



(43) International Publication Date
27 December 2012 (27.12.2012)

(10) International Publication Number
WO 2012/177537 A1

- (51) International Patent Classification:
C10M 133/06 (2006.01) *C10M 149/14* (2006.01)
- (21) International Application Number:
PCT/US2012/042882
- (22) International Filing Date:
18 June 2012 (18.06.2012)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
61/499,333 21 June 2011 (21.06.2011) US
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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))

Published:

— with international search report (Art. 21(3))

(54) Title: LUBRICATING COMPOSITION CONTAINING A DISPERSANT

(57) Abstract: The invention provides a lubricating composition containing a lubricating composition comprising an oil of lubricating viscosity and a quaternised polyester salt. The invention further relates to a method of lubricating a mechanical device (such as an internal combustion engine) with the lubricating composition. The invention further relates to the use of the quaternised polyester salt as a dispersant.



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TITLE

Lubricating Composition Containing a Dispersant

FIELD OF INVENTION

5 [0001] The invention provides a lubricating composition containing a lubricating composition comprising an oil of lubricating viscosity and a quaternised polyester salt. The invention further relates to a method of lubricating a mechanical device (such as an internal combustion engine) with the lubricating composition. The invention further relates to the use of the quaternised polyester salt as a dispersant.

BACKGROUND OF THE INVENTION

[0002] In order to reduce deposit formation, detergents and dispersants are known to assist in maintaining reduced amounts of deposits on engine components. The lubricant industry has a number of tests used to evaluate a lubricant's ability to handle deposits and sludge including the Sequence VG, Sequence IIIG, TDi, Cat 1N, and OM501LA.

[0003] With recent changes to engine specifications there is an increasing demand on the lubricant to reduce deposits. For instance, the new ILSAC GF-5 specification will require a 4.0 piston merit rating in the Sequence IIIG (vs. 3.5 for GF-4).

[0004] International Application WO2007/128740 (published 15 November, 2007) discloses the use of one or more poly (hydroxycarboxylic acid) amide salt in combination with one or more antiwear additive. Such compositions were useful for dispersing preformed sludge deposits.

[0005] International Application WO2009/053413 (published 30 April 2009) and European Patent Application EP2055729 (published 6 May 2009) both disclose compositions comprising base oil and one or more poly (hydroxycarboxylic acid) amide salt derivatives. The lubricating oils were useful for reducing wear and friction.

[0006] International Application WO2009/156393 (published 30 December 2009) discloses a lubricant with one or more poly (hydroxycarboxylic acid) amide salt with TBN less than 10. The Lubricant ameliorated piston deposits in fired engine tests such as the TU5 and Sequence IIIF.

[0007] International Application WO2010/012756 (published 4 February 2010) and US Patent Application US2010/0024286 (published 4 February 2010) both disclose a fuel composition comprising a fuel and one or more poly (hydroxycarboxylic acid) amide salts. Such fuels offered benefits such as improved lubricity by HFRR, Improved inlet valve deposits in fired engine tests and improved sludge dispersancy in the Sequence VG engine test.

[0008] International Application WO2010/014678 (published 4 February 2010) discloses a poly (hydroxycarboxylic acid) amide salt derivative wherein the anionic portion of the salt does not contain sulphur. The molecules described showed lower phosphorus volatility in Selby NOACK testing in fully formulated fluids than similar materials that had sulphur-containing anions.

[0009] International Application WO2010/015706 (published 11 February 2010) discloses a lubricant comprising base oil, a poly (hydroxycarboxylic acid) amide salt and one or more detergents. The composition is useful for dispersing preformed sludge deposits.

[0010] International Application WO2010/012763 (published 4 February 2010) and US Patent Application US2010/0024287 (published 4 February 2010) both disclose a fuel composition comprising a fuel and one or more poly (hydroxycarboxylic acid) derivative having a terminal acid group. The fuels of the disclosed composition demonstrated some improved lubricity characteristics.

[0011] International publication WO 2011/095819 (published 11 August 2011) discloses a diesel fuel composition comprising, as a fuel additive, a quaternary ammonium salt wherein the quaternising agent is an ester of a polycarboxylic acid such as dimethyl oxalate. The fuel composition disclosed has reduced occurrence of deposits in a diesel engine.

SUMMARY OF THE INVENTION

[0012] The objectives of the present invention include providing at least one of (i) dispersancy, (ii) cleanliness, or (iii) a lubricant with reduced sludge formation.

[0013] As used herein reference to the amounts of additives present in the lubricating composition disclosed are quoted on an oil free basis, i.e., amount of actives, unless otherwise indicated.

[0014] In one embodiment the present invention provides a lubricating composition comprising an oil of lubricating viscosity and a quaternised polyester salt which comprises a product obtained/obtainable by reaction of (i) a polyester containing a tertiary amino group; and (ii) a quaternising agent suitable for converting the tertiary amino group to a quaternary nitrogen, wherein the quaternising agent is selected from the group consisting of a dialkyl sulphate, a benzyl halide, an organic carbonate, an ester of a polycarboxylic acid, an organic epoxide in combination with an acid, and mixtures thereof.

[0015] In one embodiment the present invention provides a lubricating composition comprising a dispersant (typically a succinimide dispersant), an oil of lubricating viscosity and a quaternised polyester salt which comprises a product obtained/obtainable by reaction of (that is to say, which may be the reaction product of) (i) a polyester containing a tertiary amino group; and (ii) a quaternising agent suitable for converting the tertiary amino group to a quaternary nitrogen, wherein the quaternising agent is selected from the group consisting of a dialkyl sulphate, a benzyl halide, an organic carbonate (such as an alkylene carbonate or a dialkyl carbonate), an ester of a polycarboxylic acid, an organic epoxide (such as a hydrocarbyl epoxide, or ethylene oxide) in combination with an acid, and mixtures thereof.

[0016] In one embodiment the present invention provides a lubricating composition comprising :

an oil of lubricating viscosity;

0.1 wt % to 10 wt %, or 1 wt % to 8 wt % of a quaternised polyester salt which comprises a product obtained/obtainable by reaction of (i) a polyester containing a tertiary amino group; and (ii) a quaternising agent suitable for converting the tertiary amino group to a quaternary nitrogen, wherein the quaternising agent is selected from the group consisting of a dialkyl sulphate, a benzyl halide, an organic carbonate; an organic epoxide in combination with an acid or mixtures thereof; and

0.1 wt % to 15 wt %, or 0.5 wt % to 9 wt % of a dispersant (typically a succinimide dispersant).

[0017] In one embodiment the present invention provides a lubricating composition comprising:

an oil of lubricating viscosity;

2 wt % to 6.5 wt % of a quaternised polyester salt which comprises a product obtained/obtainable by reaction of (i) a polyester containing a tertiary amino group; and (ii) a quaternising agent suitable for converting the tertiary amino group to a quaternary nitrogen, wherein the quaternising agent is selected from the group consisting of a dialkyl sulphate, a benzyl halide, an organic carbonate, an ester of a polycarboxylic acid, an organic epoxide in combination with an acid, and mixtures thereof; and

2 wt % to 8.5 wt % of a dispersant (typically a succinimide dispersant).

[0018] In one embodiment the invention provides for a method of lubricating a mechanical device with a lubricating composition disclosed herein. The mechanical device may be an internal combustion engine.

[0019] The internal combustion engine may have a steel surface on at least one of a cylinder bore, cylinder block, or piston ring.

[0020] The internal combustion engine may have an aluminium alloy, or aluminium composite surface on at least one of a cylinder bore, cylinder block, or piston ring.

[0021] In one embodiment the invention provides for the use of the polyester quaternary salt of the invention as a dispersant in a lubricant for use in an internal combustion engine.

DETAILED DESCRIPTION OF THE INVENTION

[0022] The present invention provides a detergent, a process to prepare a detergent, a lubricating composition, a method for lubricating a mechanical device and a use as disclosed above.

The Polyester Quaternary Ammonium Salt

[0023] The polyester quaternary salt of the invention includes quaternised polyester amine, amide, and ester salts. The additives may also be described as quaternary polyester salts. The additives of the invention may be described as the reaction product of: a polyester containing a tertiary amino group; and a quaternising agent suitable for converting the tertiary amino group to a quaternary nitrogen. The quaternising agent may be selected from the group consisting of a dialkyl sulphate, a benzyl halide, an organic carbonate, an ester of

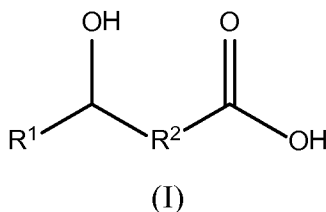
a polycarboxylic acid, an organic epoxide in combination with an acid, and mixtures thereof.

The Non-Quaternised Polyester

[0024] The polyester containing a tertiary amino group used in the preparation of the additives of the invention may also be described as a non-quaternised polyester containing a tertiary amino group.

[0025] As used herein the term “fatty carboxylic acid” used in relation to the polyester means an acid with a carbon chain of 8 to 22, or 10 to 22 carbon atoms.

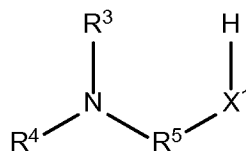
[0026] In some embodiments the polyester may be a reaction product of a fatty carboxylic acid containing at least one hydroxyl group and a compound having an oxygen or nitrogen atom capable of condensing with said acid and further having a tertiary amino group. The reaction product may be formed by adding the fatty carboxylic acid and the compound having an oxygen or nitrogen atom capable of condensing with said acid in any order. Suitable fatty carboxylic acids that may be used in the preparation of the polyesters described above may be represented by the formula:



wherein R^1 may be a hydrogen or a hydrocarbyl group containing from 1 to 20 carbon atoms and R^2 may be a hydrocarbylene group containing from 1 to 20 carbon atoms, with the proviso that the total number of carbon atoms present from R^1 and R^2 may be 6 or more, or 8 or more. In some embodiments R^1 contains from 1 to 12, 2 to 10, 4 to 8 or even 6 carbon atoms R^2 may contain from 2 to 16, 6 to 14, 8 to 12, or even 10 carbon atoms.

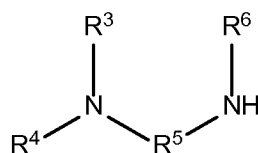
[0027] In some embodiments the fatty carboxylic acid used in the preparation of the polyester may be 12-hydroxystearic acid, ricinoleic acid, 12-hydroxy dodecanoic acid, 5-hydroxy dodecanoic acid, 5-hydroxy decanoic acid, 4-hydroxy decanoic acid, 10-hydroxy undecanoic acid, or combinations thereof.

[0028] In some embodiments the compound having an oxygen or nitrogen atom capable of condensing with said acid and further having a tertiary amino group may be represented by the formula:



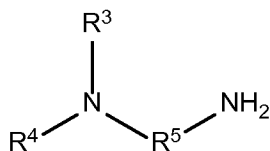
(II)

wherein R^3 may be a hydrocarbyl group containing from 1 to 10 carbon atoms; R^4 may be a hydrocarbyl group containing from 1 to 10 carbon atoms; R^5 may be a hydrocarbylene group containing from 1 to 20 carbon atoms; and X^1 may be O or NR^6 where R^6 may be a hydrogen or a hydrocarbyl group containing from 1 to 10 carbon atoms. In some embodiments R^3 contains from 1 to 6, 1 to 2, or even 1 carbon atom, R^4 contains from 1 to 6, 1 to 2, or even 1 carbon atom, R^5 contains from 2 to 12, 2 to 8 or even 3 carbon atoms, and R^6 contains from 1 to 8, or 1 to 4 carbon atoms. In some of these embodiments, formula (II) becomes:



(II-a)

or



(II-b)

wherein the various definitions provided above still apply.

[0029] Examples of nitrogen or oxygen containing compounds capable of condensing with the acylating agents, which also have a tertiary amino group, or compounds that may be alkylated into such compounds, include: 1-aminopiperidine, 1-(2-aminoethyl)piperidine, 1-(3-aminopropyl)-2-pipecoline, 1-methyl-(4-methylamino)piperidine, 4-(1-pyrrolidinyl)piperidine, 1-(2-aminoethyl)pyrrolidine, 2-(2-aminoethyl)-1-methylpyrrolidine, N,N-diethylethylenediamine, N,N-dimethylethylenediamine, N,N-dibutylethylenediamine, N,N-diethyl-1,3-diaminopropane, N,N-dimethyl-1,3-diaminopropane, N,N,N'-trimethylethylenediamine, N,N-dimethyl-N'-ethylethylenediamine, N,N-diethyl-

N'-methylethylenediamine, N,N,N'-triethylethylenediamine, 3-dimethylamino-propylamine, 3-diethylaminopropylamine, 3-dibutylaminopropylamine, N,N,N'-trimethyl-1,3-propanediamine, N,N,2,2-tetramethyl-1,3-propanediamine, 2-amino-5-diethylaminopentane, N,N,N',N'-tetraethyldiethylenetriamine, 3,3'-diamino-N-methyldipropylamine, 3,3'-iminobis(N,N-dimethylpropylamine), or combinations thereof. In such embodiments, the resulting additive includes a quaternary ammonium amide salt, containing an amide group and a quaternary ammonium salt.

[0030] The nitrogen or oxygen containing compounds may further include aminoalkyl substituted heterocyclic compounds such as 1-(3-aminopropyl)imidazole and 4-(3-aminopropyl)morpholine.

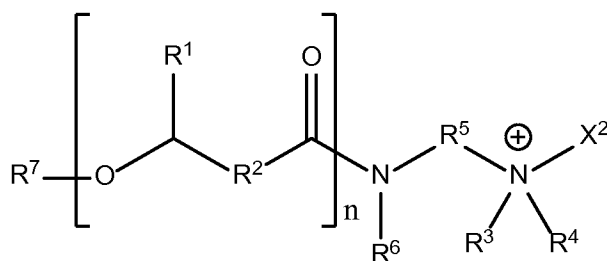
[0031] Another type of nitrogen or oxygen containing compounds capable of condensing with the acylating agent and having a tertiary amino group, in some embodiments after further alkylation, includes alkanolamines including but not limited to triethanolamine, N,N-dimethylaminopropanol, N,N-diethylaminopropanol, N,N-diethylaminobutanol, triisopropanolamine, 1-[2-hydroxyethyl]piperidine, 2-[2-(dimethylamino)ethoxy]-ethanol, N-ethyldiethanolamine, N-methyldiethanol amine, N-butyldiethanolamine, N,N-diethylaminoethanol, N,N-dimethyl aminoethanol, 2-dimethylamino-2-methyl-1-propanol. In embodiments where alkanolamines and/or similar materials are used, the resulting additive includes a quaternary ammonium ester salt, containing an ester group and a quaternary ammonium salt.

[0032] In one embodiment the nitrogen or oxygen containing compound may be triisopropanolamine, 1-[2-hydroxyethyl]piperidine, 2-[2-(dimethylamino)ethoxy]-ethanol, N-ethyldiethanolamine, N-methyldiethanolamine, N-butyldiethanolamine, N,N-diethylaminoethanol, N,N-dimethylaminoethanol, 2-dimethylamino-2-methyl-1-propanol, or combinations thereof.

[0033] In some embodiments the compound having an oxygen or nitrogen atom capable of condensing with said acid and further having a tertiary amino group comprises N,N-diethylethylenediamine, N,N-dimethylethylenediamine, N,N-dibutylethylenediamine, N,N-dimethyl-1,3-diaminopropane, N,N-diethyl-1,3-diaminopropane, N,N-dimethylaminoethanol, N,N-diethylaminoethanol, or combinations thereof.

[0034] The quaternised polyester salt may be a quaternised polyester amide salt. In such embodiments the polyester containing a tertiary amino group used to prepare the quaternised polyester salt may be a polyester amide containing a tertiary amino group. In some of these embodiments the amine or aminoalcohol may be reacted with a monomer and then the resulting material may be polymerised with additional monomer, resulting in the desired polyester amide which may then be quaternised.

[0035] In some embodiments the quaternised polyester salt includes a cation represented by the following formula:



(III)

wherein R^1 may be a hydrogen or a hydrocarbyl group containing from 1 to 20 carbon atoms and R^2 may be a hydrocarbylene group containing from 1 to 20 carbon atoms; R^3 may be a hydrocarbyl group containing from 1 to 10 carbon atoms; R^4 may be a hydrocarbyl group containing from 1 to 10 carbon atoms; R^5 may be a hydrocarbylene group containing from 1 to 20 carbon atoms; R^6 may be a hydrogen or a hydrocarbyl group containing from 1 to 10 carbon atoms; n may be a number from 1 to 10; R^7 may be hydrogen, a hydrocarbyl-substituted carbonyl group containing from 1 to 22 carbon atoms (i.e., a hydrocarbyl-substituted carbonyl group may be a hydrocarbyl group containing a carbonyl group that bonds to the -O- within $[]_n$), or a hydrocarbyl group containing from 1 to 22 carbon atoms; and X^2 may be a group derived from the quaternising agent. In some embodiments R^6 may be hydrogen.

[0036] As above, in some embodiments R^1 contains from 1 to 12, 2 to 10, 4 to 8 or even 6 carbon atoms, and R^2 contains from 2 to 16, 6 to 14, 8 to 12, or even 10 carbon atoms, R^3 contains from 1 to 6, 1 to 2, or even 1 carbon atom, R^4 contains from 1 to 6, 1 to 2, or even 1 carbon atom, R^5 contains from 2 to 12, 2 to 8 or even 3 carbon atoms, and R^6 contains from 1 to 8, or 1 to 4 carbon atoms.

In any of these embodiments n may be from 2 to 9, or 3 to 7, and R⁷ may contain from 6 to 22, or 8 to 20 carbon atoms.

[0037] In these embodiments the quaternised polyester salt may be capped with a C1-22, or a C8-20, fatty acid. Examples of suitable acids include oleic acid, palmitic acid, stearic acid, erucic acid, lauric acid, 2-ethylhexanoic acid, 9,11-linoleic acid, 9,12-linoleic acid, 9,12,15-linolenic acid, abietic acid, or combinations thereof.

[0038] The number average molecular weight (Mn) of the quaternised polyester salts of the invention may be from 500 to 3000, or from 700 to 2500.

[0039] The polyester useful in the present invention may be obtained/obtainable by heating one or more hydroxycarboxylic acids or a mixture of the hydroxycarboxylic acid and a carboxylic acid, optionally in the presence of an esterification catalyst. The hydroxycarboxylic acids may, in certain embodiments, have the formula HO-X-COOH wherein X may be a divalent saturated or unsaturated aliphatic radical containing at least 8 carbon atoms and in which there are at least 4 carbon atoms between the hydroxy and carboxylic acid groups, or from a mixture of such a hydroxycarboxylic acid and a carboxylic acid which is free from hydroxy groups. This reaction may be carried out at a temperature in the region of 160 °C to 200 °C, until the desired molecular weight has been obtained. The course of the esterification may be followed by measuring the acid value of the product, with the desired polyester, in some embodiments, having an acid value in the range of 10 to 100 mg KOH/g or in the range of 20 to 50 mg KOH/g. The indicated acid value range of 10 to 100 mg KOH/g is equivalent to a number average molecular weight range of 5600 to 560. The water formed in the esterification reaction may be removed from the reaction medium, and this may be conveniently done by passing a stream of nitrogen over the reaction mixture or by carrying out the reaction in the presence of a solvent, such as toluene or xylene, and distilling off the water as it is formed.

[0040] The resulting polyester may then be isolated in conventional manner; however, when the reaction is carried out in the presence of an organic solvent whose presence would not be harmful in the subsequent application, the resulting solution of the polyester may be used.

[0041] In the said hydroxycarboxylic acids the radical represented by X may contain from 12 to 20 carbon atoms, optionally where there are between 8 and 14 carbon atoms between the carboxylic acid and hydroxy groups. In some embodiments the hydroxycarboxylic acid may contain a second hydroxy group. Typically, the hydroxycarboxylic acid may contain one hydroxy group, and one carboxylic acid group.

[0042] Specific examples of such hydroxycarboxylic acids include ricinoleic acid, a mixture of 9- and 10-hydroxystearic acids (obtained by sulphation of oleic acid followed by hydrolysis), and 12-hydroxystearic acid, and especially the commercially available hydrogenated castor oil fatty acid which contains in addition to 12-hydroxystearic acid minor amounts of stearic acid and palmitic acid.

[0043] The carboxylic acids which may be used in conjunction with the hydroxycarboxylic acids to obtain these polyesters are preferably carboxylic acids of saturated or unsaturated aliphatic compounds, particularly alkyl and alkenyl carboxylic acids containing a chain of from 8 to 20 carbon atoms. As examples of such acids there may be mentioned lauric acid, palmitic acid, stearic acid and oleic acid.

[0044] In one embodiment the polyester may be derived from commercial 12-hydroxy-stearic acid and may have a number average molecular weight of about 1600. Polyesters such as this are described in greater detail in U.K. Patent Specification Nos. 1373660 and 1342746.

[0045] In some embodiments the components used to prepare the additives described above are substantially free of, essentially free of, or even completely free of, non-polyester-containing hydrocarbyl substituted acylating agents and/or non-polyester-containing hydrocarbyl substituted diacylating agents, such as for example polyisobutylene succinic anhydride. In some embodiments these excluded agents are the reaction product of a long chain hydrocarbon, generally a polyolefin, reacted with a monounsaturated carboxylic acid reactant, such as, (i) α,β -monounsaturated C_4 to C_{10} dicarboxylic acid, such as fumaric acid, itaconic acid, maleic acid; (ii) derivatives of (i) such as anhydrides or C_1 to C_5 alcohol derived mono- or di-esters of (i); (iii) α,β -monounsaturated C_3 to C_{10} monocarboxylic acid such as acrylic acid and methacrylic acid; or (iv)

derivatives of (iii), such as C₁ to C₅ alcohol derived esters of (iii) with any compound containing an olefinic bond represented by the general formula (R⁹)(R¹⁰)C=C(R¹¹)(CH(R⁷)(R⁸)) wherein each of R⁹ and R¹⁰ may be independently hydrogen or a hydrocarbon based group; each of R¹¹, R⁷ and R⁸ may be independently hydrogen or a hydrocarbon based group and preferably at least one may be a hydrocarbyl group containing at least 20 carbon atoms. In one embodiment, the excluded hydrocarbyl-substituted acylating agent may be a dicarboxylic acylating agent. In some of these embodiments, the excluded hydrocarbyl-substituted acylating agent is polyisobutylene succinic anhydride.

[0046] By substantially free of, it is meant that the components of the present invention are primarily composed of materials other than hydrocarbyl substituted acylating agents described above such that these agents are not significantly involved in the reaction and the compositions of the invention do not contain significant amounts of additives derived from such agents.

The Quaternising Agent

[0047] The quaternised salt of the present invention are formed when the non-quaternised polyester described above are reacted with a quaternising agent. Suitable quaternising agents include a dialkyl sulphate, a benzyl halide, an organic carbonate; an ester of a polycarboxylic acid, an organic epoxide in combination with an acid, and mixtures thereof.

[0048] In one embodiment, the quaternising agent may include an ester of a polycarboxylic acid. The ester of a polycarboxylic acid is described in international publication WO 2011/095819 (published 11 August 2011).

[0049] In this definition we mean to include dicarboxylic acids and carboxylic acids having more than 2 acidic moieties. In some embodiments the esters are alkyl esters with alkyl groups that contain from 1 to 4 carbon atoms. Suitable examples include diesters of oxalic acid, diesters of phthalic acid, diesters of maleic acid, diesters of malonic acid, diesters of tartaric acid, or diesters or triesters of citric acid.

[0050] In some embodiments the quaternizing agent is an ester of a carboxylic acid having a pK_a of less than 3.5. In such embodiments in which the compound includes more than one acid group, we mean to refer to the first dissociation constant. The quaternizing agent may be selected from an ester of a carboxylic acid selected from one or more of oxalic acid, phthalic acid, salicylic acid, maleic acid, malonic

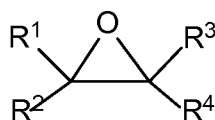
acid, citric acid, nitrobenzoic acid, aminobenzoic acid and 2, 4, 6-trihydroxybenzoic acid. In some embodiments the quaternizing agent includes dimethyl oxalate, methyl 2-nitrobenzoate and methyl salicylate.

[0051] In one embodiment, the quaternising agent may include an alkyl halide, such as a chloride, an iodide or a bromide; an alkyl sulphonate; a dialkyl sulphate, such as dimethyl sulphate; sultones; alkyl a phosphate such as, C1-12 trialkylphosphates; di C1-12 alkylphosphates; a borate; a C1-12 alkyl borate; an alkyl nitrite; an alkyl nitrate; a dialkyl carbonate; an alkyl alkanoate; an O,O-di-C1-12 alkyldithiophosphate; or mixtures thereof.

[0052] In one embodiment, the quaternising agent may be derived from a dialkyl sulphate such as dimethyl sulphate, N-oxides, sultones such as propane and butane sultone; alkyl, acyl or aralkyl halides such as methyl and ethyl chloride, bromide or iodide or benzyl chloride, and a hydrocarbyl (or alkyl) substituted carbonates. If the alkyl halide may be benzyl chloride, the aromatic ring may be optionally further substituted with alkyl or alkenyl groups.

[0053] The hydrocarbyl (or alkyl) groups of the hydrocarbyl substituted carbonates may contain 1 to 50, 1 to 20, 1 to 10 or 1 to 5 carbon atoms per group. In one embodiment, the hydrocarbyl substituted carbonates contain two hydrocarbyl groups that may be the same or different. Examples of suitable hydrocarbyl substituted carbonates include dimethyl or diethyl carbonate.

[0054] In another embodiment, the quaternising agent may be an organic epoxide, as represented by the following formula, in combination with an acid:



(IV)

wherein R^1 , R^2 , R^3 and R^4 may be independently H or a hydrocarbyl group contain from 1 to 50 carbon atoms. Examples of an organic epoxide include ethylene oxide, propylene oxide, butylene oxide, styrene oxide and combinations thereof. In one embodiment the quaternising agent does not contain styrene oxide.

[0055] In some embodiments the acid used with the hydrocarbyl epoxide may be a separate component, such as acetic acid. In other embodiments, for example

when the hydrocarbyl acylating agent may be a dicarboxylic acylating agent, no separate acid component is needed. In such embodiments, the detergent may be prepared by combining reactants which are essentially free of, or even free of, a separate acid component, such as acetic acid, and rely on the acid group of the hydrocarbyl acylating agent instead. In other embodiments, a small amount of an acid component may be present, but at <0.2 or even <0.1 moles of acid per mole of hydrocarbyl acylating agent.

[0056] In some embodiments the quaternising agent of the invention does not contain any substituent group that contains more than 20 carbon atoms. In other words, in some embodiments the long substituent group that allows for the resulting additive to be organic soluble and thus useful for the purposes of this invention is not provided by the quaternising agent but instead is brought to the additive by the non-quaternised polyester having an amine functionality to quaternising agent ratio of 1:0.1 to 2, or 1:1 to 1.5, or 1:1 to 1.3.

[0057] In certain embodiments the quaternised polyester salt may be present at 0.1 wt % to 10 wt %, or 1 wt % to 8 wt %, or 2 wt % to 6.5 wt % of the lubricating composition.

Dispersant

[0058] The lubricating composition may further include a dispersant, or mixtures thereof. The dispersant may be a succinimide dispersant, a Mannich dispersant, a succinamide dispersant, a polyolefin succinic acid ester, amide, or ester-amide, or mixtures thereof. In one embodiment the invention does include a dispersant or mixtures thereof. The dispersant may be present as a single dispersant. The dispersant may be present as a mixture of two or more (typically two or three) different dispersants, wherein at least one may be a succinimide dispersant.

[0059] The succinimide dispersant may be derived from an aliphatic polyamine, or mixtures thereof. The aliphatic polyamine may be aliphatic polyamine such as an ethylenepolyamine, a propylenepolyamine, a butylenepolyamine, or mixtures thereof. In one embodiment the aliphatic polyamine may be ethylenepolyamine. In one embodiment the aliphatic polyamine may be selected from the group consisting of ethylenediamine, diethylenetriamine, triethylenetetramine, tetra-

ethylenepentamine, pentaethylenehexamine, polyamine still bottoms, and mixtures thereof.

[0060] In one embodiment the dispersant may be a polyolefin succinic acid ester, amide, or ester-amide. For instance, a polyolefin succinic acid ester may be a polyisobutylene succinic acid ester of pentaerythritol, or mixtures thereof. A polyolefin succinic acid ester-amide may be a polyisobutylene succinic acid reacted with an alcohol (such as pentaerythritol) and an amine (such as a diamine, typically diethyleneamine).

[0061] The dispersant may be an N-substituted long chain alkenyl succinimide. An example of an N-substituted long chain alkenyl succinimide is polyisobutylene succinimide. Typically the polyisobutylene from which polyisobutylene succinic anhydride is derived has a number average molecular weight of 350 to 5000, or 550 to 3000 or 750 to 2500. Succinimide dispersants and their preparation are disclosed, for instance in US Patents 3,172,892, 3,219,666, 3,316,177, 3,340,281, 3,351,552, 3,381,022, 3,433,744, 3,444,170, 3,467,668, 3,501,405, 3,542,680, 3,576,743, 3,632,511, 4,234,435, Re 26,433, and 6,165,235, 7,238,650 and EP Patent Application 0 355 895 A.

[0062] The dispersants may also be post-treated by conventional methods by a reaction with any of a variety of agents. Among these are boron compounds (such as boric acid), urea, thiourea, dimercaptothiadiazoles, carbon disulphide, aldehydes, ketones, carboxylic acids such as terephthalic acid, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, and phosphorus compounds. In one embodiment the post-treated dispersant is borated. In one embodiment the post-treated dispersant is reacted with dimercaptothiadiazoles. In one embodiment the post-treated dispersant is reacted with phosphoric or phosphorous acid. In one embodiment the post-treated dispersant is reacted with terephthalic acid and boric acid (as described in US Patent Application US2009/0054278).

[0063] In one embodiment the dispersant may be borated or non-borated. Typically a borated dispersant may be a succinimide dispersant.

[0064] The dispersant may be prepared/obtained/obtainable from reaction of succinic anhydride by an "ene" or "thermal" reaction, by what is referred to as a "direct alkylation process." The "ene" reaction mechanism and general reaction

conditions are summarised in “Maleic Anhydride”, pages, 147-149, Edited by B.C. Trivedi and B.C. Culbertson and Published by Plenum Press in 1982. The dispersant prepared by a process that includes an “ene” reaction may be a polyisobutylene succinimide having a carbocyclic ring present on less than 50 mole %, or 0 to less than 30 mole %, or 0 to less than 20 mole %, or 0 mole % of the dispersant molecules. The “ene” reaction may have a reaction temperature of 180 °C to less than 300 °C, or 200 °C to 250 °C, or 200 °C to 220 °C.

[0065] The dispersant may also be obtained/obtainable from a chlorine-assisted process, often involving Diels-Alder chemistry, leading to formation of carbocyclic linkages. The process is known to a person skilled in the art. The chlorine-assisted process may produce a dispersant that is a polyisobutylene succinimide having a carbocyclic ring present on 50 mole % or more, or 60 to 100 mole % of the dispersant molecules. Both the thermal and chlorine-assisted processes are described in greater detail in U.S. Patent 7,615,521, columns 4-5 and preparative examples A and B.

[0066] The dispersant may have a carbonyl to nitrogen ratio (CO:N ratio) of 5:1 to 1:10, 2:1 to 1:10, or 2:1 to 1:5, or 2:1 to 1:2. In one embodiment the dispersant may have a CO:N ratio of 2:1 to 1:10, or 2:1 to 1:5, or 2:1 to 1:2, or 1:1.4 to 1:0.6.

[0067] The dispersant may be present at 0 wt % to 20 wt %, 0.1 wt % to 15 wt %, or 0.5 wt % to 9 wt %, or 1 wt % to 8.5 wt % of the lubricating composition.

Oils of Lubricating Viscosity

[0068] The lubricating composition comprises an oil of lubricating viscosity. Such oils include natural and synthetic oils, oil derived from hydrocracking, hydrogenation, and hydrofinishing, unrefined, refined, re-refined oils or mixtures thereof. A more detailed description of unrefined, refined and re-refined oils is provided in International Publication WO2008/147704, paragraphs [0054] to [0056] (a similar disclosure is provided in US Patent Application 2010/197536, see [0072] to [0073]). A more detailed description of natural and synthetic lubricating oils is described in paragraphs [0058] to [0059] respectively of WO2008/147704 (a similar disclosure is provided in US Patent Application 2010/197536, see [0075] to [0076]). Synthetic oils may also be produced by

Fischer-Tropsch reactions and typically may be hydroisomerised Fischer-Tropsch hydrocarbons or waxes. In one embodiment oils may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

[0069] Oils of lubricating viscosity may also be defined as specified in April 2008 version of "Appendix E - API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils", section 1.3 Sub-heading 1.3. "Base Stock Categories". The API Guidelines are also summarised in US Patent US 7,285,516 (see column 11, line 64 to column 12, line 10). In one embodiment the oil of lubricating viscosity may be an API Group II, Group III, Group IV oil, or mixtures thereof.

[0070] The amount of the oil of lubricating viscosity present is typically the balance remaining after subtracting from 100 wt % the sum of the amount of the compound of the invention and the other performance additives.

[0071] The lubricating composition may be in the form of a concentrate and/or a fully formulated lubricant. If the lubricating composition of the invention (comprising the additives disclosed herein) is in the form of a concentrate which may be combined with additional oil to form, in whole or in part, a finished lubricant), the ratio of the of these additives to the oil of lubricating viscosity and/or to diluent oil include the ranges of 1:99 to 99:1 by weight, or 80:20 to 10:90 by weight.

Other Performance Additives

[0072] A lubricating composition may be prepared by adding the product of the process described herein to an oil of lubricating viscosity, optionally in the presence of other performance additives (as described herein below).

[0073] The lubricating composition of the invention optionally comprises other performance additives. The other performance additives include at least one of metal deactivators, viscosity modifiers, detergents, friction modifiers, antiwear agents, corrosion inhibitors, dispersant viscosity modifiers, extreme pressure agents, antioxidants, foam inhibitors, demulsifiers, pour point depressants, seal swelling agents and mixtures thereof. Typically, fully-formulated lubricating oil will contain one or more of these performance additives.

[0074] The lubricating composition of the invention may further include other additives. In one embodiment the invention provides a lubricating composition

further comprising at least one of a dispersant, an antiwear agent, a dispersant viscosity modifier, a friction modifier, a viscosity modifier, an antioxidant, an overbased detergent, or mixtures thereof. In one embodiment the invention provides a lubricating composition further comprising at least one of a polyisobutylene succinimide dispersant, an antiwear agent, a dispersant viscosity modifier, a friction modifier, a viscosity modifier (typically an olefin copolymer such as an ethylene-propylene copolymer), an antioxidant (including phenolic and aminic antioxidants), an overbased detergent (including overbased sulphonates and phenates), or mixtures thereof.

[0075] In one embodiment the lubricating composition may be a lubricating composition further comprising a molybdenum compound. The molybdenum compound may be an antiwear agent or an antioxidant. The molybdenum compound may be selected from the group consisting of molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, amine salts of molybdenum compounds, and mixtures thereof. The molybdenum compound may provide the lubricating composition with 0 to 1000 ppm, or 5 to 1000 ppm, or 10 to 750 ppm 5 ppm to 300 ppm, or 20 ppm to 250 ppm of molybdenum.

[0076] Antioxidants include sulphurised olefins, diarylamines, alkylated diarylamines, hindered phenols, molybdenum compounds (such as molybdenum dithiocarbamates), hydroxyl thioethers, or mixtures thereof. In one embodiment the lubricating composition includes an antioxidant, or mixtures thereof. The antioxidant may be present at 0 wt % to 15 wt %, or 0.1 wt % to 10 wt %, or 0.5 wt % to 5 wt %, or 0.5 wt % to 3 wt %, or 0.3 wt % to 1.5 wt % of the lubricating composition.

[0077] The diarylamine or alkylated diarylamine may be a phenyl- α -naphthylamine (PANA), an alkylated diphenylamine, or an alkylated phenyl-naphthylamine, or mixtures thereof. The alkylated diphenylamine may include di-nonylated diphenylamine, nonyl diphenylamine, octyl diphenylamine, di-octylated diphenylamine, di-decylated diphenylamine, decyl diphenylamine and mixtures thereof. In one embodiment the diphenylamine may include nonyl diphenylamine, dinonyl diphenylamine, octyl diphenylamine, dioctyl diphenylamine, or mixtures thereof. In one embodiment the alkylated diphenylamine may include nonyl diphenylamine, or dinonyl diphenylamine. The

alkylated diarylamine may include octyl, di-octyl, nonyl, di-nonyl, decyl or di-decyl phenyl-naphthylamines.

[0078] The hindered phenol antioxidant often contains a secondary butyl and/or a tertiary butyl group as a sterically hindering group. The phenol group may be further substituted with a hydrocarbyl group (typically linear or branched alkyl) and/or a bridging group linking to a second aromatic group. Examples of suitable hindered phenol antioxidants include 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 4-propyl-2,6-di-tert-butylphenol or 4-butyl-2,6-di-tert-butylphenol, or 4-dodecyl-2,6-di-tert-butylphenol. In one embodiment the hindered phenol antioxidant may be an ester and may include, e.g., Irganox™ L-135 from Ciba. A more detailed description of suitable ester-containing hindered phenol antioxidant chemistry is found in US Patent 6,559,105.

[0079] Examples of molybdenum dithiocarbamates, which may be used as an antioxidant, include commercial materials sold under the trade names such as Vanlube 822™ and Molyvan™ A from R. T. Vanderbilt Co., Ltd., and Adeka Sakura-Lube™ S-100, S-165, S-600 and 525, or mixtures thereof.

[0080] In one embodiment the lubricating composition further includes a viscosity modifier. The viscosity modifier is known in the art and may include hydrogenated styrene-butadiene rubbers, ethylene-propylene copolymers, polymethacrylates, polyacrylates, hydrogenated styrene-isoprene polymers, hydrogenated diene polymers, polyalkyl styrenes, polyolefins, esters of maleic anhydride-olefin copolymers (such as those described in International Application WO 2010/014655), esters of maleic anhydride-styrene copolymers, or mixtures thereof.

[0081] The dispersant viscosity modifier may include functionalised polyolefins, for example, ethylene-propylene copolymers that have been functionalised with an acylating agent such as maleic anhydride and an amine; polymethacrylates functionalised with an amine, or styrene-maleic anhydride copolymers reacted with an amine. More detailed description of dispersant viscosity modifiers are disclosed in International Publication WO2006/015130 or U.S. Patents 4,863,623; 6,107,257; 6,107,258; 6,117,825; and US 7,790,661. In one embodiment the dispersant viscosity modifier may include those described in

U.S. Patent 4,863,623 (see column 2, line 15 to column 3, line 52) or in International Publication WO2006/015130 (see page 2, paragraph [0008] and preparative examples are described paragraphs [0065] to [0073]). In one embodiment the dispersant viscosity modifier may include those described in U.S. Patent US 7,790,661 column 2, line 48 to column 10, line 38.

[0082] In one embodiment the lubricating composition of the invention further comprises a dispersant viscosity modifier. The dispersant viscosity modifier may be present at 0 wt % to 5 wt %, or 0 wt % to 4 wt %, or 0.05 wt % to 2 wt %, or 0.2 wt % to 1.2 wt % of the lubricating composition..

[0083] In one embodiment the invention provides a lubricating composition further comprising an overbased metal-containing detergent. The metal of the metal-containing detergent may be zinc, sodium, calcium, barium, or magnesium. Typically the metal of the metal-containing detergent may be sodium, calcium, or magnesium.

[0084] The overbased metal-containing detergent may be selected from the group consisting of non-sulphur containing phenates, sulphur containing phenates, sulphonates, salixarates, salicylates, and mixtures thereof, or borated equivalents thereof. The overbased detergent may be borated with a borating agent such as boric acid.

[0085] The overbased metal-containing detergent may also include "hybrid" detergents formed with mixed surfactant systems including phenate and/or sulphonate components, e.g., phenate/salicylates, sulphonate/phenates, sulphonate/salicylates, sulphonates/phenates/salicylates, as described; for example, in US Patents 6,429,178; 6,429,179; 6,153,565; and 6,281,179. Where, for example, a hybrid sulphonate/phenate detergent is employed, the hybrid detergent would be considered equivalent to amounts of distinct phenate and sulphonate detergents introducing like amounts of phenate and sulphonate soaps, respectively.

[0086] Typically an overbased detergent may be sodium, calcium or magnesium salt of the phenates, sulphur containing phenates, sulphonates, salixarates and salicylates. Overbased phenates and salicylates typically have a total base number of 180 to 450 TBN. Overbased sulphonates typically have a total base number of 250 to 600, or 300 to 500. Overbased detergents are known

in the art. In one embodiment the sulphonate detergent may be a predominantly linear alkylbenzene sulphonate detergent having a metal ratio of at least 8 as is described in paragraphs [0026] to [0037] of US Patent Application 2005065045 (and granted as US 7,407,919). Linear alkyl benzenes may have the benzene ring attached anywhere on the linear chain, usually at the 2, 3, or 4 position, or mixtures thereof. The predominantly linear alkylbenzene sulphonate detergent may be particularly useful for assisting in improving fuel economy. In one embodiment the sulphonate detergent may be a metal salt of one or more oil-soluble alkyl toluene sulphonate compounds as disclosed in paragraphs [0046] to [0053] of US Patent Application 2008/0119378.

[0087] Typically the overbased metal-containing detergent may be a calcium or magnesium an overbased detergent.

[0088] Overbased detergents are known in the art. Overbased materials, otherwise referred to as overbased or superbased salts, are generally single phase, homogeneous Newtonian systems characterised by a metal content in of that which would be present for neutralization according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metal. The overbased materials are prepared by reacting an acidic material (typically an inorganic acid or lower carboxylic acid, preferably carbon dioxide) with a mixture comprising an acidic organic compound, a reaction medium comprising at least one inert, organic solvent (mineral oil, naphtha, toluene, xylene, etc.) for said acidic organic material, a stoichiometric excess of a metal base, and a promoter such as a calcium chloride, acetic acid, phenol or alcohol. The acidic organic material will normally have a sufficient number of carbon atoms to provide a degree of solubility in oil. The amount of "excess" metal (stoichiometrically) is commonly expressed in terms of metal ratio. The term "metal ratio" is the ratio of the total equivalents of the metal to the equivalents of the acidic organic compound. A neutral metal salt has a metal ratio of one. A salt having 4.5 times as much metal as present in a normal salt will have metal excess of 3.5 equivalents, or a ratio of 4.5. The term "metal ratio is also explained in standard textbook entitled "Chemistry and Technology of Lubricants", Third Edition, Edited by R. M. Mortier and S. T. Orszulik, Copyright 2010, page 219, sub-heading 7.25.

[0089] The overbased detergent (other than the detergent of the present invention) may be present at 0 wt % to 15 wt %, or 0.1 wt % to 10 wt %, or 0.2 wt % to 8 wt %, or 0.2 wt % to 3 wt %. For example in a heavy duty diesel engine the detergent may be present at 2 wt % to 3 wt % of the lubricating composition. For a passenger car engine the detergent may be present at 0.2 wt % to 1 wt % of the lubricating composition. In one embodiment, an engine lubricating composition further comprises at least one overbased detergent with a metal ratio of at least 3, or at least 8, or at least 15.

[0090] In one embodiment the friction modifier may be selected from the group consisting of long chain fatty acid derivatives of amines, long chain fatty esters, or derivatives of long chain fatty epoxides; fatty imidazolines; amine salts of alkylphosphoric acids; fatty alkyl tartrates; fatty alkyl tartrimidates; fatty alkyl tartramides; fatty glycolates; and fatty glycolamides. The friction modifier may be present at 0 wt % to 6 wt %, or 0.01 wt % to 4 wt %, or 0.05 wt % to 2 wt %, or 0.1 wt % to 2 wt % of the lubricating composition.

[0091] As used herein the term "fatty alkyl" or "fatty" in relation to friction modifiers means a carbon chain having 10 to 22 carbon atoms, typically a straight carbon chain.

[0092] Examples of suitable friction modifiers include long chain fatty acid derivatives of amines, fatty esters, or fatty epoxides; fatty imidazolines such as condensation products of carboxylic acids and polyalkylene-polyamines; amine salts of alkylphosphoric acids; fatty alkyl tartrates; fatty alkyl tartrimidates; fatty alkyl tartramides; fatty phosphonates; fatty phosphites; borated phospholipids, borated fatty epoxides; glycerol esters; borated glycerol esters; fatty amines; alkoxylated fatty amines; borated alkoxylated fatty amines; hydroxyl and polyhydroxy fatty amines including tertiary hydroxy fatty amines; hydroxy alkyl amides; metal salts of fatty acids; metal salts of alkyl salicylates; fatty oxazolines; fatty ethoxylated alcohols; condensation products of carboxylic acids and polyalkylene polyamines; or reaction products from fatty carboxylic acids with guanidine, aminoguanidine, urea, or thiourea and salts thereof.

[0093] Friction modifiers may also encompass materials such as sulphurised fatty compounds and olefins, molybdenum dialkyldithiophosphates, molybdenum

dithiocarbamates, sunflower oil or soybean oil monoester of a polyol and an aliphatic carboxylic acid.

[0094] In one embodiment the friction modifier may be a long chain fatty acid ester. In another embodiment the long chain fatty acid ester may be a mono-ester and in another embodiment the long chain fatty acid ester may be a triglyceride.

[0095] The lubricating composition optionally further includes at least one antiwear agent. Examples of suitable antiwear agents include titanium compounds, tartrates, tartrimides, oil soluble amine salts of phosphorus compounds, sulphurised olefins, metal dihydrocarbyldithiophosphates (such as zinc dialkyldithiophosphates), phosphites (such as dibutyl phosphite), phosphonates, thiocarbamate-containing compounds, such as thiocarbamate esters, thiocarbamate amides, thiocarbamic ethers, alkylene-coupled thiocarbamates, and bis(S-alkyldithiocarbamyl) disulphides.

[0096] The antiwear agent may in one embodiment include a tartrate or tartrimide as disclosed in International Publication WO 2006/044411 or Canadian Patent CA 1 183 125. The tartrate or tartrimide may contain alkyl-ester groups, where the sum of carbon atoms on the alkyl groups is at least 8. The antiwear agent may in one embodiment include a citrate as is disclosed in US Patent Application 20050198894.

[0097] The lubricating composition may further include a phosphorus-containing antiwear agent. Typically the phosphorus-containing antiwear agent may be a zinc dialkyldithiophosphate, phosphite, phosphate, phosphonate, and ammonium phosphate salts, or mixtures thereof. Zinc dialkyldithiophosphates are known in the art. The antiwear agent may be present at 0 wt % to 3 wt %, or 0.1 wt % to 1.5 wt %, or 0.5 wt % to 0.9 wt % of the lubricating composition.

[0098] Another class of additives includes oil-soluble titanium compounds as disclosed in US 7,727,943 and US2006/0014651. The oil-soluble titanium compounds may function as antiwear agents, friction modifiers, antioxidants, deposit control additives, or more than one of these functions. In one embodiment the oil soluble titanium compound is a titanium (IV) alkoxide. The titanium alkoxide is formed from a monohydric alcohol, a polyol or mixtures thereof. The monohydric alkoxides may have 2 to 16, or 3 to 10 carbon atoms.

In one embodiment, the titanium alkoxide is titanium (IV) isopropoxide. In one embodiment, the titanium alkoxide is titanium (IV) 2-ethylhexoxide. In one embodiment, the titanium compound comprises the alkoxide of a vicinal 1,2-diol or polyol. In one embodiment, the 1,2-vicinal diol comprises a fatty acid mono-ester of glycerol, often the fatty acid is oleic acid.

[0099] In one embodiment, the oil soluble titanium compound is a titanium carboxylate. In one embodiment the titanium (IV) carboxylate is titanium neodecanoate.

[00100] Useful corrosion inhibitors for an engine lubricating composition include those described in paragraphs 5 to 8 of WO2006/047486, octylamine octanoate, condensation products of dodecenyl succinic acid or anhydride and a fatty acid such as oleic acid with a polyamine. In one embodiment the corrosion inhibitors include the Synalox® corrosion inhibitor. The Synalox® corrosion inhibitor may be a homopolymer or copolymer of propylene oxide. The Synalox® corrosion inhibitor is described in more detail in a product brochure with Form No. 118-01453-0702 AMS, published by The Dow Chemical Company. The product brochure is entitled "SYNALOX Lubricants, High-Performance Polyglycols for Demanding Applications."

[00101] Foam inhibitors that may be useful in the compositions of the invention include polysiloxanes, copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate; demulsifiers including fluorinated polysiloxanes, trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers.

[00102] Pour point depressants that may be useful in the compositions of the invention include polyalphaolefins, esters of maleic anhydride-styrene copolymers, poly(meth)acrylates, polyacrylates or polyacrylamides.

[00103] Demulsifiers include trialkyl phosphates, and various polymers and copolymers of ethylene glycol, ethylene oxide, propylene oxide, or mixtures thereof.

[0100] Metal deactivators include derivatives of benzotriazoles (typically tolyltriazole), 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles or 2-alkyldithiobenzothiazoles. The metal deactivators may also be described as corrosion inhibitors.

[0101] Seal swell agents include sulpholene derivatives Exxon Necton-37™ (FN 1380) and Exxon Mineral Seal Oil™ (FN 3200).

[0102] An engine lubricating composition in different embodiments may have a composition as disclosed in the following table:

Additive	Embodiments (wt %)		
	A	B	C
Quaternised Polyester Salt	0.01 to 8	0.1 to 6	0.15 to 5
Dispersant	0 to 12	0 to 8	0.5 to 6
Dispersant Viscosity Modifier	0 to 5	0 to 4	0.05 to 2
Overbased Detergent	0.1 to 15	0.1 to 10	0.2 to 8
Antioxidant	0.1 to 13	0.1 to 10	0.5 to 5
Antiwear Agent	0.1 to 15	0.1 to 10	0.3 to 5
Friction Modifier	0.01 to 6	0.05 to 4	0.1 to 2
Viscosity Modifier	0 to 10	0.5 to 8	1 to 6
Any Other Performance Additive	0 to 10	0 to 8	0 to 6
Oil of Lubricating Viscosity	Balance to 100 %	Balance to 100 %	Balance to 100 %

5

Industrial Application

[0103] In one embodiment the invention provides a method of lubricating an internal combustion engine. The engine components may have a surface of steel or aluminium.

10

[0104] An aluminium surface may be derived from an aluminium alloy that may be a eutectic or a hyper-eutectic aluminium alloy (such as those derived from aluminium silicates, aluminium oxides, or other ceramic materials). The aluminium surface may be present on a cylinder bore, cylinder block, or piston ring having an aluminium alloy, or aluminium composite.

15

[0105] The internal combustion engine may or may not have an exhaust gas recirculation system. The internal combustion engine may be fitted with an emission control system or a turbocharger. Examples of the emission control system include diesel particulate filters (DPF), or systems employing selective catalytic reduction (SCR).

[0106] In one embodiment the internal combustion engine may be a diesel fuelled engine (typically a heavy duty diesel engine), a gasoline fuelled engine, a natural gas fuelled engine, a mixed gasoline/alcohol fuelled engine, or a hydrogen fuelled internal combustion engine. In one embodiment the internal combustion engine may be a diesel fuelled engine and in another embodiment a gasoline fuelled engine. In one embodiment the internal combustion engine may be a heavy duty diesel engine.

[0107] The internal combustion engine may be a 2-stroke or 4-stroke engine. Suitable internal combustion engines include marine diesel engines, aviation piston engines, low-load diesel engines, and automobile and truck engines. The marine diesel engine may be lubricated with a marine diesel cylinder lubricant (typically in a 2-stroke engine), a system oil (typically in a 2-stroke engine), or a crankcase lubricant (typically in a 4-stroke engine).

[0108] The lubricant composition for an internal combustion engine may be suitable for any engine lubricant irrespective of the sulphur, phosphorus or sulphated ash (ASTM D-874) content. The sulphur content of the engine oil lubricant may be 1 wt % or less, or 0.8 wt % or less, or 0.5 wt % or less, or 0.3 wt % or less. In one embodiment the sulphur content may be in the range of 0.001 wt % to 0.5 wt %, or 0.01 wt % to 0.3 wt %. The phosphorus content may be 0.2 wt % or less, or 0.12 wt % or less, or 0.1 wt % or less, or 0.085 wt % or less, or 0.08 wt % or less, or even 0.06 wt % or less, 0.055 wt % or less, or 0.05 wt % or less. In one embodiment the phosphorus content may be 0.04 wt % to 0.12 wt %. In one embodiment the phosphorus content may be 100 ppm to 1000 ppm, or 200 ppm to 600 ppm. The total sulphated ash content may be 0.3 wt % to 1.2 wt %, or 0.5 wt % to 1.1 wt % of the lubricating composition. In one embodiment the sulphated ash content may be 0.5 wt % to 1.1 wt % of the lubricating composition.

[0109] In one embodiment the lubricating composition may be an engine oil, wherein the lubricating composition may be characterised as having at least one of (i) a sulphur content of 0.5 wt % or less, (ii) a phosphorus content of 0.12 wt % or less, and (iii) a sulphated ash content of 0.5 wt % to 1.1 wt % of the lubricating composition.

[0110] The following examples provide illustrations of the invention. These examples are non-exhaustive and are not intended to limit the scope of the invention.

EXAMPLES

5 [0111] Example 1: A non-quaternised polyester amide is prepared by reacting, in a jacketed reaction vessel fitted with stirrer, condenser, feed pump attached to sub-line addition pipe, nitrogen line and thermocouple/temperature controller system, 6 moles of 12-hydroxystearic acid and 1 mole of dimethylaminopropylamine where the reaction is carried out at about 130 °C and held for about 4 hours. The
10 reaction mixture is then cooled to about 100 °C and zirconium butoxide is added, in an amount so that the catalyst makes up 0.57 percent by weight of the reaction mixture. The reaction mixture is heated to about 195 °C and held for about 12 hours. The resulting product is cooled and collected.

[0112] Example 2: A quaternised polyester amide is prepared by placing 511.7 g
15 of Example 1 in a 1L flask with 179 g methanol and 18.1 g acetic acid. The solution is heated with agitation under an atmosphere of nitrogen to 55 °C. 28.2 g propylene oxide is charged sub-surface over 4 h and the solution is stirred at 55 °C for 17 h. 184.5 g diluent oil is added and the vessel is placed under vacuum. The temperature is increased to 70 °C over 2 hours until the methanol is removed. The solution is
20 further diluted with 181.6 g diluent oil and cooled to 60 °C. 111.3 g of a C20-24 benzene sulphonic acid is added and the solution is agitated for 2 hours at 60 °C. Vacuum is applied to the vessel and the reaction is stripped of acetic acid for 2 h while the vessel is warmed to 100 °C. The isolated material has a TAN of 13.59 mg KOH/g, a TBN of 0 mg KOH/g, 0.81 % N and a kinematic viscosity at 100 °C of
25 90.32 mm/s.

[0113] Example 3: Substantially the same procedure is used as in Example 2 except that styrene oxide is used instead of propylene oxide. The isolated material has a TAN of 5.62 mg KOH/g, a TBN of 25.87 mg KOH/g, 0.73 % N and a kinematic viscosity at 100 °C of 90.9 mm/s.

30 [0114] Example 4: A mixture of xylene (348 parts) and a commercial grade of 12-hydroxystearic acid (3350 parts; having acid and hydroxyl values of 182 mg KOH/g and 160 mg KOH/g respectively) is stirred for 22 hours at 190 °C to 200 °C, the water formed in the reaction being separated from the xylene in the

distillate which is then returned to the reaction medium. After 152 parts of water have been collected, the xylene is removed by heating at 200 °C in a stream of nitrogen. The resulting pale amber coloured liquid has an acid value of 35.0 mg KOH/g. The product of this step is polyester A.

5 [0115] A mixture of polyester A (320 parts), 3-dimethylaminopropylamine (10.2 parts) and toluene (65 parts) is stirred under reflux and under a current of nitrogen using a Dean and Stark head to remove water. The temperature is raised to 165 °C and held at this temperature for 6 hours. After cooling to 20 °C to 25 °C under nitrogen, an 87.6% solution of adduct is obtained.

10 [0116] 226 parts of the adduct is stirred at 40 °C and dimethyl sulphate (6.7 parts) is added. An exotherm raises the temperature to about 50 °C which is further raised to 90 °C by external heating. After holding at 90 °C for a further 90 minutes the reaction mass is cooled to 20 °C. No free dimethyl sulphate is detected by gas/liquid chromatography.

15 [0117] Example 5: is similar to Example 4, except ricinoleic acid is used instead of 12-hydroxystearic acid.

[0118] Example 6: A mixture of 348 parts of xylene and 3350 parts of a commercial grade of 12-hydroxystearic acid (having acid and hydroxyl values of 182 mg KOH/g. and 160 mg KOH/g. respectively) is stirred for 22 hours at 190 °C to 200 °C, the water formed in the reaction being separated from the xylene in the distillate which is then returned to the reaction medium. After 152 parts of water have been collected, the xylene is removed by heating at 200 °C in a stream of nitrogen. The resulting pale amber coloured liquid has an acid value of 35.0 mg KOH/g. This is polyester B.

25 [0119] A mixture of 1600 parts of polyester B and 102 parts of 3-dimethylaminopropylamine is stirred for 2 and a half hours at 160 °C under a reflux condenser and in a current of nitrogen. 10 Parts by volume of the mixture are then distilled off; the temperature is raised to 190 °C during 20 minutes, and maintained at 190 °C to 200 °C for 2 hours 45 minutes. The resulting pale amber coloured viscous liquid partially solidifies on cooling to ambient temperature. The product is then heated to 44 °C and 183 parts of dimethyl sulphate is added. The temperature increased to 72 °C. The mixture is then heated to 90 °C to 100

°C and held for 90 minutes. The product is a pale amber coloured viscous liquid which forms a gum on cooling

[0120] Example 7: is similar to Example 6, except ricinoleic acid is used instead of 12-hydroxystearic acid.

5 [0121] Example 8: A non-quaternised polyester amide is prepared by reacting, in a jacketed reaction vessel fitted with stirrer, condenser, feed pump attached to sub-line addition pipe, nitrogen line and thermocouple/temperature controller system, 6 moles of 12-hydroxystearic acid and 1 mole of dimethylaminopropylamine where the reaction is carried out at about 130 °C and held for about 4 hours. The reaction mixture is then cooled to about 100 °C and zirconium butoxide is added, in an amount so that the catalyst makes up 0.57 percent by weight of the reaction mixture. The reaction mixture is heated to about 195 °C and held for about 12 hours. The resulting product is cooled and collected.

10 [0122] A quaternised polyester amide is prepared by placing 250g (1mol eq) of the product collected above in a 500mL flask with 64.68g dimethyl oxalate (4mol eq) and 1.48g octanoic acid (0.075mol eq). The reaction is heated with agitation under an atmosphere of nitrogen to 120 °C. Once at temperature, the reaction is held for 5 hours. After the hold, vacuum is applied to the vessel and the reaction is stripped of excess dimethyl oxalate at 120°C over a period of about 5 hours. After stripping, the quaternised polyester amide is cooled and collected without filtering.

20 [0123] Example 9: A non-quaternised polyester amide is prepared by reacting, in a jacketed reaction vessel fitted with stirrer, condenser, feed pump attached to sub-line addition pipe, nitrogen line and thermocouple/temperature controller system, 6 moles of ricinoleic acid and 1 mole of dimethylaminopropylamine where the reaction is carried out at about 130 °C and held for about 4 hours. The reaction mixture is then cooled to about 100 °C and zirconium butoxide is added, in an amount so that the catalyst makes up 0.57 percent by weight of the reaction mixture. The reaction mixture is heated to about 195 °C and held for about 12 hours. The resulting product is cooled and collected.

25 [0124] A quaternised polyester amide is prepared by placing 250g (1mol eq) of product collected above in a 500mL flask with 61.71g dimethyl oxalate (4mol eq) and 1.41g octanoic acid (0.075mol eq). The reaction is heated with agitation under an atmosphere of nitrogen to 120 °C. Once at temperature, the reaction is held for 5

hours. Vacuum is then applied and the reaction is stripped of excess dimethyl oxalate at 120°C over a period of about 5 hours. After stripping, the quaternised polyester amide is cooled and collected without filtering.

[0125] A series of engine lubricants are prepared containing the products of the examples above. The engine lubricants include both heavy diesel (HD) and gasoline passenger car (PC) lubricants.

[0126] In the lubricant examples below all amounts are expressed on an actives basis.

[0127] Comparative Lubricant Example 1 (CLE1) is a passenger car lubricant. CLE1 is an API SM capable 5W-30 lubricant containing 2 wt % of a succinimide dispersant. The lubricant contains an 1.25 wt % of antioxidant system (containing a mixture of aminic, phenolic and sulphur-containing antioxidants), 0.91 wt % of a zinc dialkyldithiophosphate, 0.62 wt % of an ethylene-propylene copolymer viscosity modifier, 0.14 wt % of pour point depressant, a 0.79 wt % of detergent system (containing a mixture of a sodium overbased sulphonate and calcium overbased sulphonate), 11 ppm of siloxane antifoam agent, and balance API Group II base oil.

[0128] Engine Lubricant 1 (EL1): is the same as CLE1 except it further contains 3 wt % of Example 4.

[0129] Engine Lubricant 2 (EL2): is the same as CLE1 except it further contains 3 wt % of Example 6.

[0130] Engine Lubricant 3 (EL3): is the same as CLE1 except it further contains 3 wt % of Example 5.

[0131] Engine Lubricant 4 (EL4): is the same as CLE1 except it further contains 3 wt % of Example 7.

[0132] Engine Lubricant 5 (EL5): is the same as CLE1 except it further contains 3 wt % of Example 2.

[0133] The PC compositions (EL1 to EL5) are tested in a panel coker apparatus. 210 g of oil to be analysed (Examples EL1 to EL5) is placed in a steel sump chamber at 105 °C. An agitator consisting of several metal tongs on a spindle is inserted into the sump and spun at 1000 rpm. The apparatus is capped with a flat aluminum plate with a constant surface temperature of 325 °C. The agitator sprays a continuous thin layer of oil onto the aluminum plate for a period of 4 hours. At the end of test, the plate is removed and optically rated. A rating scale is applied with 0 meaning a plate

completely covered in black deposits and 100 meaning a plate completely free of deposits. The results obtained for the test are presented below:

	CLE1	EL1	EL2	EL3	EL4	EL5
Rating	55	79	78	70	79	84

5 **[0134]** The data indicates that adding a quaternised polyester salt of the present invention increases the panel coker rating. This means that the addition of quaternised polyester salt improves deposit cleanliness.

10 **[0135]** Lubricant Comparative Example 1 (CLE2) is a heavy duty diesel lubricant. CLE2 is an API CJ-4 capable 15W-40 Lubricant containing 4.1 wt % of a succinimide dispersant. The lubricant contains an 1.23 wt % of antioxidant system (containing a mixture of aminic, phenolic and sulphur-containing antioxidants), 0.99 wt % of a zinc dialkyldithiophosphate, 1.24 wt % of an ethylene-propylene copolymer viscosity modifier, 0.08 wt % of pour point depressant, a 1.71 wt % of detergent system (containing a mixture of a sodium overbased sulphonate and calcium

15 overbased sulphonate), 100 ppm of siloxane antifoam agent, 0.12 wt % of corrosion inhibitor, and balance API Group II base oil.

[0136] Engine Lubricant 6 (EL6): is the same as CLE2 except it further contains 3 wt % of Example 4.

20 **[0137]** Engine Lubricant 7 (EL7): is the same as CLE2 except it further contains 3 wt % of Example 5.

[0138] Engine Lubricant 8 (EL8): is the same as CLE2 except it further contains 3 wt % of Example 7.

[0139] Engine Lubricant 9 (EL9): is the same as CLE2 except it further contains 3 wt % of Example 2.

25 **[0140]** CLE2, and EL6 to EL9 are evaluated by panel coker test as described above. The results obtained for the heavy duty diesel lubricants are as follows:

	CLE2	EL6	EL7	EL8	EL9
Rating	46	69	67	62	55

[0141] The data indicates that adding a quaternised polyester salt of the present invention increases the panel coker rating. This means that the addition of quaternised polyester salt improves deposit cleanliness.

[0142] The combination of succinimide dispersant and quaternised polyester salt of the present invention is further evaluated in the following examples and panel coker analysis. Examples EL10, EL11, and CLE1 relate to passenger car gasoline engine lubricants, and CLE2, EL12, and EL13 relate to heavy duty diesel engine lubricants.

[0143] Engine Lubricant 10 (EL10): is a passenger car gasoline engine lubricant. EL10 is an API SM capable 5W-30 Lubricant containing 0 wt % of a succinimide dispersant, and 2 wt % of the product of Example 4. The lubricant also contains 1.25 wt % of an antioxidant system (containing a mixture of aminic, phenolic and sulphur-containing antioxidants), 0.91 wt % of a zinc dialkyldithiophosphate, 0.62 wt % of an ethylene-propylene copolymer viscosity modifier, 0.14 wt % of pour point depressant, a 0.91 wt % of detergent system (containing a mixture of a sodium overbased sulphonate and calcium overbased sulphonate), 11 ppm of siloxane antifoam agent, and balance API Group II base oil.

[0144] Engine Lubricant 11 (EL11): is a passenger car gasoline engine lubricant. EL11 is an API SM capable 5W-30 Lubricant containing 1 wt % of a succinimide dispersant, and 1 wt % of the product of Example 4. The lubricant also contains 1.25 wt % of an antioxidant system (containing a mixture of aminic, phenolic and sulphur-containing antioxidants), 0.91 wt % of a zinc dialkyldithiophosphate, 0.62 wt % of an ethylene-propylene copolymer viscosity modifier, 0.14 wt % of pour point depressant, a 0.91 wt % of detergent system (containing a mixture of a sodium overbased sulphonate and calcium overbased sulphonate), 11 ppm of siloxane antifoam agent, and balance API Group II base oil.

[0145] Employing the panel coker test described above, CLE1, EL10 and EL11 are evaluated for deposit cleanliness. The results obtained are as follows:

	CLE1	EL10	EL11
Rating	55	69	77

[0146] The results obtained for CLE1, EL10 and EL11 indicate that whilst a lubricant containing dispersant of only the quaternised polyester salt of the present invention (i.e., EL10) does improve deposit cleanliness over CLE1 (i.e., rating increase from 55 to 69), even better results are obtained when both the succinimide dispersant and quaternised polyester salt are employed (i.e., as in EL11) with a rating of 77.

[0147] Engine Lubricant 12 (EL12): is an API CJ-4 capable 15W-40 Lubricant containing 0 wt % of a succinimide dispersant, and 4.1 wt % of the product of Example 4. The lubricant also contains 1.23 wt % of an antioxidant system (containing a mixture of aminic, phenolic and sulphur-containing antioxidants), 0.99 wt % of a zinc dialkyldithiophosphate, 1.24 wt % of an ethylene-propylene copolymer viscosity modifier, 0.08 wt % of pour point depressant, a 1.71 wt % of detergent system (containing a mixture of a sodium overbased sulphonate and calcium overbased sulphonate), 100 ppm of siloxane antifoam agent, 0.12 wt % of corrosion inhibitor, and balance API Group II base oil.

[0148] Engine Lubricant 13 (EL13): is an API CJ-4 capable 15W-40 Lubricant containing 2.05 wt % of a succinimide dispersant, and 2.05 wt % of the product of Example 4. The lubricant also contains 1.23 wt % of an antioxidant system (containing a mixture of aminic, phenolic and sulphur-containing antioxidants), 0.99 wt % of a zinc dialkyldithiophosphate, 1.24 wt % of an ethylene-propylene copolymer viscosity modifier, 0.08 wt % of pour point depressant, a 1.71 wt % of detergent system (containing a mixture of a sodium overbased sulphonate and calcium overbased sulphonate), 100 ppm of siloxane antifoam agent, 0.12 wt % of corrosion inhibitor, and balance API Group II base oil.

[0149] Employing the panel coker test described above, CLE2, EL12 and EL13 are evaluated for deposit cleanliness. The results obtained are as follows:

	CLE2	EL12	EL13
Rating	46	58	66

[0150] The results obtained for CLE2, EL12 and EL13 indicate that whilst a lubricant containing dispersant of only the quaternised polyester salt of the present invention (i.e., EL12) does improve deposit cleanliness over CLE2 (i.e.,

rating increase from 46 to 58), even better results are obtained when both the succinimide dispersant and quaternised polyester salt are employed (i.e., as in EL13) with a rating of 66.

[0151] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. The products formed thereby, including the products formed upon employing lubricant composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses lubricant composition prepared by admixing the components described above.

[0152] Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention may be used together with ranges or amounts for any of the other elements.

[0153] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include: hydrocarbon substituents, including aliphatic, alicyclic, and aromatic substituents; substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in

the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent; and hetero substituents, that is, substituents which similarly have a predominantly hydrocarbon character but contain other than carbon in a ring or chain. A more detailed definition of the term "hydrocarbyl substituent" or "hydrocarbyl group" is described in paragraphs [0118] to [0119] of International Publication WO2008147704, or a similar definition in paragraphs [0137] to [0141] of published application US 2010-0197536.

[0154] While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

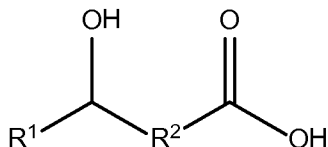
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What is claimed is:

1. A lubricating composition comprising an oil of lubricating viscosity and a quaternised polyester salt which comprises a product obtained/obtainable by reaction of (i) a polyester containing a tertiary amino group; and (ii) a quaternising agent suitable for converting the tertiary amino group to a quaternary nitrogen, wherein the quaternising agent is selected from the group consisting of a dialkyl sulphate, a benzyl halide, an organic carbonate, an ester of a polycarboxylic acid, an organic epoxide in combination with an acid, and mixtures thereof.

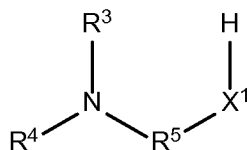
2. The lubricating composition of claim 1 wherein the polyester comprises the reaction product of a fatty carboxylic acid containing at least one hydroxyl group and a compound having an oxygen or nitrogen atom capable of condensing with said acid and further having a tertiary amino group.

3. The lubricating composition of claim 2 wherein the fatty carboxylic acid is represented by the formula:



where R^1 is a hydrogen or a hydrocarbyl group containing from 1 to 20 carbon atoms and R^2 is a hydrocarbylene group containing from 1 to 20 carbon atoms, with the proviso that the total number of carbon atoms present from R^1 and R^2 is 6 or more, or 8 or more; and

wherein the compound having an oxygen or nitrogen atom capable of condensing with said acid and further having a tertiary amino group is represented by the formula:

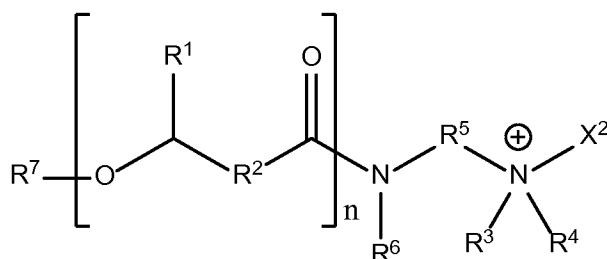


where R^3 is a hydrocarbyl group containing from 1 to 10 carbon atoms; R^4 is a hydrocarbyl group containing from 1 to 10 carbon atoms; R^5 is a hydrocarbylene

group containing from 1 to 20 carbon atoms; and X^1 is O or NR^6 where R^6 is a hydrogen or a hydrocarbyl group containing from 1 to 10 carbon atoms.

4. The lubricating composition of any preceding claim, wherein the quaternised polyester salt comprises a quaternised polyester amide salt wherein the polyester containing a tertiary amino group used to prepare said quaternised polyester salt comprises a polyester amide containing a tertiary amino group.

5. The lubricating composition of any preceding claim, wherein the quaternised polyester salt comprises a cation represented by the following formula:



where R^1 is a hydrogen or a hydrocarbyl group containing from 1 to 20 carbon atoms and R^2 is a hydrocarbylene group containing from 1 to 20 carbon atoms; R^3 is a hydrocarbyl group containing from 1 to 10 carbon atoms; R^4 is a hydrocarbyl group containing from 1 to 10 carbon atoms; R^5 is a hydrocarbylene group containing from 1 to 20 carbon atoms; R^6 is a hydrogen or a hydrocarbyl group containing from 1 to 10 carbon atoms; n is a number from 1 to 10; R^7 is hydrogen, a hydrocarbyl-substituted carbonyl group containing from 1 to 22 carbon atoms, or a hydrocarbyl group containing from 1 to 22 carbon atoms; and X^2 is a group derived from the quaternising agent.

6. The lubricating composition of claim 2 wherein the compound having an oxygen or nitrogen atom capable of condensing with said acid and further having a tertiary amino group comprises N,N-diethylethylenediamine, N,N-dimethylethylenediamine, N,N-dibutylethylenediamine, N,N-dimethyl-1,3-diaminopropane, N,N-diethyl-1,3-diaminopropane, N,N-dimethylaminoethanol, N,N-diethylaminoethanol, or combinations thereof.

7. The lubricating composition of claim 2 wherein the fatty carboxylic acid containing at least one hydroxyl group comprises: 12-hydroxystearic acid; ricinoleic acid; 12-hydroxy dodecanoic acid; 5-hydroxy

dodecanoic acid; 5-hydroxy decanoic acid; 4-hydroxy decanoic acid; 10-hydroxy undecanoic acid; or combinations thereof.

8. The lubricating composition of any preceding claim, wherein the quaternising agent comprises ethylene oxide, propylene oxide, butylene oxide, styrene oxide, or combinations thereof in combination with an acid.

9. The lubricating composition of any preceding claim, wherein the quaternised polyester salt is present at 0.1 wt % to 10 wt %, or 1 wt % to 8 wt %, or 2 wt % to 6.5 wt % of the lubricating composition.

10. The lubricating composition of any preceding claim further comprising a dispersant.

11. The lubricating composition of claim 10, wherein the dispersant is a succinimide dispersant, a Mannich dispersant, a succinamide dispersant, a polyolefin succinic acid ester, amide, or ester-amide, or mixtures thereof.

12. The lubricating composition of any preceding claim 10 to 11, wherein the dispersant is a succinimide dispersant, or mixtures thereof.

13. The lubricating composition of any preceding claim 10 to 12, wherein the dispersant is a polyisobutylene succinimide, wherein the polyisobutylene from which the polyisobutylene succinimide is derived has a number average molecular weight in the range of 350 to 5000, or 500 to 3000, or 750 to 2200.

14. The lubricating composition of any preceding claim 10 to 13, wherein the dispersant is a polyisobutylene succinimide derived from an aliphatic polyamine selected from the group consisting of ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenhexamine, polyamine still bottoms, and mixtures thereof.

15. The lubricating composition of any preceding claim 10 to 14, wherein the dispersant is a polyisobutylene succinimide derived from an aliphatic polyamine selected from the group consisting of tetraethylenepentamine, pentaethylenhexamine, polyamine still bottoms, and mixtures thereof.

16. The lubricating composition of any preceding claim 10 to 15, wherein the dispersant is a polyisobutylene succinimide having a carbocyclic ring present on less than 50 mole % of the dispersant molecules.

17. The lubricating composition of any preceding claim 10 to 15, wherein the dispersant is a polyisobutylene succinimide having a carbocyclic ring present on 50 mole % or more of the dispersant molecules.

18. The lubricating composition of any preceding claim 10 to 17, wherein the dispersant is present at 0.1 wt % to 15 wt %, or 0.5 wt % to 9 wt %, or 1 wt % to 8.5 wt % of the lubricating composition.

19. A method of lubricating an internal combustion engine comprising supplying to the internal combustion engine a lubricating composition of any preceding claim 1 to 18.

20. The method of claim 19, wherein the internal combustion engine has a steel surface on a cylinder bore, cylinder block, or piston ring.

21. The method of claim 19, wherein the internal combustion engine has a surface of steel, or an aluminium alloy, or an aluminium composite.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/042882

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10M133/06 C10M133/08 C10M149/14
ADD. C10N30/04 C10N40/25

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EP0-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2008/026973 A1 (NELSON DAVID C [GB] ET AL) 31 January 2008 (2008-01-31) cited in the application paragraphs [0088], [0090]; claim 1; examples 1,2 -----	1-21
X	WO 2009/156393 A1 (SHELL INT RESEARCH [NL]; FRANK JANE ELIZABETH [GB]; SOUTHBY MARK CLIFT) 30 December 2009 (2009-12-30) cited in the application page 12, lines 12-19; table 1 -----	1-21
X	WO 2010/149712 A1 (SHELL INT RESEARCH [NL]; KRUCHININ DENNIS BORISOVICH [GB]; TREDGET CAR) 29 December 2010 (2010-12-29) page 14, lines 3-10; table 3 ----- -/-	1-21

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

3 September 2012

Date of mailing of the international search report

17/09/2012

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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2012/042882

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 139 692 A (POWELL BOB R [US] ET AL) 18 August 1992 (1992-08-18) column 3, lines 4-10; claim 1 -----	1-7

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2012/042882

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US 5139692	A	18-08-1992	NONE
