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(54) **LUBRICATING COMPOSITION COMPRISING POLY(HYDROXYCARBOXYLIC ACID) AMIDE AND DETERGENT**

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(57) **ABSTRACT**

The present invention provides a lubricating composition comprising: a base oil; one or more poly (hydroxycarboxylic acid) amide salt derivatives having Formula (III): $[Y—CO[O\text{-}A\text{-}CO]_n—Z—R^+]m\ pX^{q-}$ 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; and one or more detergents; wherein the soap concentration as provided by a detergent selected from the group of sulphonate and salicylate detergents is less than 3.75 mmol soap per wt. % of the one or more poly (hydroxycarboxylic acid) amide salt derivatives having Formula (III).

LUBRICATING COMPOSITION COMPRISING POLY(HYDROXYCARBOXYLIC ACID) AMIDE AND DETERGENT

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

[0002] WO 2007/128740 discloses a lubricating composition containing poly(hydroxycarboxylic acid) amide salts derivatives in order to reduce deposits in an internal combustion engine. On page 16, line 25-page 17, line 5 of WO 2007/128740 it is disclosed that the lubricating composition may comprise one or more detergents, in particular one or more salicylate-, phenate- or sulphonate-type detergents. In the Examples of WO 2007/128740 a conventional additive package is used, containing sulphonate and phenate detergents having TBNs (TBN=total base number) in the range of from 30 to 350 mg·KOH/g, PIB succinimide dispersant, zinc dithiophosphate and diluent oil.

[0003] It has now surprisingly been found according to the present invention that there is a benefit in using phenate-type detergents rather than sulphonate or salicylate-type detergents in the reduction of deposits such as sludge and varnish.

[0004] Accordingly, the present invention provides lubricating composition comprising:

[0005] a base oil;

[0006] one or more poly(hydroxycarboxylic acid) amide salt derivatives having formula (III):

$$[Y\text{—}CO[O\text{-}A\text{-}CO]_n\text{—}Z\text{—}R^+]_m pX^{q-} \qquad \text{(III)}$$

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; and

[0007] one or more detergents;

wherein the soap concentration as provided by a detergent selected from the group of sulphonate and salicylate detergents or a mixture thereof is less than 3.75 mmol soap per wt. % of the one or more poly(hydroxycarboxylic acid) amide salt derivatives having formula (III), preferably less than 3.0 mmol soap, more preferably less than 2.5 mmol soap, even more preferably less than 2.0 mmol soap, most preferably less than 1.0 mmol soap.

[0008] In formula (III) R^+ may be a primary, secondary, tertiary or quaternary ammonium group. R^+ is preferably a quaternary ammonium group.

[0009] In formula (III), A is preferably a divalent straight chain or branched hydrocarbyl group as hereafter described for formulae (I) and (II).

[0010] 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.

[0011] 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.

[0012] 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.

[0013] In formula (III), Y is preferably an optionally substituted hydrocarbyl group as hereinafter described for formula (I).

[0014] 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.

[0015] 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, stibenzyl and phenylmethylphenyl.

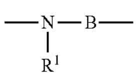
[0016] In the present invention, the optionally substituted hydrocarbyl group Y in formula (III) may contain one or more functional groups such as carbonyl, carboxyl, nitro, hydroxy, halo, alkoxy, amino, preferably tertiary amino (no N—H linkages), oxy, cyano, sulphonyl and sulphoxyl. The majority of 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.

[0017] 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 sulphoxyl in a substituted hydrocarbyl group will displace a —CH— or —CH_2— moiety of the hydrocarbyl.

[0018] 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 alkoxy.

[0019] Most preferably, the optionally substituted hydrocarbyl group Y in formula (III) is a stearyl group, 12-hydroxystearyl group, an oleyl group or a 12-hydroxyoleyl group, and that derived from naturally occurring oil such as tall oil fatty acid.

[0020] In formula (III), Z is preferably an optionally substituted divalent bridging group represented by formula (IV)



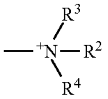
$$\text{—}\underset{\displaystyle R^1}{\underset{|}{N}}\text{—}B\text{—} \qquad \text{(IV)}$$

wherein R^1 is hydrogen or a hydrocarbyl group and B is an optionally substituted alkylene group.

[0021] Examples of hydrocarbyl groups that may represent R^1 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.

[0022] Examples of preferred Z moieties in formula (III) include —$NHCH_2CH_2$—, —$NHCH_2C(CH_3)_2CH_2$— and —$NH(CH_2)_3$—. Preferably, R^+ may be represented by formula (V)



$$—{}^{+}N(R^2)(R^3)(R^4) \quad (V)$$

wherein R^2, R^3 and R^4 may be selected from hydrogen and alkyl groups such as methyl.

[0023] 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.

[0024] 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)

$$Y—CO[O\text{-}A\text{-}CO]_n—OH \qquad (I)$$

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.

[0025] 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).

[0026] 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.

[0027] 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.

[0028] 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.

[0029] 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.

[0030] Other examples of said optionally substituted hydrocarbyl group Y in formula (I) 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, stibenzyl and phenylmethylphenyl.

[0031] 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 sulphoxyl. 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.

[0032] 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 sulphoxyl in a substituted hydrocarbyl group will displace a —CH— or —CH_2— moiety of the hydrocarbyl.

[0033] 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 C_{1-4} alkoxy.

[0034] 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.

[0035] 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.

[0036] 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.

[0037] 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, U.S. Pat. No. 5,536,445, GB 2 001 083, GB 1 342 746, GB 1 373 660, U.S. Pat. No. 5,000,792 and U.S. Pat. No. 4,349,389.

[0038] The preparation of the poly(hydroxycarboxylic acid)s of formula (I) may be made by the interesterification of one or more hydroxycarboxylic acids of formula (II)

$$HO\text{-}A\text{-}COOH \qquad (II)$$

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 U.S. Pat. No. 3,996,059, GB 1 373 660 and GB 1 342 746.

[0039] The chain terminator in said interesterification may be a non-hydroxycarboxylic acid.

[0040] 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.

[0041] 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.

[0042] The reaction may be carried out at a temperature up to –250° C., conveniently at the reflux temperature of the solvent.

[0043] 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.

[0044] 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.

[0045] 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.

[0046] 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.

[0047] 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 C_{1-4} alkoxy groups.

[0048] The hydroxyl group in the hydroxycarboxylic acids of formula (II) is preferably a secondary hydroxyl group.

[0049] 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.

[0050] 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.

[0051] The group (—O-A-CO—) in the compounds of formulae (I) and (II) is preferably a 12-oxystearyl group, 12-oxyoleyl group or a 6-oxycaproyl group.

[0052] Preferred poly(hydroxycarboxylic acid)s of formula (I) for reaction with amine include poly(hydroxystearic acid) and poly(hydroxyoleic acid).

[0053] 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.

[0054] For example, various amines and their preparations are described in U.S. Pat. No. 3,275,554, U.S. Pat. No. 3,438,757, U.S. Pat. No. 3,454,555, U.S. Pat. No. 3,565,804, U.S. Pat. No. 3,755,433 and U.S. Pat. No. 3,822,209.

[0055] The amine reactant is preferably a diamine, a triamine or a polyamine.

[0056] Preferred amine reactants are diamines selected from ethylenediamine, N,N-dimethyl-1,3-propanediamine, triamines and polyamines selected from dietheylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine and tris(2-aminoethyl)amine.

[0057] 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.

[0058] The poly(hydroxycarboxylic acid) amide intermediate formed from reaction of the amine and the poly(hydroxycarboxylic acid) of formula (I) may be reacted with an acid or a quaternizing agent to form a salt derivative, according to well-known methods.

[0059] 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.

[0060] 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.

[0061] 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.

[0062] Quaternization is a well-known method in the art. For example, quaternization using dimethyl sulphate is described in U.S. Pat. No. 3,996,059, U.S. Pat. No. 4,349,389 and GB 1 373 660.

[0063] 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. %, based on the total weight of the lubricating composition. According to an especially preferred embodiment of the present invention, the composition comprises less than 2.5 wt. %, preferably less than 2.0 wt. %, more preferably less than 1.5 wt. %, even more preferably less than 1.2 wt. % of the one or more poly(hydroxycarboxylic acid) amide salt derivatives, based on the total weight of the lubricant composition.

[0064] 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.

[0065] Examples of poly(hydroxycarboxylic acid) amide salt derivatives that are available commercially include that available from Lubrizol under the trade designation "SOLSPERSE 17000" (a reaction product of poly(12-hydroxystearic acid) with N,N-dimethyl-1,3-propanediamine and dimethyl sulphate) and those available under the trade designations "CH-5" and "CH-7" from Shanghai Sanzheng Polymer Company.

[0066] Typically, the lubricating composition comprises one or more detergents such as one or more of salicylate, phenate or sulphonate detergents. The one or more salicylate, phenate or sulphonate detergents are preferably selected from alkali metal or alkaline earth metal salicylate, phenate or sulphonate detergents. Calcium and magnesium salicylates, phenates and sulphonates are particularly preferred.

[0067] The total amount of detergents as used in the composition is preferably in the range of 0.05 to 12.5 wt. %, more preferably from 0.5 to 9.0 wt. % and most preferably in the range of from 0.8 to 5.0 wt. %, based on the total weight of the lubricating composition.

[0068] According to the present invention, the lubricating composition comprises less than 1.5 wt. %, preferably less than 1.0 wt. %, more preferably less than 0.5 wt % of a detergent selected from the group of sulphonate and salicylate detergents, based on the total weight of the composition. It is even more preferred that less than 0.2 wt. %, or even less than 0.1 wt. % of a detergent selected from the group of sulphonate and salicylate detergents is present.

[0069] Preferably the combined amount of sulphonate and salicylate detergents is also less than the above indicated amounts.

[0070] Preferably, the detergent comprises no detergent selected from the group of sulphonate and salicylate detergents. It is even more preferred that the detergent(s) consists of one or more phenate detergents.

[0071] Examples of commercially available phenate detergents are obtainable from Oronite under the trade designation "OLOA® 219C", from Lubrizol under the trade designation "LZ6503" and from Infineum under the trade designation "M7152".

[0072] Furthermore, the lubricating composition according to the present invention typically comprises one or more anti-wear additives. The one or more anti-wear additives are preferably present in an amount in the range of from 0.01 to 10.0 wt. %, based on the total weight of the lubricating composition.

[0073] 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.

[0074] For preferred zinc dithiophosphates reference is made to page 15, line 19-page 16, line 17 of WO 2007/128740, the teaching of which is incorporated by specific reference.

[0075] The lubricating composition according to the present invention preferably comprises in the range of from 0.01 to 10.0 wt. % of zinc dithiophosphates, based on total weight of the lubricating composition.

[0076] Additional or alternative anti-wear additives may be conveniently used in the lubricating composition of the present invention.

[0077] There are no particular limitations regarding the base oil used in the present invention, and various conventional known mineral oils and synthetic oils may be conveniently used.

[0078] The base oil used in the present invention may conveniently comprise mixtures of one or more mineral oils and/or one or more synthetic oils.

[0079] Mineral oils include liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oil of the paraffinic, naphthenic, or mixed paraffinic/naphthenic type which may be further refined by hydrofinishing processes and/or dewaxing.

[0080] Naphthenic base oils have low viscosity index (VI) (generally 40-80) and a low pour point. Such base oils are produced from feedstocks rich in naphthenes and low in wax content and are used mainly for lubricants in which colour and colour stability are important, and VI and oxidation stability are of secondary importance.

[0081] Paraffinic base oils have higher VI (generally >95) and a high pour point. Said base oils are produced from feedstocks rich in paraffins, and are used for lubricants in which VI and oxidation stability are important.

[0082] 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.

[0083] Synthetic processes enable molecules to be built from simpler substances or to have their structures modified to give the precise properties required.

[0084] 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.

[0085] 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.

[0086] 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.

[0087] Preferably, the viscosity index of the base oil is more than 80, more preferably more than 120, as measured according to ASTM D2270.

[0088] 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.

[0089] Preferably, the lubricating composition has a kinematic viscosity in the range of from 2 to 80 mm^2/s at 100° C., more preferably in the range of from 3 to 70 mm^2/s, most preferably in the range of from 4 to 50 mm^2/s.

[0090] 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.

[0091] 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.

[0092] Antioxidants that may be conveniently used include those selected from the group of aminic antioxidants and/or phenolic antioxidants.

[0093] 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.

[0094] For examples of suitable or preferred aminic and phenolic antioxidants, reference is made to page 19, line 18-page 21, line 32 of WO 2007/128740, the teaching of which is hereby incorporated by specific reference.

[0095] 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.

[0096] Examples of ash-free dispersants which may be used include the polyalkenyl succinimides and polyalkenyl succininic 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.

[0097] Examples of viscosity index 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.

[0098] Such viscosity index 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.

[0099] Polymethacrylates may be conveniently employed in the lubricating compositions of the present invention as effective pour point depressants.

[0100] 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.

[0101] Compounds such as polysiloxanes, dimethyl polycyclohexane and polyacrylates may be conveniently used in the lubricating composition of the present invention as defoaming agents.

[0102] 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.

[0103] 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.

[0104] In another aspect the present invention provides a method of improving the reduction of deposits in an internal combustion engine, which method comprises lubricating with a lubricating composition according to the invention.

[0105] Further, the present invention provides the use of a lubricating composition for improving the reduction of deposits in an internal combustion engine, in particular when compared with similar compositions containing sulphonate or salicylate detergents instead of phenate detergents.

[0106] 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, especially where the reduction of deposits plays a role.

[0107] 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

[0108] Table 1 indicates the composition of the lubricating oil compositions that were tested; the amounts of the components are given in wt. %, based on the total weight of the fully formulated formulations.

[0109] The lubricating oil compositions were formulated such that a concentration of 7.5 mmoles of soap was obtained, whilst using commercially available detergents having TBNs in the range of from 30 to 350 mg·KOH/g. In this respect it is noted that the person skilled in the art will readily understand that the actual detergent treat rate may depend on the detergents used, i.e. the actual amount of detergent needed in order to achieve the same soap concentration may vary from one detergent to another.

[0110] The person skilled in the art of lubricant formulation readily knows how to achieve such a soap concentration; as acknowledged in e.g. paragraphs [0151] and [0152] of US 2003/0096716 A1, suitable methods for determining the soap concentration include potentiometric acid titration of the metal salts associated with organic acids. In the case of metal sulphonate ASTM D3712 may be used to determine the metal associated with the sulphonate. Also, paragraph [0060] of EP 1 728 848 A1 mentions the incorporation of a salicylate detergent in an amount introducing a certain amount of salicylate soap in the final composition. From the above it can be appreciated that the person skilled in the art of lubricant formulation readily knows how to achieve such a soap concentration.

[0111] Examples of commercially available phenate detergents are obtainable from e.g. Oronite under the trade designation "OLOA® 219C", from Lubrizol under the trade designation "LZ6503" and from Infineum under the trade designation "M7152".

Examples of commercially available sulphonate detergents are obtainable from e.g. Oronite under the trade designation "OLOA® 246S" and from Lubrizol under the trade designation "LZ6477".

[0112] Examples of commercially available salicylate detergents are obtainable from e.g. Infineum under the trade designation "M7101" and "M7125".

[0113] The "base oil" as used in the examples was a commercially available API Group I base oil. By "Group I" base oil is meant a Group I base oil according to the definitions of American Petroleum Institute (API). Such API categories are defined in API Publication 1509, 15th Edition, Appendix E, April 2002.

[0114] As the poly(hydroxycarboxylic acid) amide salt derivative a product available commercially from Shanghai Sanzheng Polymer Company under the trade designation "CH-5" was used. "CH-5" product has a TBN value of approximately 2.0 mg·KOH/g, as measured by ASTM D 4739. Furthermore, "CH-5" product has a sulphur content of approximately 0.86 wt. %, as measured by ICP-AES.

[0115] The compositions of the Examples and Comparative Examples were obtained by simply mixing the base oil, the poly(hydroxycarboxylic acid) amide salt derivative, and the detergent, using a laboratory paddle mixer.

TABLE 1

Component [wt. %]	Ex. 1	Ex. 2	Ex. 3	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6
"CH-5" product	1.0	1.5	2.0	1.0	1.5	2.0	1.0	1.5	2.0
Phenate-type detergent	1.0	1.0	1.0	—	—	—	—	—	—
Salicylate-type detergent	—	—	—	1.5	1.5	1.5	—	—	—
Sulphonate-type detergent	—	—	—	—	—	—	1.87	1.87	1.87
API Group I Base Oil	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder
TOTAL	100	100	100	100	100	100	100	100	100
Soap concentration [mmol]	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5
Soap concentration per wt. % CH-5 provided by a sulphonate/ salicylate detergent [mmol]	0	0	0	7.5	5.0	3.8	7.5	5.0	3.8

Bench Screener Test

[0116] The same bench screener test as disclosed on page 28, line 11-page 29, line 4 of WO 2007/128740 (except for numerical ratings) was used in order to demonstrate deposit control specifically in relation to the ability of a lubricant to "clean-up" real engine sludge rather than just "keep clean".

1. A cam-baffle was obtained from a VG engine after running the dirty-up phase of the modified Sequence VG test as described above.
2. 1 cm×1 cm samples were cut from the cam-baffle, using a lever-press to avoid contamination with cutting fluid.
3. Cam-baffle samples were dipped in lubricating oil compositions to be tested and allowed to drain before initial cleanliness ratings for sludge and varnish were made and photographs were taken for each sample.
4. Cam-baffle samples were then suspended in the lubricating oil compositions to be tested (100 g). The lubricating oil compositions were then stirred and maintained at 80° C. for a period of up to 14 days.
5. Cleanliness ratings and photographs were taken at intermediate time-intervals to assess the performance of the lubricating oil compositions tested.

[0117] A rating "clean" means that the sample was completely clean with no sludge or varnish thereon, whilst a rating "not clean" means that the sample contained clearly visible sludge and varnish thereon. The ratings are given in Table 2.

TABLE 2

Example	Amount of "CH-5" product [wt. %]	Rating
Example 1	1.0	Clean
Example 2	1.5	Clean
Example 3	2.0	Clean
Comp. Ex. 1	1.0	Not clean
Comp. Ex. 2	1.5	Not clean
Comp. Ex. 3	2.0	Clean
Comp. Ex. 4	1.0	Not clean
Comp. Ex. 5	1.5	Not clean
Comp. Ex. 6	2.0	Clean

Discussion

[0118] As is clearly shown in the Table 2, there is a benefit in using phenate-type detergents, rather than salicylate- or sulphonate-type detergents. In this respect it is noted that, although Comparative Examples 1, 2, 4 and 5 received a rating "not clean", they performed significantly better when compared with compositions not containing the poly(hydroxycarboxylic acid) amide salt derivative.

[0119] Although Examples 3 and Comparative Examples 3 and 6 show that an amount of 2.0 wt. % of the poly(hydroxycarboxylic acid) amide salt derivative in the presence of 7.5 mmols soap as provided by the phenate, sulphonate or salicylate detergent give a desirable "clean" rating, it has been found according to the present invention that the phenate detergent is more effective to provide cleansing than the sulphonate or salicylate detergent.

[0120] Examples 1 and 2 according to the present invention (using a phenate detergent) also give a "clean" rating at lower amounts of the poly(hydroxycarboxylic acid) amide salt derivative used, whilst this is not the case when using sulphonate or salicylate detergents.

[0121] Thus, it has surprisingly been found according to the present invention that substantially less of the (relatively expensive) poly(hydroxycarboxylic acid) amide salt derivative is needed to provide cleansing in the presence of phenate-type detergents when compared to salicylate- and sulphonate-type detergents at the same soap concentration as provided by the detergent(s).

[0122] To this end the present invention suggests that the soap concentration in the lubricating composition as provided by a detergent selected from the group of sulphonate and salicylate detergents or a mixture thereof is less than 5.0 mmol soap per wt. % of the one or more poly(hydroxycarboxylic acid) amide salt derivatives, preferably less than 4.5 mmol soap, less than 4.0, less than 3.5, less than 3.0, less than 2.5, less than 2.0, less than 1.5, less than 1.0 mmol soap, most preferably less than 0.5 mmol soap.

1. A lubricating composition comprising:

a base oil;

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

$$[Y—CO[O\text{-}A\text{-}CO]_n—Z—R^+]_m pX^{q-} \quad (III)$$

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; and

one or more detergents;

wherein the soap concentration as provided by a detergent selected from the group of sulphonate and salicylate detergents or a mixture thereof is less than 3.75 mmol soap per wt. % of the one or more poly(hydroxycarboxylic acid) amide salt derivatives having formula (III), preferably less than 3.0 mmol soap, more preferably less than 2.5 mmol soap, even more preferably less than 2.0 mmol soap, most preferably less than 1.0 mmol soap.

2. The lubricating composition according to claim **1**, wherein the one or more detergents comprise no detergent selected from the group of sulphonate and salicylate detergents.

3. The lubricating composition according to claim **1** wherein the one or more detergents consist of one or more phenate detergents.

4. The lubricating composition according to claim **1** 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.

5. The lubricating composition according to claim **1**, wherein the composition comprises less than 2.5 wt. %, preferably less than 2.0 wt. %, more preferably less than 1.5 wt. %, even more preferably less than 1.2 wt. % of the one or more poly(hydroxycarboxylic acid) amide salt derivatives having formula (III), based on the total weight of the lubricant composition.

6. (canceled)

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