

(19)



(11)

EP 2 055 729 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

06.05.2009 Bulletin 2009/19

(51) Int Cl.:

C08G 63/685 (2006.01)**C08G 63/06** (2006.01)**C10M 141/06** (2006.01)**C10M 141/10** (2006.01)**C10M 161/00** (2006.01)**C10M 163/00** (2006.01)(21) Application number: **07119030.0**(22) Date of filing: **23.10.2007**

(84) Designated Contracting States:

**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LT LU LV MC MT NL PL PT RO SE
SI SK TR**

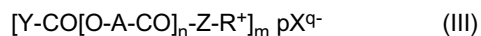
Designated Extension States:

AL BA HR MK RS(71) Applicant: **SHELL INTERNATIONALE RESEARCH****MAATSCHAPPIJ B.V.****2596 HR Den Haag (NL)**(72) Inventor: **The designation of the inventor has not
yet been filed**(74) Representative: **Zeestraten, Albertus W. J.****Shell International B.V.****Intellectual Property Services****P.O. Box 384****2501 CJ The Hague (NL)**(54) **Lubricating composition**

(57) The present invention provides a lubricating composition comprising:

- a base oil; and

- one or more poly(hydroxycarboxylic acid) amide salt derivatives having formula (III):



wherein Y is hydrogen or an optionally substituted hydrocarbyl group, A is a divalent optionally substituted hydrocarbyl group, n is from 1 to 100, preferably from 1 to 10, m is from 1 to 4, q is from 1 to 4 and p is an integer such that pq = m, Z is an optionally substituted divalent bridging group which is attached to the carbonyl group through a nitrogen atom, R⁺ is an ammonium group and X^{q-} is an anion.

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Description

[0001] The present invention relates to a lubricating oil or grease composition for particular use in internal combustion engines.

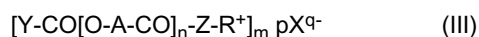
[0002] In practice various lubricating compositions are known.

[0003] As an example, EP 0 194 718 discloses lubricating oil compositions which contain one or more lubricating oils, one or more basic salts of polyvalent metals and one or more polyesters or salts thereof which are either derived from one or more hydroxycarboxylic acids of the general formula HO-X-COOH, wherein X represents a bivalent saturated or unsaturated aliphatic radical which contains at least 8 carbon atoms and in which at least 4 carbon atoms are situated between the hydroxyl group and the carboxyl group, or derived from a mixture of one or more such hydroxycarboxylic acids and one or more carboxylic acids containing no hydroxyl groups.

[0004] There has been surprisingly found in the present invention a lubricating composition for particular use in internal combustion engines, which lubricating composition not only suppresses internal combustion engine fouling and exhibits advantageous cleaning performance in the reduction of deposits such as sludge and varnish, but also shows surprisingly advantageous friction reduction and anti-wear properties.

[0005] Accordingly, the present invention provides a lubricating composition comprising:

- a base oil; and
- one or more poly(hydroxycarboxylic acid) amide salt derivatives having formula (III):



wherein Y is hydrogen or optionally substituted hydrocarbyl group, A is a divalent optionally substituted hydrocarbyl group, n is from 1 to 100, preferably from 1 to 10, m is from 1 to 4, q is from 1 to 4 and p is an integer such that $pq = m$, Z is an optionally substituted divalent bridging group which is attached to the carbonyl group through a nitrogen atom, R^+ is an ammonium group and X^{q-} is an anion.

[0006] R^+ may be a primary, secondary, tertiary or quaternary ammonium group. R^+ is preferably a quaternary ammonium group.

[0007] In formula (III), A is preferably a divalent straight chain or branched hydrocarbyl group as hereafter described for formulae (I) and (II).

[0008] That is to say, in formula (III), A is preferably an optionally substituted aromatic, aliphatic or cycloaliphatic straight chain or branched divalent hydrocarbyl group. More preferably, A is an arylene, alkylene or alkenylene group, in particular an arylene, alkylene or alkenylene group containing in the range of from 4 to 25 carbon atoms, more preferably in the range of from 12 to 20 carbon atoms.

[0009] Preferably, in said compound of formula (III), there are at least 4 carbon atoms, more preferably in the range of from 8 to 14 carbon atoms connected directly between the carbonyl group and the oxygen atom derived from the hydroxyl group.

[0010] In the compound of formula (III), the optional substituents in the group A are preferably selected from hydroxy, halo or alkoxy groups, especially C_{1-4} alkoxy groups.

[0011] In formula (III), Y is preferably an optionally substituted hydrocarbyl group as hereinbefore described for formula (I).

[0012] That is to say, the optionally substituted hydrocarbyl group Y in formula (III) is preferably aryl, alkyl or alkenyl containing up to 50 carbon atoms, more preferably in the range of from 7 to 25 carbon atoms. For example, the optionally substituted hydrocarbyl group Y may be conveniently selected from heptyl, octyl, undecyl, lauryl, heptadecyl, heptadecyl, heptadecadienyl, stearyl, oleyl and linoleyl.

[0013] Other examples of said optionally substituted hydrocarbyl group Y in formula (III) herein include C_{4-8} cycloalkyls such as cyclohexyl; polycycloalkyls such as polycyclic terpenyl groups which are derived from naturally occurring acids such as abietic acid; aryls such as phenyl; aralkyls such as benzyl; and polyaryls such as naphthyl, biphenyl, stibenyl and phenylmethylphenyl.

[0014] In the present invention, the optionally substituted hydrocarbyl group Y in formula (III) may contain one or more functional groups such as carbonyl, carboxyl, nitro, hydroxy, halo, alkoxy, amino, preferably tertiary amino (no N-H linkages), oxy, cyano, sulphonyl and sulphonyl. The majority of the atoms, other than hydrogen, in substituted hydrocarbyl groups are generally carbon, with the heteroatoms (e.g., oxygen, nitrogen and sulphur) generally representing only a minority, about 33% or less, of the total non-hydrogen atoms present.

[0015] Those skilled in the art will appreciate that functional groups such as hydroxy, halo, alkoxy, nitro and cyano in a substituted hydrocarbyl group Y will displace one of the hydrogen atoms of the hydrocarbyl, whilst functional groups such as carbonyl, carboxyl, tertiary amino (-N-), oxy, sulphonyl and sulphonyl in a substituted hydrocarbyl group will

displace a -CH- or -CH₂- moiety of the hydrocarbyl.

[0016] More preferably, the hydrocarbyl group Y in formula (III) is unsubstituted or substituted by a group selected from hydroxy, halo or alkoxy group, even more preferably C₁₋₄ alkoxy.

[0017] Most preferably, the optionally substituted hydrocarbyl group Y in formula (III) is a stearyl group, 12-hydroxy-stearyl group, an oleyl group or a 12-hydroxyoleyl group, and that derived from naturally occurring oil such as tall oil fatty acid.

[0018] In formula (III), Z is preferably an optionally substituted divalent bridging group represented by formula (IV)



wherein R¹ is hydrogen or a hydrocarbyl group and B is an optionally substituted alkylene group.

[0019] Examples of hydrocarbyl groups that may represent R¹ include methyl, ethyl, n-propyl, n-butyl and octadecyl. Examples of optionally substituted alkylene groups that may represent B include ethylene, trimethylene, tetramethylene and hexamethylene.

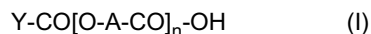
[0020] Examples of preferred Z moieties in formula (III) include -NHCH₂CH₂-, -NHCH₂C(CH₃)₂CH₂- and -NH(CH₂)₃-. Preferably, R⁺ may be represented by formula (V)



wherein R², R³ and R⁴ may be selected from hydrogen and alkyl groups such as methyl.

[0021] Preferably, the anion X^{q-} of the compound of formula (III) is a sulphur-containing anion. More preferably said anion is selected from sulphate and sulphonate anions.

[0022] The one or more poly(hydroxycarboxylic acid) amide salt derivatives may be obtained by reaction of an amine and a poly(hydroxycarboxylic acid) of formula (I)



wherein Y is hydrogen or optionally substituted hydrocarbyl group, A is a divalent optionally substituted hydrocarbyl group and n is from 1 to 100, preferably from 1 to 10, with an acid or a quaternizing agent.

[0023] As used herein, the term "hydrocarbyl" represents a radical formed by removal of one or more hydrogen atoms from a carbon atom of a hydrocarbon (not necessarily the same carbon atoms in case more hydrogen atoms are removed).

[0024] Hydrocarbyl groups may be aromatic, aliphatic, acyclic or cyclic groups. Preferably, hydrocarbyl groups are aryl, cycloalkyl, alkyl or alkenyl, in which case they may be straight-chain or branched-chain groups. Representative hydrocarbyl groups include phenyl, naphthyl, methyl, ethyl, butyl, pentyl, methylpentyl, hexenyl, dimethylhexyl, octenyl, cyclooctenyl, methylcyclooctenyl, dimethylcyclooctyl, ethylhexyl, octyl, isooctyl, dodecyl, hexadecenyl, eicosyl, hexacosyl, triacontyl and phenylethyl.

[0025] In the present invention, the phrase "optionally substituted hydrocarbyl" is used to describe hydrocarbyl groups optionally containing one or more "inert" heteroatom-containing functional groups. By "inert" is meant that the functional groups do not interfere to any substantial degree with the function of the compound.

[0026] The optionally substituted hydrocarbyl group Y in formula (I) herein is preferably aryl, alkyl or alkenyl containing up to 50 carbon atoms, more preferably in the range of from 7 to 25 carbon atoms. For example, the optionally substituted hydrocarbyl group Y may be conveniently selected from heptyl, octyl, undecyl, lauryl, heptadecyl, heptadenyl, heptadecadienyl, stearyl, oleyl and linoleyl.

[0027] Other examples of said optionally substituted hydrocarbyl group Y in formula (I) herein include C₄₋₈ cycloalkyls such as cyclohexyl; polycycloalkyls such as polycyclic terpenyl groups which are derived from naturally occurring acids such as abietic acid; aryls such as phenyl; aralkyls such as benzyl; and polyaryls such as naphthyl, biphenyl, stilbenyl and phenylmethylphenyl.

[0028] In the present invention, the optionally substituted hydrocarbyl group Y may contain one or more functional groups such as carbonyl, carboxyl, nitro, hydroxy, halo, alkoxy, tertiary amino (no N-H linkages), oxy, cyano, sulphonyl

and sulphonyl. The majority of the atoms, other than hydrogen, in substituted hydrocarbyl groups are generally carbon, with the heteroatoms (e.g., oxygen, nitrogen and sulphur) generally representing only a minority, about 33% or less, of the total non-hydrogen atoms present.

[0029] Those skilled in the art will appreciate that functional groups such as hydroxy, halo, alkoxy, nitro and cyano in a substituted hydrocarbyl group Y will displace one of the hydrogen atoms of the hydrocarbyl, whilst functional groups such as carbonyl, carboxyl, tertiary amino (-N-), oxy, sulphonyl and sulphonyl in a substituted hydrocarbyl group will displace a -CH- or -CH₂- moiety of the hydrocarbyl.

[0030] The hydrocarbyl group Y in formula (I) is more preferably unsubstituted or substituted by a group selected from hydroxy, halo or alkoxy group, even more preferably C₁₋₄ alkoxy.

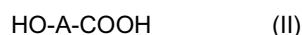
[0031] Most preferably, the optionally substituted hydrocarbyl group Y in formula (I) is a stearyl group, 12-hydroxystearyl group, an oleyl group, a 12-hydroxyoleyl group or a group derived from naturally occurring oil such as tall oil fatty acid.

[0032] In a preferred embodiment of the present invention, the one or more poly(hydroxycarboxylic acid) amide salt derivatives are sulphur-containing poly(hydroxycarboxylic acid) amide salt derivatives.

[0033] More preferably, said one or more poly(hydroxycarboxylic acid) amide salt derivatives have a sulphur content in the range of from 0.1 to 2.0 wt.%, even more preferably in the range of from 0.6 to 1.2 wt.% sulphur, as measured by ICP-AES, based on the total weight of said poly(hydroxycarboxylic acid) amide salt derivatives.

[0034] The preparation of poly(hydroxycarboxylic acid) and its amide or other derivatives is known and is described, for instance, in EP 0 164 817, WO 95/17473, WO 96/07689, US 5 536 445, GB 2 001 083, GB 1 342 746, GB 1 373 660, US 5 000 792 and US 4 349 389.

[0035] The poly(hydroxycarboxylic acid)s of formula (I) may be made by the interesterification of one or more hydroxycarboxylic acids of formula (II)



wherein A is a divalent optionally substituted hydrocarbyl group, optionally in the presence of a catalyst according to well known methods. Such methods are described, for example, in US 3 996 059, GB 1 373 660 and GB 1 342 746.

[0036] The chain terminator in said interesterification may be a non-hydroxycarboxylic acid.

[0037] The hydroxyl group in the hydroxycarboxylic acid and the carboxylic acid group in the hydroxycarboxylic acid or the non-hydroxycarboxylic acid may be primary, secondary or tertiary in character.

[0038] The interesterification of the hydroxycarboxylic acid and the non-hydroxycarboxylic acid chain terminator may be effected by heating the starting materials, optionally in a suitable hydrocarbon solvent such as toluene or xylene, and azeotroping off the formed water. The reaction may be carried out at a temperature up to -250°C, conveniently at the reflux temperature of the solvent.

[0039] Where the hydroxyl group in the hydroxycarboxylic acid is secondary or tertiary, the temperature employed should not be so high as to lead to dehydration of the acid molecule.

[0040] Catalysts for the interesterification, such as p-toluenesulphonic acid, zinc acetate, zirconium naphthenate or tetrabutyl titanate, may be included, with the objective of either increasing the rate of reaction at a given temperature or of reducing the temperature required for a given rate of reaction.

[0041] In the compounds of formulae (I) and (II), A is preferably an optionally substituted aromatic, aliphatic or cycloaliphatic straight chain or branched divalent hydrocarbyl group. Preferably, A is an arylene, alkylene or alkenylene group, in particular an arylene, alkylene or alkenylene group containing in the range of from 4 to 25 carbon atoms, more preferably in the range of from 12 to 20 carbon atoms.

[0042] Preferably, in said compounds of formulae (I) and (II), there are at least 4 carbon atoms, more preferably in the range of from 8 to 14 carbon atoms connected directly between the carbonyl group and the oxygen atom derived from the hydroxyl group.

[0043] In the compounds of formulae (I) and (II), the optional substituents in the group A are preferably selected from hydroxy, halo or alkoxy groups, more preferably C₁₋₄ alkoxy groups.

[0044] The hydroxyl group in the hydroxycarboxylic acids of formula (II) is preferably a secondary hydroxyl group. Examples of suitable hydroxycarboxylic acids are 9-hydroxystearic acid, 10-hydroxystearic acid, 12-hydroxystearic acid, 12-hydroxy-9-oleic acid (ricinoleic acid), 6-hydroxycaproic acid, preferably 12-hydroxystearic acid. Commercial 12-hydroxystearic acid (hydrogenated castor oil fatty acid) normally contains up to 15% wt of stearic acid and other non-hydroxycarboxylic acids as impurities and can conveniently be used without further admixture to produce a polymer of molecular weight about 1000-2000.

[0045] Where the non-hydroxycarboxylic acid is introduced separately to the reaction, the proportion which is required in order to produce a polymer or oligomer of a given molecular weight can be determined either by simple experiment or by calculation by the person skilled in the art.

[0046] The group (-O-A-CO-) in the compounds of formulae (I) and (II) is preferably a 12-oxystearyl group, 12-oxyleyl group or a 6-oxycaproyl group.

[0047] Preferred poly(hydroxycarboxylic acid)s of formula (I) for reaction with amine include poly(hydroxystearic acid) and poly(hydroxyoleic acid).

[0048] The amines which react with poly(hydroxycarboxylic acid)s of formula (I) to form poly(hydroxycarboxylic acid) amide intermediates may include those defined in WO 97/41092.

[0049] For example, various amines and their preparations are described in US 3 275 554, US 3 438 757, US 3 454 555, US 3 565 804, US 3 755 433 and

[0050] US 3 822 209.

[0051] The amine reactant is preferably a diamine, a triamine or a polyamine.

[0052] Preferred amine reactants are diamines selected from ethylenediamine, N,N-dimethyl-1,3-propanediamine, triamines and polyamines selected from diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenhexamine and tris(2-aminoethyl)amine.

[0053] The amidation between the amine reactant and the (poly(hydroxycarboxylic acid) of formula (I) may be carried out according to methods known to those skilled in the art, by heating the poly(hydroxycarboxylic acid) with the amine reactant, optionally in a suitable hydrocarbon solvent such as toluene or xylene, and azeotroping off the formed water. Said reaction may be carried out in the presence of a catalyst such as p-toluenesulphonic acid, zinc acetate, zirconium naphthenate or tetrabutyl titanate.

[0054] Various patent documents disclose poly(hydroxycarboxylic acid) amide derivatives.

[0055] For instance, GB 1 373 660 discloses poly(hydroxycarboxylic acid) amide derivatives with amines such as 3-dimethylaminopropylamine and ethylenediamine for use as dispersing agents in dispersions of pigments in organic liquids.

[0056] GB 2 001 083 discloses poly(hydroxycarboxylic acid) amide derivatives with poly(ethyleneimine) (PEI) having a molecular weight (MW) greater than 500 for a similar use.

[0057] In US 5 000 792, poly(hydroxycarboxylic acid) amide derivatives with amines of the formula of $\text{NH}_2\text{-R}'\text{-N(R'')-R'''-NH}_2$ are disclosed for use as pigment dispersing agent.

[0058] WO 95/17473 discloses poly(hydroxycarboxylic acid) amide derivatives with amines such as 3-dimethylaminopropylamine, ethylenediamine, poly(ethyleneimine) (PEI) having a molecular weight (MW) greater than 500 and amines of the formula of $\text{NH}_2\text{-R}'\text{-N(R'')-R'''-NH}_2$ for use in a method of preparing a non-aqueous dispersion of copper phthalocyanine.

[0059] US 4 349 389 discloses poly(hydroxycarboxylic acid) amide derivatives with amines such as 3-dimethylaminopropylamine, poly(ethyleneimine) (PEI) having a molecular weight (MW) greater than 500 as dispersing agent in the preparation of a dispersible inorganic pigment composition.

[0060] EP 0 164 817 discloses poly(hydroxycarboxylic acid) amide derivatives with polyamines (ethylenediamine, diethylenetriamine, etc.), aminoalcohols (diethanolamine, etc.) and ester derivatives with polyols (glycerol, etc.) for use as surfactant suitable for stabilising dispersions of solids in organic liquids and oil/water emulsions.

[0061] However, none of the afore-mentioned patent documents disclose the use of one or more poly(hydroxycarboxylic acid) amide salt derivatives as disclosed herein in lubricating compositions.

[0062] The poly(hydroxycarboxylic acid) amide intermediate formed from reaction of the amine and the poly(hydroxycarboxylic acid) of formula (I) is reacted with an acid or a quaternizing agent to form a salt derivative, according to well-known methods.

[0063] Acids that may be used to form the salt derivative may be selected from organic or inorganic acids. Said acids are preferably sulphur-containing organic or inorganic acids. Preferably, said acids are selected from sulphuric acid, methanesulphonic acid and benzenesulphonic acid.

[0064] Quaternizing agents that may be used to form the salt derivative may be selected from dimethylsulphuric acid, a dialkyl sulphate having from 1 to 4 carbon atoms, an alkyl halide such as methyl chloride, methyl bromide, aryl halide such as benzyl chloride.

[0065] In a preferred embodiment, the quaternizing agent is a sulphur-containing quaternizing agent, in particular dimethylsulphuric acid or an dialkyl sulphate having from 1 to 4 carbon atoms. The quaternizing agent is preferably dimethyl sulphate.

[0066] Quaternization is a well-known method in the art. For example, quaternization using dimethyl sulphate is described in US 3 996 059, US 4 349 389 and GB 1 373 660.

[0067] According to preferred embodiment of the present invention, the one or more poly(hydroxycarboxylic acid) amide salt derivatives are present in the lubricating composition of the present invention in an amount in the range of from 0.1 to 10.0 wt. %, more preferably in an amount in the range of from 0.1 to 5.0 wt. % and most preferably in an amount in the range of from 0.2 to 4.0 wt. %, based on the total weight of the lubricating composition.

[0068] Poly(hydroxycarboxylic acid) amide salt derivatives that are preferred in the present invention are those which each have a TBN (total base number) value of less than 10 mg.KOH/g, as measured by ASTM D 4739. More preferably, the poly(hydroxycarboxylic acid) amide salt derivatives each have a TBN value of less than 5 mg.KOH/g, most preferably 2 mg.KOH/g or less, as measured by ASTM D 4739.

[0071] Preferably, the one or more anti-wear additives present in the lubricating composition may comprise zinc dithiophosphates. The or each zinc dithiophosphate may be selected from zinc dialkyl-, diaryl- or alkylaryl-dithiophosphates.

$$\begin{array}{c} \text{R}^5\text{O} \\ \diagdown \\ \text{P} \\ \diagup \\ \text{R}^6\text{O} \end{array} - \text{S} - \text{Zn} - \text{S} - \begin{array}{c} \diagup \\ \text{P} \\ \diagdown \\ \text{OR}^7 \\ \text{OR}^8 \end{array}$$

[0086] Fischer-Tropsch derived base oils may be conveniently used as the base oil in the lubricating composition of

the present invention, for example, the Fischer-Tropsch derived base oils disclosed in EP 0 776 959, EP 0 668 342, WO 97/21788, WO 00/15736, WO 00/14188, WO 00/14187, WO 00/14183, WO 00/14179, WO 00/08115, WO 99/41332, EP 1 029 029, WO 01/18156 and WO 01/57166.

[0087] Synthetic processes enable molecules to be built from simpler substances or to have their structures modified to give the precise properties required.

[0088] Synthetic oils include hydrocarbon oils such as olefin oligomers (PAOs), dibasic acid esters, polyol esters, and dewaxed waxy raffinate. Synthetic hydrocarbon base oils sold by the Shell Group under the designation "XHVI" (trade mark) may be conveniently used.

[0089] Preferably, the base oil is constituted from mineral oils and/or synthetic oils which contain more than 80% wt of saturates, preferably more than 90 % wt., as measured according to ASTM D2007.

[0090] It is further preferred that the base oil contains less than 1.0 wt. %, preferably less than 0.1 wt. % of sulphur, calculated as elemental sulphur and measured according to ASTM D2622, ASTM D4294, ASTM D4927 or ASTM D3120.

[0091] Preferably, the viscosity index of the base oil is more than 80, more preferably more than 120, as measured according to ASTM D2270.

[0092] The total amount of base oil incorporated in the lubricating composition of the present invention is preferably present in an amount in the range of from 60 to 92 wt. %, more preferably in an amount in the range of from 75 to 90 wt. % and most preferably in an amount in the range of from 75 to 88 wt. %, with respect to the total weight of the lubricating composition.

[0093] Preferably, the lubricating composition has a kinematic viscosity in the range of from 2 to 80 mm²/s at 100 °C, more preferably in the range of from 3 to 70 mm²/s, most preferably in the range of from 4 to 50 mm²/s.

[0094] As the lubricating composition may also be in the form of a grease, the base oil as contained in the lubricating composition may contain or be compounded with one or more thickeners such as metallic soaps, organic substances or inorganic substances, for example, lithium soaps, lithium complex soaps, sodium terephthalate, urea/urethane compounds and clays.

[0095] The lubricating composition of the present invention may further comprise additional additives such as antioxidants, dispersants, friction modifiers, viscosity index improvers, pour point depressants, corrosion inhibitors, defoaming agents and seal fix or seal compatibility agents.

[0096] Antioxidants that may be conveniently used include those selected from the group of aminic antioxidants and/or phenolic antioxidants.

[0097] In a preferred embodiment, said antioxidants are present in an amount in the range of from 0.1 to 5.0 wt. %, more preferably in an amount in the range of from 0.3 to 3.0 wt. %, and most preferably in an amount of in the range of from 0.5 to 1.5 wt. %, based on the total weight of the lubricating composition.

[0098] Examples of aminic antioxidants which may be conveniently used include alkylated diphenylamines, phenyl- α -naphthylamines, phenyl- β -naphthylamines and alkylated α -naphthylamines.

[0099] Preferred aminic antioxidants include dialkyldiphenylamines such as p,p'-dioctyl-diphenylamine, p,p'-di- α -methylbenzyl-diphenylamine and N-p-butylphenyl-N-p'-octylphenylamine, monoalkyldiphenylamines such as mono-t-butylidiphenylamine and mono-octyldiphenylamine, bis(dialkylphenyl)amines such as di-(2,4-diethylphenyl)amine and di(2-ethyl-4-nonylphenyl)amine, alkylphenyl-1-naphthylamines such as octylphenyl-1-naphthylamine and n-t-dodecylphenyl-1-naphthylamine, 1-naphthylamine, aryl-naphthylamines such as phenyl-1-naphthylamine, phenyl-2-naphthylamine, N-hexylphenyl-2-naphthylamine and N-octylphenyl-2-naphthylamine, phenylenediamines such as N,N'-diisopropyl-p-phenylenediamine and N,N'-diphenyl-p-phenylenediamine, and phenothiazines such as phenothiazine and 3,7-dioctylphenothiazine.

[0100] Preferred aminic antioxidants include those available under the following trade designations: "Sonoflex OD-3" (ex. Seiko Kagaku Co.), "Irganox L-57" (ex. Ciba Specialty Chemicals Co.) and phenothiazine (ex. Hodogaya Kagaku Co.).

[0101] Examples of phenolic antioxidants which may be conveniently used include C7-C9 branched alkyl esters of 3,5-bis(1,1-dimethyl-ethyl)-4-hydroxy-benzenepropanoic acid, 2-t-butylphenol, 2-t-butyl-4-methylphenol, 2-t-butyl-5-methylphenol, 2,4-di-t-butylphenol, 2,4-dimethyl-6-t-butylphenol, 2-t-butyl-4-methoxyphenol, 3-t-butyl-4-methoxyphenol, 2,5-di-t-butylhydroquinone, 2,6-di-t-butyl-4-alkylphenols such as 2,6-di-t-butylphenol, 2,6-di-t-butyl-4-methylphenol and 2,6-di-t-butyl-4-ethylphenol, 2,6-di-t-butyl-4-alkoxyphenols such as 2,6-di-t-butyl-4-methoxyphenol and 2,6-di-t-butyl-4-ethoxyphenol, 3,5-di-t-butyl-4-hydroxybenzylmercaptooctylacetate, alkyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionates such as n-octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, n-butyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate and 2'-ethylhexyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, 2,6-d-t-butyl- α -dimethylamino-p-cresol, 2,2'-methylene-bis(4-alkyl-6-t-butylphenol) such as 2,2'-methylenebis(4-methyl-6-t-butylphenol), and 2,2'-methylenebis(4-ethyl-6-t-butylphenol), bisphenols such as 4,4'-butylidenebis(3-methyl-6-t-butylphenol), 4,4'-methylenebis(2,6-di-t-butylphenol), 4,4'-bis(2,6-di-t-butylphenol), 2,2-(di-p-hydroxyphenyl)propane, 2,2-bis(3,5-di-t-butyl-4-hydroxyphenyl)propane, 4,4'-cyclohexylidenebis(2,6-t-butylphenol), hexamethyleneglycol-bis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], triethyleneglycolbis[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionate], 2,2'-thio-[diethyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], 3,9-bis{1,1-dimethyl-2-[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionyloxy]ethyl}2,4,8,10-

tetraoxaspiro[5,5]undecane, 4,4'-thiobis(3-methyl-6-t-butylphenol) and 2,2'-thiobis(4,6-di-t-butylresorcinol), polyphenols such as tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate]methane, 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene, bis-[3,3'-bis(4'-hydroxy-3'-t-butylphenyl)butyric acid]glycol ester, 2-(3',5'-di-t-butyl-4-hydroxyphenyl)methyl-4-(2'',4''-di-t-butyl-3''-hydroxyphenyl)methyl-6-t-butylphenol and 2,6-bis(2'-hydroxy-3'-t-butyl-5'-methylbenzyl)-4-methylphenol, and p-t-butylphenol - formaldehyde condensates and p-t-butylphenol - acetaldehyde condensates.

[0102] Preferred phenolic antioxidants include those available under the following trade designations: "Irganox L-135" (ex. Ciba Specialty Chemicals Co.), "Yoshinox SS" (ex. Yoshitomi Seiyaku Co.), "Antage W-400" (ex. Kawaguchi Kagaku Co.), "Antage W-500" (ex. Kawaguchi Kagaku Co.), "Antage W-300" (ex. Kawaguchi Kagaku Co.), "Irganox L-109" (ex. Ciba Specialty Chemicals Co.), "Tominox 917" (ex. Yoshitomi Seiyaku Co.), "Irganox L-115" (ex. Ciba Specialty Chemicals Co.), "Sumilizer GA80" (ex. Sumitomo Kagaku), "Antage RC" (ex. Kawaguchi Kagaku Co.), "Irganox L-101" (ex. Ciba Specialty Chemicals Co.), "Yoshinox 930" (ex. Yoshitomi Seiyaku Co.).

[0103] The lubricating composition of the present invention may comprise mixtures of one or more phenolic antioxidants with one or more aminic antioxidants.

[0104] The lubricating compositions of the present invention may additionally contain an ash-free dispersant which is preferably admixed in an amount in the range of from 5 to 15 wt. %, based on the total weight of the lubricating composition.

[0105] Examples of ash-free dispersants which may be used include the polyalkenyl succinimides and polyalkenyl succinic acid esters disclosed in Japanese Laid-Open Patent Application Nos. JP 53-050291 A, JP 56-120679 A, JP 53-056610 A and JP 58-171488 A. Preferred dispersants include borated succinimides.

[0106] Examples of viscosity index improver improvers which may conveniently be used in the lubricating composition of the present invention include the styrene-butadiene copolymers, styrene-isoprene stellate copolymers and the polymethacrylate copolymer and ethylene-propylene copolymers. Dispersant-viscosity index improvers may be used in the lubricating composition of the present invention.

[0107] Such viscosity index improver improvers may be conveniently employed in an amount in the range of from 1 to 20 wt. %, based on the total weight of the lubricating composition.

[0108] Polymethacrylates may be conveniently employed in the lubricating compositions of the present invention as effective pour point depressants.

[0109] Furthermore, compounds such as alkenyl succinic acid or ester moieties thereof, benzotriazole-based compounds and thiodiazole-based compounds may be conveniently used in the lubricating composition of the present invention as corrosion inhibitors.

[0110] Compounds such as polysiloxanes, dimethyl polycyclohexane and polyacrylates may be conveniently used in the lubricating composition of the present invention as defoaming agents.

[0111] Compounds which may be conveniently used in the lubricating composition of the present invention as seal fix or seal compatibility agents include, for example, commercially available aromatic esters.

[0112] The lubricating compositions of the present invention may be conveniently prepared by admixing the one or more poly(hydroxycarboxylic acid) amide salt derivatives and, optionally, one or more anti-wear additives, one or more detergents and further additives that are usually present in lubricating compositions, for example as herein before described, with mineral and/or synthetic base oil.

[0113] In another aspect the present invention provides a method of improving friction reduction and/or anti-wear properties, preferably in an internal combustion engine, which method comprises lubricating (preferably said internal combustion engine) with the lubricating composition according to the present invention.

[0114] Also the present invention provides the use of the lubricating composition according to the present invention in order to improve friction reduction and/or anti-wear properties, preferably in an internal combustion engine.

[0115] The person skilled in the art will readily understand that the lubricating composition may also be suitably used for other uses than in an internal combustion engine, where friction reduction and anti-wear properties play a role.

[0116] The present invention is described below with reference to the following Examples, which are not intended to limit the scope of the present invention in any way.

EXAMPLES

Lubricating oil compositions

[0117] Table 1 indicates the composition of the lubricating oil compositions that were tested; the amounts of the components are given in wt. %.

[0118] "ILSAC GF-4" specification lubricant and "API SG/CD" specification lubricant available from SOPS products and Shell Lubricants, respectively. "ILSAC GF-4" is a 5W30 engine oil, and "API SG/CD" a 15W40 engine oil.

[0119] Poly(hydroxycarboxylic acid) amide salt derivatives according to the present invention that were used in testing were products available commercially from Shanghai Sanzheng Polymer Company under the trade designations "CH-

5" and "CH-7".

[0120] "CH-5" and "CH-7" products both have a TBN value of approximately 1.9 mg.KOH, as measured by ASTM D 4739. Furthermore, "CH-5" product and "CH-7" product have sulphur contents of approximately 0.95 wt.% and 0.86 wt.%, respectively, as measured by ICP-AES.

[0121] A comparative product ("SOLSPERSE 11200") was tested which was a poly(hydroxycarboxylic acid) derivative that is not according to the teaching of the present invention. "SOLSPERSE 11200" is commercially available from Lubrizol under the trade designation "SOLSPERSE 11200". "SOLSPERSE 11200" product has a TBN value of approximately 35 mg.KOH/g, as measured by ASTM D 4739 and a sulphur content of < 0.01 wt. %, as measured by ICP-AES.

TABLE 1

Component (wt. %)	Example 1	Example 2	Example 3	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
"ILSAC GF-4" lubricant	99.5	99.5	-	100	-	-	-
"API SG/CD" lubricant	-	-	97.0	-	100	97.0	97.0
"CH-5" additive	0.5	-	-	-	-	-	-
"CH-7" additive	-	0.5	3.0	-	-	-	-
"SOLSPERSE 11200" additive	-	-	-	-	-	3.0	-
"SAP 230" additive	-	-	-	-	-	-	3.0
TOTAL	100	100	100	100	100	100	100

Cameron-Plint test

[0122] In order to demonstrate the improved friction properties of the present invention, friction coefficient measurements were made on a Cameron-Plint TE77 rig with a pin-on-plate geometry (available from Phoenix Tribology Ltd, Newbury, England).

[0123] The test methodology used is described in amongst others H. Ji et al., "Zinc-dialkyl-dithiophosphate antiwear films: dependence on contact pressure and sliding speed", Wear 258 (2005) 789-799; and G. Pereira et al., "A variable temperature mechanical analysis of ZDDP-derived antiwear films formed on 52100 steel", Wear 262 (2007) 461-470.

[0124] In the test, the boundary friction properties of the composition of Examples 1 and 2 and Comparative Example 1 (see Table 1) were tested using the Cameron-Plint TE77 high frequency friction machine in a pin-on-plate test mode. The cylindrical side of the pin was in contact with a ground hardened steel plate (ground parallel to direction of pin travel). A 15 minute friction test was performed, friction coefficient measurements were averaged over the last 10 minutes of test time.

[0125] The following test conditions were used:

- Temperature: 135 °C;
- Load: 100 N
- Speed: 15 Hz
- Stroke length: 1.5 cm;
- Pin: 52100 steel 6x16 mm (TE77/L);
- Plate: annealed ground gauge (TE77/F3).

[0126] The measured friction coefficients are indicated in Table 2 below.

TABLE 2

	Friction coefficient	Percent reduction
Example 1	0.1076	9.4
Example 2	0.1037	12.7
Comp. Ex. 1	0.1188	-

[0127] As can be learned from Table 2, the friction coefficients for Examples 1 and 2 were significantly reduced when compared with Comparative Example 1.

[0128] As all compositions contained the same engine oil "ILSAC GF-4" (see Table 1) this indicates thus that the use of the poly(hydroxycarboxylic acid) amide salt derivatives according to the present invention in a lubricant composition will result in a significant friction reduction.

Rolling and Sliding Environment Controlled Rig No. 1 (RASER1) test

[0129] In order to demonstrate the improved anti-wear properties of the present invention, RASER1 friction and wear measurements were made using a Cameron Flint TE77 reciprocating wear and friction test machine (available from Phoenix Tribology Ltd, Newbury, England) modified to produce a contact between one reciprocating component and a rotating component, similar to a Reciprocating Amsler machine (as described in e.g. SAE paper 952473 of October 1995).

[0130] A difference between the RASER1 and the Reciprocating Amsler rig concerns the contact geometry. The Reciprocating Amsler rig involves a line-contact between the contacting components, whilst for the RASER1, however, the block specimen representing the cam follower is barrelled in the direction orthogonal to the direction of motion, so that the contact geometry is elliptical. This enables a higher contact pressure to be produced from a given applied load. Nevertheless, the contact conditions of the test are still based around those of the pivoted valve-train systems used as the basis of the Reciprocating Amsler rig.

[0131] The test specimens as used in the RASER1 test were both made of hardened steel, with the disc specimen having the greater hardness and roughness, so that most wear occurred on the block specimen. During testing, the rotating and reciprocating components were operated in loaded contact with each other, while partially immersed in a temperature-controlled oil bath. The maximum Hertzian pressure of the contact was 0.64 GPa. The surface velocity of the disc was 1.1 m.s⁻¹, while the block motion varied sinusoidally with an amplitude of 0.47 m.s⁻¹. The test involved two temperature stages, firstly at 40°C oil temperature for 2 hours, then at 100°C oil temperature for a further 2 hours. The humidity was maintained at a dew-point of 25°C during the low temperature stage; it was not controlled during the high temperature stage. The conditions are also indicated in Table 3 below.

[0132] Friction and electrical contact resistance were measured continuously during the test, of which the latter permitted monitoring of the rate of formation and integrity of anti-wear films. Since the test involved an elliptical contact between one rotating and one reciprocating component, the resulting wear-scar grew with time and so a measurement of wear-scar width provided an indication of the amount of wear that had occurred. The contact conditions were more severe at the ends of the reciprocating motion than in the centre, which generally resulted in more wear at the ends.

TABLE 3

	Stage 1	Stage 2
Stroke length [mm]	15 (i.e. +/- 7.5)	15 (i.e. +/- 7.5)
Load [N]	100	100
Speed [Hz] ([rpm])	10 (600)	10 (600)
Bulk oil temperature [°C]	40	100
Duration [h]	2	2
Humidity	Dew-point at 25 °C	Not controlled

[0133] The RASER1 friction results for the compositions of Example 3 and Comparative Examples 2-4 (all containing the same "API SG/CD" engine oil) are shown in Table 4.

TABLE 4

	Example 3	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
Friction coefficient (after stage 2)	0.083	0.095	0.090	0.105
Friction reduction [%]	12.6	-	5.2	-10.5 (increase)
Wear (average end stroke) [mm]	1.21	1.45	1.45	1.33
Wear reduction [%]	16.6	-	-	8.3
Wear (mid stroke) [mm]	0.87	0.97	0.99	0.87
Wear reduction [%]	10.3	-	-2.1 (increase)	10.3

[0134] As can be learned from Table 4, the friction coefficient and wear for Example 3 were significantly reduced when compared with Comparative Example 2 (only containing the engine oil).

[0135] Although the friction coefficient in the case of Comparative Example 3 (using "SOLSPERSE 11200") was also reduced compared with Comparative Example 2 (but in a far lesser extent than in the case of Example 3), Comparative Example 3 resulted in a neutral (end stroke) or negative (mid stroke) wear effect.

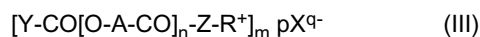
[0136] On the other hand, Comparative Example 4 ("SAP 230") resulted in some wear reduction, but showed an increase in friction when compared with Comparative Example 2.

[0137] The above test results thus surprisingly show that the use of the poly(hydroxycarboxylic acid) amide salt derivatives according to the present invention in a lubricant composition result at the same time in a significant friction and wear reduction.

Claims

1. A lubricating composition comprising:

- a base oil; and
- one or more poly(hydroxycarboxylic acid) amide salt derivatives having formula (III):



wherein Y is hydrogen or an optionally substituted hydrocarbyl group, A is a divalent optionally substituted hydrocarbyl group, n is from 1 to 100, preferably from 1 to 10, m is from 1 to 4, q is from 1 to 4 and p is an integer such that pq = m, Z is an optionally substituted divalent bridging group which is attached to the carbonyl group through a nitrogen atom, R⁺ is an ammonium group and X^{q-} is an anion.

2. Lubricating composition according to claim 1 wherein the anion is selected from sulphate and sulphonate anions.

3. Lubricating composition according to claim 1 or 2, wherein the one or more poly(hydroxycarboxylic acid) amide salt derivatives are present in an amount in the range of from 0.1 to 10.0 wt. %, based on the total weight of the lubricating composition.

4. Lubricating composition according to any one of claims 1 to 3, further comprising one or more anti-wear additives.

5. Lubricating composition according to any one of claims 1 to 4, further comprising one or more detergents selected from alkali metal or alkaline earth metal salicylate, phenate or sulphonate detergents.

6. Lubricating composition according to any one of claims 1 to 5, wherein one or more of the poly(hydroxycarboxylic acid) amide salt derivatives have a TBN (total base number) value of less than 10 mg.KOH/g.

7. Lubricating composition according to any one of claims 1 to 6, wherein one or more of the poly(hydroxycarboxylic acid) amide salt derivatives have a sulphur content in the range of from 0.1 to 2.0 wt. %, based on the total weight of said poly(hydroxycarboxylic acid) amide salt derivatives.

8. Lubricating composition according to any one of claims 1 to 6, wherein it is in the form of a grease and comprises

one or more thickeners.

5 9. A method of improving friction reduction properties, preferably in an internal combustion engine, which method comprises lubricating with a lubricating composition as described in any one of Claims 1 to 8.

10 10. Use of a lubricating composition according to any one of claims 1 to 8 in order to improve friction reduction properties, preferably in an internal combustion engine.

11. A method of improving anti-wear properties, preferably in an internal combustion engine, which method comprises lubricating with a lubricating composition as described in any one of Claims 1 to 8.

12. A method according to claim 11, wherein the friction reduction properties are improved at the same time.

15 13. Use of a lubricating composition according to any one of claims 1 to 8 in order to improve anti-wear properties, preferably in an internal combustion engine.

14. Use according to claim 12 wherein the friction reduction properties are improved at the same time.

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EUROPEAN SEARCH REPORT

Application Number
EP 07 11 9030

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X,E	WO 2007/128740 A (SHELL INT RESEARCH [NL]; NELSON DAVID CHARLES [GB]; SOUTHBY MARK CLIFT) 15 November 2007 (2007-11-15) * claims 1-11 *	1-14	INV. C08G63/685 C08G63/06 C10M141/06 C10M141/10 C10M161/00 C10M163/00
X	WO 2006/054045 A (ICI PLC [GB]; OLDFIELD ANDREW SIMON [GB]; IRVINE DEREK JOHN [GB]) 26 May 2006 (2006-05-26) * page 4, line 21 - page 5, line 5; figures 1,2; example 1; tables 3,4 * * page 6, line 8 - line 15 *	1-14	
Y,D	EP 0 736 070 A (ZENECA LTD [GB]) 9 October 1996 (1996-10-09) * paragraphs [0012], [0030], [0060], [0061]; claim 3 *	1,2,7	
Y	WO 2006/047745 A (LUBRIZOL CORP [US]; WILKES MARK F [GB]; DAVIES MARK C [GB]) 4 May 2006 (2006-05-04) * paragraphs [0010] - [0013]; examples *	1-14	
Y	WO 00/34418 A (INFINEUM HOLDINGS B V [NL]) 15 June 2000 (2000-06-15) * page 7, line 14 - page 10, line 8; claims 1-8 *	1-14	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (IPC) C10M C08G
Place of search Munich		Date of completion of the search 10 January 2008	Examiner Pöllmann, Klaus
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 07 11 9030

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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10-01-2008

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 2007128740	A	15-11-2007	NONE	

WO 2006054045	A	26-05-2006	EP 1812539 A1	01-08-2007
			KR 20070084350 A	24-08-2007

EP 0736070	A	09-10-1996	AT 176918 T	15-03-1999
			AU 680084 B2	17-07-1997
			AU 1277695 A	10-07-1995
			BR 9408366 A	26-08-1997
			CA 2179749 A1	29-06-1995
			DE 69416695 D1	01-04-1999
			DE 69416695 T2	08-07-1999
			DK 736070 T3	23-08-1999
			ES 2128036 T3	01-05-1999
			WO 9517473 A1	29-06-1995
			IN 190998 A1	06-09-2003
			JP 9506922 T	08-07-1997
			US 5753022 A	19-05-1998

WO 2006047745	A	04-05-2006	CA 2584787 A1	04-05-2006
			EP 1807480 A1	18-07-2007

WO 0034418	A	15-06-2000	AU 1973900 A	26-06-2000
			JP 2002531684 T	24-09-2002
			US 6458173 B1	01-10-2002

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- EP 0194718 A [0003]
- EP 0164817 A [0034] [0060]
- WO 9517473 A [0034] [0058]
- WO 9607689 A [0034]
- US 5536445 A [0034]
- GB 2001083 A [0034] [0056]
- GB 1342746 A [0034] [0035]
- GB 1373660 A [0034] [0035] [0055] [0066]
- US 5000792 A [0034] [0057]
- US 4349389 A [0034] [0059] [0066]
- US 3996059 A [0035] [0066]
- WO 9741092 A [0048]
- US 3275554 A [0049]
- US 3438757 A [0049]
- US 3454555 A [0049]
- US 3565804 A [0049]
- US 3755433 A [0049]
- US 3822209 A [0050]
- EP 0776959 A [0086]
- EP 0668342 A [0086]
- WO 9721788 A [0086]
- WO 0015736 A [0086]
- WO 0014188 A [0086]
- WO 0014187 A [0086]
- WO 0014183 A [0086]
- WO 0014179 A [0086]
- WO 0008115 A [0086]
- WO 9941332 A [0086]
- EP 1029029 A [0086]
- WO 0118156 A [0086]
- WO 0157166 A [0086]
- JP 53050291 A [0105]
- JP 56120679 A [0105]
- JP 53056610 A [0105]
- JP 58171488 A [0105]

Non-patent literature cited in the description

- **H. JI et al.** Zinc-dialkyl-dithiophosphate antiwear films: dependence on contact pressure and sliding speed. *Wear*, 2005, vol. 258, 789-799 [0123]
- **G. PEREIRA et al.** A variable temperature mechanical analysis of ZDDP-derived antiwear films formed on 52100 steel. *Wear*, 2007, vol. 262, 461-470 [0123]