10 % en masse, sur la base de la masse totale de la composition d'huile lubrifiante, ledit moteur étant alimenté au moins en partie avec un biocarburant.

- 5 **15.** Moteur suivant la revendication 14, ledit moteur fonctionnant avec le carburant comprenant ledit biocarburant et ledit moteur étant lubrifié avec ladite composition d'huile lubrifiante.

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- EP 2055761 A [0008]
- US 6410490 B [0070]
- US 3202678 A [0100]
- US 3154560 A [0100]
- US 3172892 A [0100]
- US 3024195 A [0100]
- US 3024237 A [0100]
- US 3219666 A [0100]
- US 3216936 A [0100]
- US 3087936 A [0100]
- US 3254025 A [0100]
- EP 330522 A [0115]

Non-patent literature cited in the description

- Engine Oil Licensing and Certification System. American Petroleum Institute, December 1996 [0038]