



(11) **EP 2 290 038 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
21.03.2012 Bulletin 2012/12

(21) Application number: **10171307.1**

(22) Date of filing: **29.07.2010**

(51) Int Cl.:
C10M 159/22 (2006.01) **C10N 10/02** (2006.01)
C10N 10/04 (2006.01) **C10N 10/12** (2006.01)
C10N 30/04 (2006.01) **C10N 30/10** (2006.01)
C10N 30/12 (2006.01) **C10N 40/25** (2006.01)
C10N 40/26 (2006.01) **C10N 70/00** (2006.01)

(54) **A lubricating oil composition**

Schmierölzusammensetzung

Composition d'huile de lubrification

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

(30) Priority: **14.10.2009 GB 0917983**
24.08.2009 EP 09010811

(43) Date of publication of application:
02.03.2011 Bulletin 2011/09

(60) Divisional application:
11169302.4 / 2 365 049

(73) Proprietor: **Infineum International Limited**
Abingdon,
Oxfordshire OX13 6BB (GB)

(72) Inventors:
• **Strickland, Keith**
Abingdon, Oxfordshire OX13 6BB (GB)

• **McTavish, Stuart James**
Abingdon, Oxfordshire OX13 6BB (GB)
• **Richard, Katherine**
Abingdon, Oxfordshire OX13 6BB (GB)
• **Shaw, Robert**
Abingdon, Oxfordshire OX13 6BB (GB)

(74) Representative: **Goddard, Frances Anna et al**
PO Box 1
Milton Hill
Abingdon, Oxfordshire OX13 6BB (GB)

(56) References cited:
EP-A2- 2 055 761 WO-A1-2008/117776
WO-A1-2009/050984 WO-A1-2009/054322
WO-A1-2009/085943 GB-A- 2 446 277
US-A- 5 739 088 US-A1- 2008 026 962

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 2 290 038 B1

Description**FIELD OF THE INVENTION**

[0001] The present invention relates to automotive lubricating oil compositions, more especially to automotive lubricating oil compositions for use in compression-ignited internal combustion engines fuelled at least in part with a biodiesel fuel, crankcase lubrication, such compositions being referred to as crankcase lubricants.

[0002] 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, that exhibit improved antioxidant properties and/or improved inhibition of the corrosion of the metallic engine parts during operation of the engine which is fuelled with a biofuel; and to the use of additives in such compositions for improving the antioxidant and/or anti-corrosion properties of the lubricating oil composition.

BACKGROUND OF THE INVENTION

[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.

[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 metallic) engine parts such as the lead and copper based bearing materials. 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.

[0005] European patent application No. 2141220 A discloses a lubricating oil composition comprising a borated dispersant and an alkaline earth metal detergent for improved detergency in biodiesel applications. European patent application No. 2204438 A discloses a low ash containing lubricating oil composition comprising an alkali metal borate for improved detergency and oxidation stability in biodiesel applications. European patent application No. 2223992 A discloses use of a polyol ester base oil for improved detergency in biofuel applications. United States patent No. 5,739,088 discloses the use of an alkaline earth metal borate in alcohol fuelled engines.

[0006] European patent application No. 2055 761 A2 discloses a lubricating oil compositions comprising a base oil, and a metal phenate detergent, particularly an alkaline metal phenate, wherein the composition further contains at least 0.3 wt% of a biodiesel fuel or decomposition products thereof.

[0007] 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 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 metallic) 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.

[0008] A similar increase in the corrosion of the metallic engine parts, particularly the softer metallic (i.e. non-ferrous metallic) 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.

[0009] Additionally, it has been found that contamination of a crankcase lubricant with a biofuel (e.g. biodiesel or bioethanol), especially with biodiesel, and the decomposition products thereof accelerates oxidation of the lubricant. Oxidation of the lubricant yields corrosive acids and an undesirable increase in viscosity, thereby shortening the useful life of the lubricant.

[0010] Still further, it has been found that the use of a biofuel, particularly biodiesel, to fuel an internal combustion engine typically promotes the formation of engine and piston deposits which may increase the tendency of piston ring-sticking during operation of the engine.

[0011] 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 metallic) engine components such as those containing copper and/or lead (e.g. bearing materials), need to be identified. Accordingly, lubricants with improved antioxidant properties also need to be identified. Still further, lubricants which exhibit improved piston cleanliness need to be identified.

SUMMARY OF THE INVENTION

[0012] 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 metallic) engine components, such as those containing lead and/or copper, and/or improved antioxidant properties and/or improved piston cleanliness.

[0013] In accordance with a first aspect, the present invention provides a lubricating oil composition comprising:

- (A) an oil of lubricating viscosity in a major amount, comprising a Group III base stock;
- (B) a metal detergent system, as an additive component in a minor amount, comprising one or more oil-soluble overbased alkaline earth metal salicylates including one or more oil soluble overbased magnesium salicylates; 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 biodiesel or a decomposition product thereof and wherein the one or more overbased alkaline earth metal salicylates provides from 50 to 4000 ppm by mass of atoms of metal, based on the mass of the lubricating oil composition.

[0014] Preferably, the lubricating oil composition according to the present invention is a crankcase lubricant.

[0015] It has unexpectedly been found that the inclusion of a metal detergent system as claimed in a lubricating oil composition, particularly a lubricating oil composition comprising a Group III base stock, provides a lubricant that exhibits improved inhibition and/or a reduction in the corrosion of the metallic engine components, particularly the softer metallic (i.e. non-ferrous metallic) engine components, in use, in the lubrication of a spark-ignited or compression-ignited internal combustion engine which is fuelled at least in part with a biofuel.

[0016] Additionally, or alternatively, the inclusion of a metal detergent system as claimed in a lubricating oil composition, particularly one including a Group III base stock, improves the antioxidant properties of the lubricant, in use, in the lubrication of an internal combustion engine which is fuelled at least in part with a biofuel.

[0017] Still further, the inclusion of a metal detergent system as claimed in a lubricating oil composition, particularly one including a Group III base stock, improves the engine piston cleanliness and reduces piston ring-sticking, in use, in the lubrication of an internal combustion engine which is fuelled at least in part with a biofuel.

[0018] In particular, the inclusion of such a salicylate detergent system in a lubricant comprising a Group III base stock typically provides, in use, a positive credit in terms of reduced corrosion of the metallic engine components and/or reduced oxidation of the lubricant and/or improved piston cleanliness, whereas the use of a metal sulfonate and/or phenate detergent system typically accelerates metal corrosion and/or oxidation of the lubricant and/or provides inferior engine piston cleanliness.

[0019] According to a second aspect, the present invention provides a method of lubricating a compression-ignited internal combustion engine which is fuelled with biodiesel, comprising operating the engine with a lubricating oil composition according to the first aspect of the invention.

[0020] Suitably, the method of the second aspect of the present invention reduces and/or inhibits the corrosion of the metallic, particularly the non-ferrous metallic, engine components.

[0021] According to a third aspect, the present invention provides the use, in the lubrication of a compression-ignited internal combustion engine which is fuelled with biodiesel, of a lubricating oil composition according to the first aspect of the invention to reduce and/or inhibit the corrosion of the metallic engine components during operation of the engine.

[0022] According to a fourth aspect, the present invention provides the use, in the lubrication of a compression-ignited internal combustion engine which is fuelled with biodiesel, of a metal detergent system according to any one of claims 1 to 4 hereof, as an additive component in a minor amount in a lubricating oil composition, to reduce and/or inhibit the corrosion of the metallic engine components, during operation of the engine wherein the lubricating oil composition becomes contaminated with biodiesel or a decomposition product thereof during operation of the engine. Preferably, the lubricating oil composition comprises a major amount of an oil of lubricating viscosity comprising a Group III base stock.

[0023] In accordance with the present invention, the metal detergent system comprising one or more metal salicylates includes one or more overbased magnesium salicylates. Unexpectedly, it has been found that magnesium salicylates

offer performance credits in respect of soft metal corrosion and/or lubricant oxidative stability compared with other metal salicylates.

[0024] Preferably, the lubricating oil compositions as defined in the second to fourth aspects of the invention 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.

[0025] Preferably, the metal detergent system of the present invention (i.e. additive component (B)) forms 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), 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 comprising the Group III base stock.

[0026] Suitably, the lubricating oil composition may further include one or more co-additives in a minor amount, other than additive component (B), selected from ashless dispersants, metal detergents, corrosion inhibitors, antioxidants, pour point depressants, antiwear agents, friction modifiers, demulsifiers, antifoam agents and viscosity modifiers.

[0027] Preferably, the soft metallic engine components (i.e. non-ferrous metallic) of the metallic engine components of the third and fourth aspects comprise components which include copper or lead and mixtures thereof, especially lead, such as the lead and copper based bearing materials.

[0028] 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;

deposit formation (i.e. a measure of engine piston cleanliness) for a lubricating oil composition in the presence of biodiesel is measured using the TEOST MHT-4 Test in accordance with ASTM D7097 and, when appropriate, modified accordingly by the addition of a biofuel;

"hydrocarbyl" means a chemical group (i.e. substituent) 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. Such substituents include the following:

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

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

"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 an 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;

"oxidative stability" is measured by determining the oxidation induction time (OIT) by differential scanning calorimetry using the Hot Surface Oxidation Test as described 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 (mg KOH/g) 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.

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

[0030] Also, it will be understood that various components used, essential as well as optimal and customary, may react under conditions of formulation, storage or use and that the invention also provides the product obtainable or

obtained as a result of any such reaction.

[0031] Further, it is understood that any upper and lower quantity, range and ratio limits set forth herein may be independently combined.

DETAILED DESCRIPTION OF THE INVENTION

[0032] 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)

[0033] The oil of lubricating viscosity (sometimes referred to as "base stock" or "base oil") is the primary liquid constituent of a lubricant, into which additives and possibly other oils are blended, for example to produce a final lubricant (or lubricant composition). A base oil is useful for making concentrates as well as for making lubricating oil compositions therefrom, and may be selected from natural (vegetable, animal or mineral) and synthetic lubricating oils and mixtures thereof.

[0034] The oil of lubricating viscosity comprises a Group III base stock. The base stock groups are defined in the American Petroleum Institute (API) publication "Engine Oil Licensing and Certification System", Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998. Typically, the base stock will have a viscosity preferably of 3-12, more preferably 4-10, most preferably 4.5-8, mm²/s (cSt) at 100°C.

[0035] 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

[0036] Preferably, 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.

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

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

[0038] Synthetic lubricating oils include hydrocarbon oils such as polymerized and interpolymerized olefins (e.g. polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes)); alkylbenzenes (e.g. dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes); polyphenols (e.g. biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogues and homologues thereof.

[0039] Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g. phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, 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.

[0040] 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.

[0041] Unrefined, refined and re-refined oils can be used in the compositions of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from distillation or ester oil obtained directly from an esterification process and used without further treatment would be unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation are known to those skilled in the art. Re-refined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such re-refined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for approval of spent additive and oil breakdown products.

[0042] Other examples of base oil are gas-to-liquid ("GTL") base oils, i.e. the base oil may be an oil derived from Fischer-Tropsch synthesised hydrocarbons made from synthesis gas containing 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.

[0043] The oil of lubricating viscosity may also comprise a Group I, Group II, Group IV or Group V base stocks or base oil blends of the aforementioned base stocks.

[0044] 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.

[0045] The oil of lubricating viscosity is provided in a major amount, in combination with a minor amount of additive component (B), 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.

[0046] 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.

[0047] 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.

[0048] 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.

[0049] 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.

[0050] 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.

[0051] 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.

[0052] 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.

Metal Detergent System (B)

[0053] Metal detergents are additives that reduce formation of piston deposits in engines and that may have acid-neutralising properties, and the term 'detergent' is used herein to define a material capable of providing either or both of these functions within the lubricating oil composition. They are based on metal "soaps", that is metal salts of acidic organic compounds, sometimes referred to as surfactants, and that generally comprise a polar head with a long hydrophobic tail. Large amounts of a metal base can be included by reacting an excess of a metal base, such as an oxide or hydroxide, with an acidic gas such as carbon dioxide to give an overbased detergent which comprises neutralised detergent as the outer layer of a metal base (e.g. carbonate) micelle.

[0054] As stated, the metal detergent system (B) comprises one or more oil soluble overbased alkaline earth metal salicylates i.e. one or more metal salts of salicylic acids, including one or more oil soluble overbased magnesium salicylates.

[0055] Salicylic acids are typically prepared by the carboxylation, by the Kolbe-Schmitt process, of phenoxides, and in that case, will generally be obtained (normally in a diluent) in admixture with uncarboxylated phenol. Salicylic acids may be non-sulphurized or sulphurized, and may be chemically modified and/or contain additional substituents. Processes for sulphurizing a hydrocarbyl-substituted salicylic acid are well known to those skilled in the art, and are described, for example, in US 2007/0027057. Preferably, the salicylic acids are non-sulphurized.

[0056] Preferably, the one or more metal salicylates comprise one or more hydrocarbyl-substituted salicylates, namely the surfactant of the soap comprises one or more hydrocarbyl-substituted salicylic acids. More preferably, each surfactant moiety of the soap comprises a hydrocarbyl-substituted salicylic acid, more preferably each surfactant moiety comprises an alkyl substituted salicylic acid, most preferably each surfactant moiety independently represents a C₈ to C₃₀ alkyl substituted salicylic acid. Examples of suitable alkyl groups include: octyl, nonyl, decyl, dodecyl, pentadecyl, octadecyl, eicosyl, docosyl, tricosyl, hexacosyl, triacontyl, dimethylcyclohexyl, ethylcyclohexyl, methylcyclohexylmethyl and cyclohexylethyl.

[0057] Preferably, the alkaline earth metal of the one or more alkaline earth metal salicylates is e.g. calcium, magnesium, barium or strontium. More preferably, the alkaline earth metal is calcium or magnesium.

[0058] Unexpectedly it has been found that the use of a magnesium salicylate detergent in a lubricating oil composition enhances the level of lead corrosion control performance still further compared with the use of a calcium salicylate detergent at the same levels of soap, TBN and/or sulphated ash.

[0059] Unexpectedly it has also been found that the use of a magnesium salicylate detergent in a lubricating oil composition reduces oxidation of the lubricating oil composition still further compared with the use of a calcium salicylate detergent at the same levels of soap, TBN and/or sulphated ash.

[0060] Magnesium salicylate detergents typically provide enhanced detergency than the corresponding calcium salicylate detergents, whereas the calcium salicylate detergents typically provide better anti-wear credits than the magnesium counterparts. Thus, by the appropriate combination of a calcium salicylate detergent and a magnesium salicylate detergent in a lubricating oil composition it may be possible to optimise lead corrosion control performance, anti-wear performance and detergency performance. Thus according to a further preferred embodiment of the present invention, the lubricating oil composition comprises a combination of one or more calcium salicylates and one or more magnesium salicylates, preferably one or more overbased calcium salicylates and one or more overbased magnesium salicylates.

[0061] The salts may contain a substantially stoichiometric amount of the metal when they are usually described as normal or neutral salts and would typically have a total base number or TBN (as may be measured by ASTM D2896) of from 0 to 80. Large amounts of a metal base can be included by reaction of an excess of a metal compound, such as an oxide or hydroxide, with an acidic gas such as carbon dioxide. The resulting overbased detergent comprises neutralised detergent as an outer layer of a metal base (e.g. carbonate) micelle. Such overbased detergents may have a TBN of

100 or greater, and typically of from 250 to 500.

[0062] Preferably, the metal detergent system comprises one or more overbased calcium salicylate.

[0063] The metal detergent system may contain two or more different metal detergents of the same surfactant, for example an alkali metal salicylate and an alkaline earth metal salicylate, or a magnesium salicylate and a calcium salicylate. The metal detergent system may also contain two or more different detergents having a different surfactant type, for example one or more metal salicylates plus one or more metal sulphonates and/or metal phenates. Metal detergent systems including two or more different detergents having a different surfactant type include "hybrid" detergents formed with mixed surfactant systems, e.g., phenate/salicylates (sometimes referred to as "phenalates"), sulfonate/salicylates, sulfonates/phenates/salicylates, as described, for example, in U.S. Patent Nos. 6,153,565; 6,281,179; 6,429,178; and 6,429,179.

[0064] Although the lubricating composition may include other metal detergents apart from the metal salicylate, for example metal phenate detergents, preferably the one or more metal salicylates is the predominant metal detergent in the lubricating oil composition. In other words, the one or more metal salicylates contribute greater than 50 %, preferably greater than 60 %, more preferably greater than 70 %, even more preferably greater than 80 %, most preferably greater than 90 %, of the total TBN from all of the ash forming metal detergents in the lubricating composition. In a preferred embodiment, the one or more metal salicylates is essentially the sole metal detergent of the metal detergent system in the lubricating oil composition.

[0065] Thus, according to a preferred embodiment, the lubricating composition includes a metal detergent system from which metal phenates and metal sulfonates are substantially, or more preferably completely, absent.

[0066] Typically, the metal detergent system of the lubricating oil composition is used in amounts which provide the lubricating oil composition with a TBN of from about 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, preferably from about 7 to 12. In a passenger car diesel engine lubricating oil composition (PCDO) and a passenger car motor oil for a spark-ignited engine (PCMO), a detergent is generally added in amounts that provide the lubricating oil composition with a TBN of from about 5.0 to about 12.0, such as from about 5.0 to about 11.0.

[0067] Preferably, the metal detergent system, is used in an amount which introduces at least about 6 mmols, preferably at least 9 mmols, more preferably at least 15 mmols, such as at least about 18 mmols, even more preferably at least 20 mmols, even more preferably at least about 24 mmols, of soap (i.e. salicylate) per kilogram of finished lubricant. Unexpectedly, it has been found that the level of both copper and lead corrosion control performance is enhanced by increasing the level of soap introduced into the lubricating oil composition by the one or more metal salicylates.

[0068] The one or more oil soluble overbased alkaline earth metal salicylates provide from 50 to 4,000 preferably from 100 to 3,000, ppm by mass of atoms of metal, based on the mass of the lubricating oil composition.

ENGINES

[0069] The lubricating oil compositions of the invention may be used to lubricate mechanical engine components, particularly in internal combustion engines, e.g. spark-ignited or compression-ignited two- or four- stroke reciprocating engines, by adding the composition thereto. The engines may be conventional gasoline or diesel engines designed to be powered by gasoline or petroleum diesel, respectively; alternatively, the engines may be specifically modified to be powered by an alcohol based fuel or biodiesel fuel. Preferably, the lubricating oil compositions are crankcase lubricants.

[0070] Preferably, the lubricating oil composition is for use in the lubrication of a compression-ignited internal combustion 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. More preferably, the lubricating oil composition is for use in the lubrication of the crankcase of the aforementioned engines.

[0071] When the lubricating oil composition, such as a crankcase lubricant, 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.

[0072] The biofuel comprises an alcohol based fuel in the case of spark-ignited internal combustion engines, preferably a bioalcohol fuel, especially bioethanol fuel.

[0073] The biofuel comprises biodiesel in the case of compression ignited internal combustion engines.

BIOFUELS

[0074] 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", irrespective of the source of the alcohol (i.e. the alcohol may be derived from a renewable biological source or a non-renewable source, such as petroleum).

Alcohol Based Fuels

[0075] 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.

[0076] Preferably, the alcohol based fuel comprises an ethanol based fuel. More preferably, the alcohol based fuel comprises a bioalcohol fuel, especially a bioethanol fuel.

[0077] 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.

[0078] 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

[0079] 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.

[0080] 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.

[0081] 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.

[0082] 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.

[0083] 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

[0084] Co-additives, with representative effective amounts, that may also be present, different from additive component

(B), are listed below. All the values listed are stated as mass percent active ingredient.

	Additive	Mass %	Mass %
		(Broad)	(Preferred)
5	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
10	Metal Dihydrocarbyl Dithiophosphate	0 - 10	0 - 4
	Anti-Oxidants	0 - 5	0.01 - 3
	Pour Point Depressant	0.01 - 5	0.01 - 1.5
	Anti-Foaming Agent	0 - 5	0.001 - 0.13
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.			

[0085] 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.

[0086] 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.

[0087] 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.

[0088] 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.

[0089] 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.

[0090] 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.

[0091] Preferably, the lubricating oil composition includes an oil-soluble boron containing compound, especially a borated dispersant. Preferably, the borated dispersant comprises an ashless nitrogen containing borated dispersant, such as a borated polyalkenyl succinimide, especially a borated polyisobutenyl succinimide.

[0092] A detergent, in addition to additive component B, may be present in the lubricating oil compositions. Detergents which may be used include oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, 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.

[0093] Preferably, the detergent system comprising one or more metal salicylates (i.e. additive component (B)) is the sole detergent in the lubricating oil composition.

[0094] 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, ethoxylated tallow amine and ethoxylated tallow ether amine.

[0095] 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.

[0096] 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.

[0097] 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.

[0098] 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.

[0099] 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.

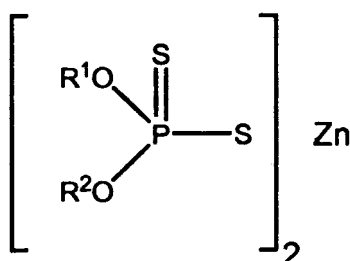
[0100] They may be classified as radical scavengers (e.g. sterically hindered phenols, secondary aromatic amines, and organo-copper salts); hydroperoxide decomposers (e.g., organosulfur and organophosphorus additives); and multifunctionals (e.g. zinc dihydrocarbyl dithiophosphates, which may also function as anti-wear additives, and organo-molybdenum compounds, which may also function as friction modifiers and anti-wear additives).

[0101] Examples of suitable antioxidants are selected from copper-containing antioxidants, sulfur-containing antioxidants, aromatic amine-containing antioxidants, hindered phenolic antioxidants, dithiophosphates derivatives, metal thio-carbamates, and molybdenum-containing compounds. Preferred anti-oxidants are aromatic amine-containing antioxidants, molybdenum-containing compounds and mixtures thereof, particularly aromatic amine-containing antioxidants. Preferably, an antioxidant is present in the lubricating oil composition.

[0102] Anti-wear agents reduce friction and excessive wear and are usually based on compounds containing sulfur or phosphorous or both, for example that are capable of depositing polysulfide films on the surfaces involved. Noteworthy are dihydrocarbyl dithiophosphate metal salts wherein the metal may be an alkali or alkaline earth metal, or aluminium, lead, tin, molybdenum, manganese, nickel, copper, or preferably, zinc. Preferably, the lubricating oil composition includes a dihydrocarbyl dithiophosphate metal salt as defined herein.

[0103] 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.

[0104] 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, especially primary alkyl groups (i.e. R¹ and R² are derived from predominantly primary alcohols). 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.

[0105] Preferably, the lubricating oil composition contains an amount of dihydrocarbyl dithiophosphate metal salt that introduces 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.

[0106] To limit the amount of phosphorus introduced into the lubricating oil composition 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 1.3 mass % (a.i.), based upon the total mass of the lubricating oil composition.

[0107] Examples of ashless anti-wear agents include 1,2,3-triazoles, benzotriazoles, sulfurised fatty acid esters, and dithiocarbamate derivatives.

[0108] 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.

[0109] Pour point depressants, otherwise known as lube oil flow improvers, lower the minimum temperature at which the oil will flow or can be poured. Such additives are well known. Typical of these additive are C₈ to C₁₈ dialkyl fumarate/vinyl acetate copolymers and polyalkylmethacrylates.

[0110] Additives of the polysiloxane type, for example silicone oil or polydimethyl siloxane, can provide foam control.

[0111] 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.

[0112] 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.

[0113] 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.

[0114] 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.

[0115] 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.

[0116] Preferably, the metal detergent system comprising one or more metal salicylates (i.e. additive component (B)) forms 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 component (B), 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 comprising a Group III base stock.

EXAMPLES

[0117] 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)

[0118] 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.

[0119] 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.

[0120] 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.

Oxidative Stability: Hot Surface Oxidation Test

[0121] Oxidative stability is measured using the Hot Surface Oxidation Test which determines the Oxidation Induction Time (OIT) of a lubricating oil composition by Pressure Differential Scanning Calorimetry (PDSC).

[0122] A measured sample (3 mg) of a lubricating oil composition is placed in a test cell of a Pressure Differential Scanning Calorimeter (Netzsch 204 HPDSC) and the cell pressurised to 689.5 KPa (100 psi) with clean dry air. The cell is then heated at a rate of 40°C per minute until the isothermal test temperature of 210°C is attained and the sample maintained at this temperature for a maximum of 240 minutes. The calorimeter provides a value of the OIT i.e. the time taken for the sample to oxidise; a larger OIT indicates the sample is more stable to oxidation than a sample having a smaller OIT.

Piston Cleanliness - Deposit Formation: TEOST MHT-4 Test

[0123] The deposit forming tendency of a lubricating oil composition under temperature and environmental conditions as being significant in internal combustion engines is measured using the TEOST MHT-4 Test in accordance with ASTM D7097, and modified accordingly by the addition of biofuel to the lubricant where appropriate.

[0124] A sample of the lubricating oil composition, including a biofuel where appropriate, is placed in the TEOST test apparatus (available from Tannas, Midland MI, USA) along with a proprietary catalyst (0.01g of catalyst per 1g of lubricant, available from Tannas). The lubricant is then cycled down (approximately 0.25 g/min) the outside of a pre-weighed depositor rod, which is resistively heated to a constant temperature of 285°C in a mantle chamber, for 24 hours. During this time dry air is forced to flow through the mantle chamber at a rate of 10 ml/min. At the end of the test, the depositor rod is removed from the mantle chamber and soaked in cyclohexane (3 x 300 ml). The cyclohexane is filtered and any deposits collected and weighed. The total mass of deposits (in mg) formed is determined by weighing the mass of the rod to determine the mass of deposits remaining on the rod and adding this to the mass of deposits collected by filtration. A lower total mass of deposits formed is indicative of improved piston cleanliness.

Example 1 Corrosion Control - Soap Type

[0125] A series of 5W-30 multigrade lubricating oil compositions, as detailed in Table 1, were prepared by admixing

an identical Group III base stock with known additives including a detergent selected from an overbased calcium salicylate detergent (TBN 217) or a mixture of an overbased calcium sulphonate detergent (TBN 300) and an overbased calcium phenate detergent (TBN 140), a dispersant, ZDDP, an aminic antioxidant, a phenolic antioxidant and a viscosity modifier concentrate. All additives described herein are available as standard from lubricant additive companies such as Infineum UK Ltd, Lubrizol Corporation, Afton Chemicals Corp, for example.

[0126] Reference Lubricants 1 and 2 did not include any biodiesel fuel (i.e. the lubricants *per se*), whereas Lubricant 1 and Lubricant 2 included 5 mass % B50 biodiesel fuel (i.e. 5 mass % of a fuel comprising B100 biodiesel fuel (50 mass %) and petroleum diesel fuel (50 mass %)) to simulate contamination of the oil during operation of a diesel engine fuelled with a biodiesel fuel. Reference Lubricant 1 and Lubricant 1 included the overbased calcium salicylate detergent, whereas Reference Lubricant 2 and Lubricant 2 included a comparable amount of the overbased calcium sulphonate detergent and calcium phenate detergent. Both Lubricant 1 and Lubricant 2 had a phosphorus content of 0.2 mass %, a sulphated ash content of 1 mass % and a TBN of 8.85. each of the Lubricants were evaluated for copper and lead corrosion control using the High Temperature Corrosion Bench Test. The results are detailed in Table 1 below.

Table 1.

	Reference Lubricant 1 (wt %)	Reference Lubricant 2 (wt %)	Lubricant 1 (wt %)	Lubricant 2 (wt %)
Ca salicylate detergent	2.5	0	2.5	0
Ca sulphonate detergent	0	0.9	0	0.9
Ca phenate detergent	0	2.0	0	2.0
Dispersant	5.5	5.5	5.5	5.5
ZDDP	1.1	1.1	1.1	1.1
Aminic antioxidant	2.0	2.0	1.0	1.0
Phenolic antioxidant	1.0	0	0.5	0.5
Viscosity modifier concentrate	5.5	5.5	5.5	5.5
B50 Biodiesel	0	0	5	5
Group III base stock	balance	balance	balance	balance
Copper Corrosion ppm	6.1	6.8	7.4	151.4
Lead Corrosion ppm	11.6	50.6	142.5	836.7

[0127] The results indicate that both a lubricant including an overbased salicylate detergent (Reference Lubricant 1) or a lubricant including overbased sulphonate and phenate detergents (Reference Lubricant 2), in the absence of a biofuel, display excellent corrosion control performance. In the presence of a biofuel, a lubricant including an overbased salicylate detergent (Lubricant 1) still displays good copper and lead corrosion control performance. Moreover, the copper and lead corrosion control performance of a lubricant including an overbased salicylate detergent (Lubricant 1) is far superior to that of a corresponding lubricant including overbased sulphonate and phenate detergents (Lubricant 2).

Example 2 Oxidation Stability - Soap Type

[0128] Two 5W-30 multigrade lubricating oil compositions (Lubricant 3 and Lubricant 4), as detailed in Table 2, were prepared by admixing an identical Group III base stock with known additives including a detergent selected from an overbased calcium salicylate detergent (TBN 217) or a mixture of an overbased calcium sulphonate detergent (TBN 300) and an overbased calcium phenate detergent (TBN 140), a dispersant, an organo-molybdenum dithiocarbamate compound, ZDDP, an aminic antioxidant, a hindered phenol ester antioxidant and a viscosity modifier concentrate.

[0129] Lubricant 3 included the overbased calcium salicylate detergent, whereas Lubricant 4 included a comparable amount of the overbased calcium sulphonate detergent and a calcium phenate detergent. Both of the lubricants had a

phosphorus content of 0.08 mass %, a sulphated ash content of 0.83 mass % and a TBN of 7.85. B50 biodiesel fuel (i.e. 5 mass % of a fuel comprising B100 biodiesel fuel (50 mass %) and petroleum diesel fuel (50 mass %)) was added to both of the lubricants to simulate contamination of the oil during operation of a diesel engine fuelled with a biodiesel fuel. The oxidative stability of each lubricant was determined using the Hot Surface Oxidation Test. The results are also detailed in Table 2.

[0130] The results demonstrate that a lubricant including an overbased salicylate detergent (Lubricant 3) is far more stable to oxidation, in the presence of a biofuel, than a comparable lubricant including overbased sulphonate and phenate detergents (Lubricant 4).

Table 2

	Lubricant 3 (wt %)	Lubricant 4 (wt %)
Ca salicylate detergent	2.5	0
Ca sulphonate detergent	0	0.9
Ca phenate detergent	0	2.0
Dispersant	5.5	5.5
Molybdenum	0.1	0.1
ZDDP	0.9	0.9
Aminic antioxidant	0.5	0.5
Phenolic antioxidant	0.5	0.5
Viscosity modifier concentrate	5.5	5.5
B50 Biodiesel	5	5
Group III base stock	balance	balance
OIT (minutes)	161.9	126.1

Example 3 Corrosion Control and Piston Cleanliness - Soap Type

[0131] A series of 5W-30 multigrade lubricating oil compositions, as detailed in Table 3, were prepared by admixing an identical Group III base stock with known additives including a detergent selected from an overbased calcium salicylate detergent (TBN 217) or an overbased calcium sulphonate detergent (TBN 300) plus a neutral calcium sulphonate detergent (TBN 17) or an overbased calcium phenate detergent (TBN 250), a dispersant, a ZDDP, an aminic antioxidant and a viscosity modifier concentrate.

[0132] Lubricants 6 and 9 included the overbased calcium sulphonate detergent plus a neutral calcium sulphonate detergent; Lubricants 7 and 10 included the overbased calcium phenate detergent; whereas, Lubricants 5 and 8 included the overbased calcium salicylate detergent. 10 mass % B50 biodiesel fuel (i.e. 5 mass % of a fuel comprising B100 biodiesel fuel (50 mass %) and petroleum diesel fuel (50 mass %)) was added to each of the lubricants to simulate contamination of the oil during operation of a diesel engine fuelled with a biodiesel fuel. Each of the lubricants were evaluated for copper and lead corrosion control using the High Temperature Corrosion Bench Test, deposit formation (piston cleanliness) using the TEOST MHT-4 test and oxidation stability using the Hot Surface Oxidation Test. The results are also detailed in Table 3.

[0133] The results indicate that a lubricant comprising a salicylate detergent exhibits improved copper and lead corrosion control performance, in the presence of a biofuel, compared with a comparable lubricant, having the same level of soap and TBN, including a sulphonate detergent or a phenate detergent (compare Lubricant 5 with Lubricants 6 and 7 or compare Lubricant 8 with Lubricants 9 and 10).

[0134] The results also indicate that the level of copper and lead corrosion control is enhanced still further in a lubricating oil composition including a salicylate detergent by increasing the level of soap in the lubricating oil composition (compare Lubricant 5 with Lubricant 8).

[0135] The results also demonstrate that a lubricant comprising a salicylate detergent exhibits reduced deposit formation (i.e. indicative of enhanced piston cleanliness), in the presence of a biofuel, compared with a comparable lubricant, having the same level of soap and TBN, including a sulphonate detergent or a phenate detergent (compare Lubricant 5 with Lubricants 6 and 7).

[0136] Additionally, the results also demonstrate that a lubricant comprising a salicylate detergent is more stable to oxidation, in the presence of a biofuel, compared with a comparable lubricant, having the same level of soap and TBN including a sulphonate detergent or a phenate detergent (compare oxidation induction time (OIT) of Lubricant 5 with Lubricant 6 and Lubricant 7). Furthermore, increasing the concentration of salicylate soap in Lubricant 5 by 50 mole % to form Lubricant 8 results in a significant increase in oxidation stability in the presence of a biofuel. In contrast, increasing the level of soap in Lubricant 6 or Lubricant 7 by 50 mole % to form Lubricants 9 and 10, respectively, does not significantly increase the oxidation stability of the resulting lubricants in the presence of a biofuel.

Table 3

	Lubricant 5 (wt %)	Lubricant 6 (wt %)	Lubricant 7 (wt %)	Lubricant 8 (wt %)	Lubricant 9 (wt)	Lubricant 10 (wt %)
Casalicylate detergent	2.5	0	0	3.75	0	0
Ca sulphonate detergent (TBN 300)	0	1.73	0	0	2.60	0
Ca sulphonate detergent (TBN 17)	0	2.66	0	0	3.99	0
Ca phenate detergent	0	0	2.17	0	0	3.26
Dispersant	5.5	5.5	5.5	5.5	5.5	5.5
ZDDP	1.0	1.0	1.0	1.0	1.0	1.0
Antioxidant	1.0	1.0	1.0	1.0	1.0	1.0
Viscosity modifier concentrate	5.5	5.5	5.5	5.5	5.5	5.5
B50 Biodiesel	10	10	10	10	10	10
Group III base stock	balance	balance	balance	balance	balance	balance
TBN	5.63	5.66	5.68	8.44	8.50	8.51
Soap (mmol/kg)	15.90	15.90	15.88	23.85	23.84	23.83
Ash (mass)	0.83	1.01	0.85	1.16	1.43	1.19
Phosphorus (mass %)	0.08	0.08	0.08	0.08	0.08	0.08
Copper Corrosion ppm	98.3	153.9	216.6	82.6	113.9	340.2
Lead Corrosion ppm	1369.6	4276.4	1935.5	1199.6	3943.4	3047.4
Deposits (mg)	12.9	49.8	23.7	-	-	-
OIT (mins)	99	72	75	279	77	105

Example 4 Corrosion Control and Oxidative Stability - Soap Counterion

[0137] A series of 5W-30 multigrade lubricating oil compositions (Lubricant 11 of the invention and Lubricants 12 and 13), as detailed in Table 4, were prepared by admixing an identical Group III base stock with known additives including a detergent selected from a mixture of overbased calcium salicylate detergents (TBN 217 and TBN of 335) or an overbased magnesium salicylate detergent (TBN 340), a dispersant, a ZDDP, an aminic antioxidant and a viscosity modifier concentrate. 10 mass % B50 biodiesel fuel (i.e. 5 mass % of a fuel comprising B100 biodiesel fuel (50 mass %) and petroleum diesel fuel (50 mass %)) was added to each of the lubricants to simulate contamination of the oil during operation of a diesel engine fuelled with a biodiesel fuel. Each of the lubricants were evaluated for copper and lead corrosion control using the High Temperature Corrosion Bench Test and oxidative stability using the Hot Surface Oxidation Test. The results are also detailed in Table 4.

[0138] The results indicate that a lubricant including a magnesium salicylate detergent exhibits essentially the same copper corrosion control performance, in the presence of a biofuel, as a comparable lubricant including a calcium salicylate detergent, having the same level of soap, TBN and/or sulphated ash (compare Lubricant 11 with Lubricant 12 and also Lubricant 11 with Lubricant 13). However, a lubricant including a magnesium salicylate detergent exhibits far superior lead corrosion control performance, in the presence of a biofuel, compared to a comparable lubricant including a calcium salicylate detergent, having the same level of soap, TBN and/or sulphated ash (compare Lubricant 11 with Lubricant 12 and also Lubricant 11 with Lubricant 13). Additionally, a lubricant including a magnesium salicylate detergent is more stable to oxidation, in the presence of a biofuel, than a comparable lubricant including a calcium salicylate detergent, having the same level of soap, TBN and/or sulphated ash (compare Lubricant 11 with Lubricant 12 and also Lubricant 11 with Lubricant 13).

Table 4

	Lubricant 11 (wt %)	Lubricant 12 (wt %)	Lubricant 13 (wt %)
Mg salicylate detergent	3.0	0	0
Ca salicylate detergent (TBN 335)	0	2.75	1.65
Ca salicylate detergent (TBN 217)	0	0.30	0.95
Dispersant	5.5	5.5	5.5
ZDDP	1.0	1.0	1.0
Aminic antioxidant	1.0	1.0	1.0
Viscosity modifier concentrate	5.5	5.5	5.5
B50 Biodiesel	10	10	10
Group III base stock	balance	balance	balance
TBN	10.26	10.26	7.91
Soap (mmol/kg)	12.51	12.52	12.49
Ash (mass %)	1.10	1.38	1.10
Phosphorus (mass %)	0.08	0.08	0.08
Copper Corrosion ppm	83.8	83.6	83.1
Lead Corrosion ppm	932.4	2007.3	1677.5
OIT (minutes)	142	83	80

Claims

1. A lubricating oil composition comprising:

- (A) an oil of lubricating viscosity in a major amount, comprising a Group III base stock;
- (B) a metal detergent system, as an additive component in a minor amount, comprising one or more oil-soluble overbased alkaline earth metal salicylates including one or more oil-soluble overbased magnesium salicylates; 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 biodiesel or a decomposition product thereof and wherein the one or more oil-soluble overbased alkaline earth metal salicylates provides from 50 to 4000 ppm by mass of atoms of metal, based on the mass of the lubricating oil composition.

2. The lubricating oil composition as claimed in claim 1, wherein the metal detergent system comprises a combination of said one or more oil-soluble overbased magnesium salicylates and one or more oil-soluble overbased calcium salicylates.
3. The lubricating oil composition as claimed in claim 1 or 2, wherein the metal detergent system consists essentially of said one or more oil-soluble overbased alkaline earth metal salicylates.
4. The lubricating oil composition as claimed in any one of the preceding claims, wherein the one or more oil-soluble overbased alkaline earth metal salicylates introduces at least 6 mmols of soap per kilogram of finished lubricant.
5. The lubricating oil composition as claimed in any one of the preceding claims, wherein the composition has a phosphorus concentration, expressed as atoms of phosphorus, of not greater than 0.10 mass %.
6. 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 component (B), selected from ashless dispersants, metal detergents, corrosion inhibitors, antioxidants, pour point depressants, antiwear agents, friction modifiers, demulsifiers, antifoam agents and viscosity modifiers.
7. The use, in the lubrication of a compression-ignited internal combustion engine which is fuelled with biodiesel, of a metal detergent system, as defined in any one of claims 1 to 4, as an additive component in a minor amount, in a lubricating oil composition, to reduce and/or inhibit the corrosion of the metallic engine components during operation of the engine, wherein the lubricating oil composition becomes contaminated with biodiesel or a decomposition product thereof during operation of the engine.
8. The use as claimed in claim 7, wherein the metallic engine components comprise lead, copper or mixtures thereof.
9. The use as claimed in claim 8, wherein the metallic engine components comprise lead.
10. The use as claimed in any one of claims 7 to 9, wherein the lubricating oil composition is contaminated with at least 0.3 mass %, based on the total mass of the lubricating oil composition, of biodiesel or a decomposition product thereof.
11. The use as claimed in any one of claims 7 to 10, wherein the lubricating oil composition comprises an oil of lubricating viscosity in a major amount comprising a Group III base stock.
12. A method of lubricating a compression-ignited internal combustion engine which is fuelled with biodiesel, comprising operating the engine with a lubricating oil composition as claimed in any one of claims 1 to 6.
13. The use, in the lubrication of a compression-ignited internal combustion engine which is fuelled with biodiesel, of a lubricating oil composition as claimed in any one of claims 1 to 6, to reduce and/or inhibit the corrosion of the metallic engine components, during operation of the engine.

Patentansprüche

1. Schmierölszusammensetzung, die:

(A) in einer größeren Menge Öl mit Schmierviskosität, das Basismaterial aus Gruppe III umfasst,
 (B) in einer geringeren Menge ein Metaldetergenzsystem als Additivbestandteil umfasst, das ein oder mehrere öllöslichen überbasische Erdalkalimetallsalicylate umfasst, die ein oder mehrere öllösliche überbasische Magnesiumsalicylate umfassen, und

wobei die Schmierölszusammensetzung mit mindestens 0,3 Masse-%, bezogen auf die gesamte Masse der Schmierölszusammensetzung, Biodiesel oder eines Zersetzungsprodukts davon kontaminiert ist und wobei das eine oder

die mehreren öllöslichen Erdalkalimetallsalicylate von 50 bis 4000 Masse-ppm Metallatome zur Verfügung stellen, bezogen auf die Masse der Schmierölszusammensetzung.

2. Schmierölszusammensetzung wie in Anspruch 1 beansprucht, wobei das Metaldetergenzsystem eine Kombination des einen oder der mehreren öllöslichen überbasischen Magnesiumsalicylate und des einen oder der mehreren öllöslichen überbasischen Calciumsalicylate umfasst.
3. Schmierölszusammensetzung wie in Anspruch 1 oder Anspruch 2 beansprucht, wobei das Metaldetergenzsystem im Wesentlichen aus dem einen oder den mehreren öllöslichen überbasischen Erdalkalimetallsalicylaten besteht.
4. Schmierölszusammensetzung wie in einem der vorhergehenden Ansprüche beansprucht, wobei das eine oder die mehreren öllöslichen überbasischen Erdalkalimetallsalicylate mindestens 6 mmol Seife pro Kilogramm fertiges Schmiermittel einbringen.
5. Schmierölszusammensetzung wie in einem der vorhergehenden Ansprüche beansprucht, wobei die Zusammensetzung eine Phosphorkonzentration von nicht größer als 0,10 Masse-% aufweist, ausgedrückt als Phosphoratome.
6. Schmierölszusammensetzung nach einem der vorhergehenden Ansprüche, die ferner in einer geringeren Menge ein oder mehrere Co-Additive umfasst, die sich von Additivbestandteil (B) unterscheiden und die ausgewählt sind aus aschefreien Dispergiemitteln, Metaldetergenzien, Korrosionsinhibitoren, Antioxidantien, Stockpunktsenkungsmitteln, Antiverschleißmitteln, Reibungsmodifizierungsmitteln, Demulgatoren, Antischaummitteln und Viskositätsmodifizierungsmitteln.
7. Verwendung eines Metaldetergenzsystems wie in einem der Ansprüche 1 bis 4 definiert in einer geringeren Menge als Additivbestandteil in einer Schmierölszusammensetzung bei der Schmierung eines kompressionsgezündeten Verbrennungsmotors, der mit Biodiesel betrieben wird, um die Korrosion der metallischen Motorkomponenten während des Betriebs des Motors zu vermindern und/oder zu inhibieren, wobei die Schmierölszusammensetzung während des Betriebs des Motors mit Biodiesel oder einem Zersetzungsprodukt desselben kontaminiert wird.
8. Verwendung wie in Anspruch 7 beansprucht, wobei die metallischen Motorkomponenten Blei, Kupfer oder Mischungen davon umfassen.
9. Verwendung wie in Anspruch 8 beansprucht, wobei die metallischen Motorkomponenten Blei umfassen.
10. Verwendung wie in einem der Ansprüche 7 bis 9 beansprucht, wobei die Schmierölszusammensetzung mit mindestens 0,3 Masse-% Biodiesel oder eines Zersetzungsprodukts desselben kontaminiert ist, bezogen auf die Gesamtmasse der Schmierölszusammensetzung.
11. Verwendung wie in einem der Ansprüche 7 bis 10 beansprucht, wobei die Schmierölszusammensetzung in einer größeren Menge Öl mit Schmierviskosität umfasst, das Basismaterial aus Gruppe III umfasst.
12. Verfahren zum Schmieren eines kompressionsgezündeten Verbrennungsmotors, der mit Biodiesel betrieben wird, wobei der Motor mit einer Schmierölszusammensetzung wie in einem der Ansprüche 1 bis 6 beansprucht betrieben wird.
13. Verwendung einer Schmierölszusammensetzung wie in einem der Ansprüche 1 bis 6 beansprucht, bei der Schmierung eines kompressionsgezündeten Verbrennungsmotors, der mit Biodiesel betrieben wird, zur Verminderung und/oder Inhibierung der Korrosion der metallischen Motorenkomponenten während des Betriebs des Motors.

Revendications

1. Composition d'huile lubrifiante comprenant :

- (A) une huile de viscosité propre à la lubrification en une quantité dominante, comprenant une huile de base du Groupe III ;
- (B) un système détergent métallique, comme constituant servant d'additif en une petite quantité, comprenant un ou plusieurs salicylates de métaux alcalino-terreux surbasiques solubles dans l'huile comprenant un ou

plusieurs salicylates de magnésium surbasiques solubles dans l'huile ; 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 biodiesel ou d'un de ses produits de décomposition, et ledit ou lesdits salicylates de métaux alcalino-terreux surbasiques solubles dans l'huile fournissant 50 à 4000 ppm en masse d'atomes de métal, sur la base de la masse de la composition d'huile lubrifiante.

2. Composition d'huile lubrifiante suivant la revendication 1, dans laquelle le système détergent métallique comprend une association dudit ou desdits salicylates de magnésium surbasiques solubles dans l'huile et d'un ou plusieurs salicylates de calcium surbasiques solubles dans l'huile.
3. Composition d'huile lubrifiante suivant la revendication 1 ou 2, dans laquelle le système détergent métallique consiste essentiellement en ledit ou lesdits salicylates de métaux alcalino-terreux surbasiques solubles dans l'huile.
4. Composition d'huile lubrifiante suivant l'une quelconque des revendications précédentes, dans laquelle ledit ou lesdits salicylates de métaux alcalino-terreux surbasiques solubles dans l'huile introduisent au moins 6 mmol de savon par kilogramme de lubrifiant fini.
5. Composition d'huile lubrifiante suivant l'une quelconque des revendications précédentes, ladite composition ayant une concentration en phosphore, exprimée en atomes de phosphore, non supérieure à 0,10 % en masse.
6. 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 le constituant servant d'additif (B), choisis entre des dispersants sans cendres, des détergents métalliques, des inhibiteurs de corrosion, des antioxydants, des agents abaissant le point d'écoulement, des agents anti-usure, des modificateurs de frottement, des désémulsifiants, des agents antimousse et des modificateurs de viscosité.
7. Utilisation, dans la lubrification d'un moteur à combustion interne à allumage par compression qui est alimenté avec un biodiesel, d'un système détergent métallique, tel que défini dans l'une quelconque des revendications 1 à 4, comme constituant servant d'additif en une petite quantité, dans une composition d'huile lubrifiante, pour réduire et/ou inhiber la corrosion des composants métalliques du moteur au cours du fonctionnement du moteur, dans laquelle la composition d'huile lubrifiante devient contaminée par le biodiesel ou un de ses produits de décomposition au cours du fonctionnement du moteur.
8. Utilisation suivant la revendication 7, dans laquelle les composants métalliques du moteur comprennent le plomb, le cuivre ou leurs mélanges.
9. Utilisation suivant la revendication 8, dans laquelle les composants métalliques du moteur comprennent le plomb.
10. Utilisation suivant l'une quelconque des revendications 7 à 9, dans laquelle la composition d'huile lubrifiante est contaminée par au moins 0,3 % en masse, sur la base de la masse totale de la composition d'huile lubrifiante, par le biodiesel ou un de ses produits de décomposition.
11. Utilisation suivant l'une quelconque des revendications 7 à 10, dans laquelle la composition d'huile lubrifiante comprend une huile de viscosité propre à la lubrification en une quantité dominante comprenant une huile de base du Groupe III.
12. Procédé pour lubrifier un moteur à combustion interne à allumage par compression qui est alimenté avec un biodiesel, comprenant le fonctionnement du moteur avec une composition d'huile lubrifiante suivant l'une quelconque des revendications 1 à 6.
13. Utilisation, dans la lubrification d'un moteur à combustion interne à allumage par compression qui est alimenté avec un biodiesel, d'une composition d'huile lubrifiante suivant l'une quelconque des revendications 1 à 6, pour réduire et/ou inhiber la corrosion des composants métalliques du moteur, au cours du fonctionnement du moteur.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- EP 2141220 A [0005]
- EP 2204438 A [0005]
- EP 2223992 A [0005]
- US 5739088 A [0005]
- EP 2055761 A2 [0006]
- US 20070027057 A [0055]
- US 6153565 A [0063]
- US 6281179 A [0063]
- US 6429178 A [0063]
- US 6429179 A [0063]
- US 3202678 A [0090]
- US 3154560 A [0090]
- US 3172892 A [0090]
- US 3024195 A [0090]
- US 3024237 A [0090]
- US 3219666 A [0090]
- US 3216936 A [0090]
- US 3087936 A [0090]
- US 3254025 A [0090]
- EP 330522 A [0111]

Non-patent literature cited in the description

- Engine Oil Licensing and Certification System. Industry Services Department. December 1996 [0034]
[0035]