

LIQUID FUEL COMPOSITIONS

Field of the Invention

The present invention relates to liquid fuel compositions comprising a major portion of a base fuel suitable for use in an internal combustion engine, in particular liquid fuel compositions comprising a major portion of a base fuel suitable for use in an internal combustion engine and a hyperdispersant.

Background of the Invention

EP 0164817 A2 discloses a surfactant comprising a carboxylic acid ester or amide carrying a terminal strong acid group selected from carboxymethyl, sulphate, sulphonate, phosphate and phosphonate, suitable for stabilising dispersions of solids in organic liquids and oil/water emulsions. A preferred species of the surfactant is a poly(hydroxyalkanecarboxylic acid) having the strong acid group attached, either directly or through a linking group, to a terminal hydroxy or carboxylic acid group. The use of such surfactants in fuels is not disclosed therein.

EP 0233684 A1 discloses an ester or polyester having (i) a terminal group containing at least two aliphatic carbon-carbon double bonds and (ii) an acidic or basic amino group which is suitable for use as a dispersant for solids in organic liquids. The use of such surfactants in fuels is not disclosed therein.

GB 2197312 A discloses oil soluble dispersant additives, wherein said dispersant additives are poly (C₅-C₉ lactone) adducts which have been prepared by first reacting a C₅-C₉ lactone with a polyamine, a polyol or an amino alcohol to form an intermediate adduct, whereafter

the intermediate adduct is reacted with an aliphatic hydrocarbyl monocarboxylic or dicarboxylic acylating agent having from about 1 to about 165 total carbon atoms. The use of the dispersant additives in lubricating oils and fuels is also disclosed in GB 2197312 A.

EP 0802255 A2 discloses hydroxyl group containing acylated nitrogen compounds which are useful as low chlorine containing additives for lubricating oils and normally liquid fuels and a process for preparing the compounds.

WO 00/34418 A1 discloses the use of poly(hydroxycarboxylic acid)amide or -ester derivatives in fuel compositions as a lubricity additive. It is also disclosed in WO 00/34418 A1 that the use of the poly(hydroxycarboxylic acid)amide or -ester derivatives disclosed therein may also result in attaining one or more of a number of effects such as inlet system cleanliness (intake valves, fuel injectors, carburetors), combustion chamber cleanliness (in each case either or both of keep clean and clean-up effects), anti-corrosion (including anti-rust) and reduction or elimination of valve-stick.

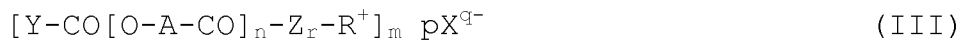
It has now been found that the use of poly(hydroxycarboxylic acid) amide salt derivatives can also surprisingly provides benefits in terms of improving the lubricity of liquid fuel compositions incorporated them.

Summary of the Invention

The present invention provides a liquid fuel composition comprising:

- a liquid base fuel suitable for use in an internal combustion engine; and

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



wherein Y is hydrogen or an optionally substituted hydrocarbyl group, A is a divalent optionally substituted hydrocarbyl group, n is from 1 to 100, 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 0 or 1, R^+ is an ammonium group and X^{q-} is an anion.

The present invention further provides a method for preparing a liquid fuel composition of the present invention comprising admixing the one or more poly(hydroxycarboxylic acid) amide salt derivatives with a base fuel suitable for use in an internal combustion engine.

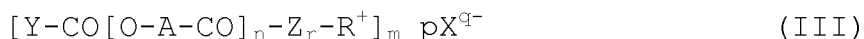
The present invention yet further provides a method of operating an internal combustion engine, which method involves introducing into a combustion chamber of the engine a liquid fuel composition according to the present invention

Detailed Description of the Invention

The liquid fuel composition of the present invention comprises a base fuel suitable for use in an internal combustion engine and one or more poly(hydroxycarboxylic acid) amide salt derivatives. Typically, the base fuel suitable for use in an internal combustion engine is a gasoline or a diesel fuel, and therefore the liquid fuel composition of the present invention is typically a gasoline composition or a diesel fuel composition.

The poly(hydroxycarboxylic acid) amide salt derivatives used in the present invention may also be referred to as hyperdispersants.

The one or more poly(hydroxycarboxylic acid) amide salt derivatives in the liquid fuel compositions of the present invention are poly(hydroxycarboxylic acid) amide salt derivatives having formula (III):



wherein Y is hydrogen or optionally substituted hydrocarbyl group, A is a divalent optionally substituted hydrocarbyl group, n is from 1 to 100, 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 0 or 1, R^+ is an ammonium group and X^{q-} is an anion.

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

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

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 6 to 25 carbon atoms, more preferably in the range of from 8 to 24 carbon atoms, more preferably in the range of from 10 to 22 carbon atoms, and most preferably in the range of from 12 to 20 carbon atoms.

Preferably, in said compound of formula (III), there are at least 4 carbon atoms, more preferably at least 6 carbon atoms, and even 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.

In the compound of formula (III), the optional substituents in the group A are preferably selected from hydroxy, halo or alkoxy groups, especially C₁₋₄ alkoxy groups.

In formula (III) (and formula (I)), n is in the range of from 1 to 100. Preferably, the lower limit of the range for n is 1, more preferably 2, even more preferably 3; preferably the upper limit of the range for n is 100, more preferably 60, more preferably 40, more preferably 20, and even more preferably 10 (i.e. n may be selected from any of the following ranges: from 1 to 100; from 2 to 100; from 3 to 100; from 1 to 60; from 2 to 60; from 3 to 60; from 1 to 40; from 2 to 40; from 3 to 40; from 1 to 20; from 2 to 20; from 3 to 20; from 1 to 10; from 2 to 10; and, from 3 to 10).

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

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, heptadenyl, heptadecadienyl, stearyl, oleyl and linoleyl.

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

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 sulfoxyl. 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.

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 sulfoxyl in a substituted hydrocarbyl group will displace a -CH- or -CH₂- moiety of the hydrocarbyl.

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

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.

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



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

Examples of hydrocarbyl groups that may represent R^1 include methyl, ethyl, n-propyl, n-butyl and octadecyl.

10 Examples of optionally substituted alkylene groups that may represent B include ethylene, trimethylene, tetramethylene and hexamethylene.

Examples of preferred Z moieties in formula (III) include $\text{-NHCH}_2\text{CH}_2\text{-}$, $\text{-NHCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{-}$ and $\text{-NH}(\text{CH}_2)_3\text{-}$.

15 In formula (III), r is preferably 1, i.e. the poly(hydroxycarboxylic acid) amide salt derivative having formula (III) must contain the optionally substituted divalent bridging group Z.

Preferably, R^+ may be represented by formula (V)



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

The anion $\text{X}^{\text{q-}}$ of the compound of formula (III) is not critical and can be any anion (or mixture of anions) suitable to balance the positive charge of the
 25 poly(hydroxycarboxylic acid) amide cation.

The anion X^{q-} of the compound of formula (III) may conveniently be a sulphur-containing anion, such as an anion selected from sulphate and sulphonate anions.

However, since it is desirable to maintain a low sulphur content in gasoline and diesel fuels, the use of non-sulphur-containing anions in the compounds of formula (III) may be desirable depending upon the concentration of sulphur in the liquid base fuel and/or the desired concentration of sulphur in the liquid fuel composition containing the one or more poly(hydroxycarboxylic acid) amide salt derivatives.

Therefore, the anion X^{q-} of the compound of formula (III) can also be any non-sulphur-containing anion (or mixture of anions) suitable to balance the positive charge of the poly(hydroxycarboxylic acid) amide cation, such as a non-sulphur-containing organic anion or a non-sulphur-containing inorganic anion.

Non-limiting examples of suitable anions are OH^- , CH^- , NH_3^- , HCO_3^- , $HCOO^-$, CH_3COO^- , H^- , BO_3^{3-} , CO_3^{2-} , $C_2H_3O_2^-$, HCO^{2-} , $C_2O_4^{2-}$, $HC_2O_4^-$, NO_3^- , NO_2^- , N^{3-} , NH_2^- , O^{2-} , O_2^{2-} , BeF_3^- , F^- , Na^- , $[Al(H_2O)_2(OH)_4]^-$, SiO_3^{2-} , SiF_6^{2-} , $H_2PO_4^-$, P^{3-} , PO_4^{3-} , HPO_4^{2-} , Cl^- , ClO_3^- , ClO_4^- , ClO^- , KO^- , $SbOH_6^-$, $SnCl_6^{2-}$, $[SnTe_4]^{4-}$, CrO_4^{2-} , $Cr_2O_7^{2-}$, MnO_4^- , $NiCl_6^{2-}$, $[Cu(CO_3)_2(OH)_2]^{4-}$, AsO_4^{3-} , Br^- , BrO_3^- , IO_3^- , I^- , CN^- , OCN^- , etc.

Suitable anions may also include anions derived from compounds containing a carboxylic acid group (e.g. a carboxylate anion), anions derived from compounds containing a hydroxyl group (e.g. an alkoxide, phenoxide or enolate anion), nitrogen based anions such as nitrate and nitrite, phosphorus based anions such as phosphates and phosphonates, or mixtures thereof.

Non-limiting examples of suitable anions derived from compounds containing a carboxylic acid group include acetate, oleate, salicylate anions, and mixtures thereof.

Non-limiting examples of suitable anions derived from compounds containing a hydroxyl group include phenate anions, and mixtures thereof.

In a preferred embodiment of the present invention, the anion X^{q-} is a non-sulfur-containing anion selected from the group consisting of OH, a phenate group, a salicylate group, an oleate group and an acetate group; more preferably the anion X^{q-} is OH.

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



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

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).

Hydrocarbyl groups may be aromatic, aliphatic, acyclic or cyclic groups. Preferably, hydrocarbyl groups are aryl, cycloalkyl, alkyl or alkenyl, in which case they may be straight-chain or branched-chain groups.

Representative hydrocarbyl groups include phenyl, naphthyl, methyl, ethyl, butyl, pentyl, methylpentyl, hexenyl, dimethylhexyl, octenyl, cyclooctenyl, methylcyclooctenyl, dimethylcyclooctyl, ethylhexyl,

octyl, isooctyl, dodecyl, hexadecenyl, eicosyl, hexacosyl, triacontyl and phenylethyl.

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.

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.

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

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 sulfoxyl. 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.

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

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

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.

In one embodiment of the present invention, at least one of, or all of, the one or more poly(hydroxycarboxylic acid) amide salt derivatives are sulphur-containing poly(hydroxycarboxylic acid) amide salt derivatives.

In such an embodiment, said one or more poly(hydroxycarboxylic acid) amide salt derivatives preferably have a sulphur content of at most 2.5 wt.%, such as a sulphur content in the range of from 0.1 to 2.0 wt.%, conveniently 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.

In another embodiment of the present invention, the one or more poly(hydroxycarboxylic acid) amide salt

derivatives are non-sulphur-containing
poly(hydroxycarboxylic acid) amide salt derivatives.

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

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



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

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

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.

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

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.

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.

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 6 to 25 carbon atoms, more preferably in the range of from 8 to 24 carbon atoms, more preferably in the range of from 10 to 22 carbon atoms, and most preferably in the range of from 12 to 20 carbon atoms.

Preferably, in said compounds of formulae (I) and (II), there are at least 4 carbon atoms, more preferably at least 6 carbon atoms, and even 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.

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

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

Examples of suitable hydroxycarboxylic acids are 9-hydroxystearic acid, 10-hydroxystearic acid,

12-hydroxystearic acid, 12-hydroxy-9-oleic acid (ricinoleic acid), 6-hydroxycaproic acid, preferably 12-hydroxystearic acid. Commercial 12-hydroxystearic acid (hydrogenated castor oil fatty acid) normally contains up to 15% wt of stearic acid and other non-hydroxycarboxylic acids as impurities and can conveniently be used without further admixture to produce a polymer of molecular weight about 1000-2000.

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.

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

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

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.

For example, various amines and their preparations are described in US 3 275 554, US 3 438 757, US 3 454 555, US 3 565 804, US 3 755 433 and US 3 822 209.

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

Preferred amine reactants are diamines selected from ethylenediamine, N,N-dimethyl-1,3-propanediamine, triamines and polyamines selected from

diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine and tris(2-aminoethyl)amine.

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.

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

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

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

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

WO 95/17473 discloses poly(hydroxycarboxylic acid) amide derivatives with amines such as 3-dimethylaminopropylamine, ethylenediamine, poly(ethyleneimine) (PEI) having a molecular weight (MW) greater than 500 and amines of the formula of

$\text{NH}_2\text{-R}'\text{-N(R}'')\text{-R}'''\text{-NH}_2$ for use in a method of preparing a non-aqueous dispersion of copper phthalocyanine.

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

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

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

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

Acids that may be used to form the salt derivative may be selected from organic or inorganic acids. Said acids are conveniently selected from carboxylic acids, nitrogen-containing organic and inorganic acids, sulphur-containing organic or inorganic acids (such as sulphuric acid, methanesulphonic acid and benzenesulphonic acid).

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.

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

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

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
15 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.

Examples of poly(hydroxycarboxylic acid) amide salt derivatives that are available commercially include that
20 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
25 trade designations "CH-5" and "CH-7" from Shanghai Sanzheng Polymer Company.

In the liquid fuel compositions of the present invention, if the base fuel used is a gasoline, then the gasoline may be any gasoline suitable for use in an
30 internal combustion engine of the spark-ignition (petrol) type known in the art. The gasoline used as the base fuel in the liquid fuel composition of the present

invention may conveniently also be referred to as 'base gasoline'.

Gasolines typically comprise mixtures of hydrocarbons boiling in the range from 25 to 230 °C (EN-ISO 3405), the optimal ranges and distillation curves typically varying according to climate and season of the year. The hydrocarbons in a gasoline may be derived by any means known in the art, conveniently the hydrocarbons may be derived in any known manner from straight-run gasoline, synthetically-produced aromatic hydrocarbon mixtures, thermally or catalytically cracked hydrocarbons, hydro-cracked petroleum fractions, catalytically reformed hydrocarbons or mixtures of these.

The specific distillation curve, hydrocarbon composition, research octane number (RON) and motor octane number (MON) of the gasoline are not critical.

Conveniently, the research octane number (RON) of the gasoline may be at least 80, for instance in the range of from 80 to 110, preferably the RON of the gasoline will be at least 90, for instance in the range of from 90 to 110, more preferably the RON of the gasoline will be at least 91, for instance in the range of from 91 to 105, even more preferably the RON of the gasoline will be at least 92, for instance in the range of from 92 to 103, even more preferably the RON of the gasoline will be at least 93, for instance in the range of from 93 to 102, and most preferably the RON of the gasoline will be at least 94, for instance in the range of from 94 to 100 (EN 25164); the motor octane number (MON) of the gasoline may conveniently be at least 70, for instance in the range of from 70 to 110, preferably the MON of the gasoline will be at least 75, for instance in the range of from 75 to 105, more preferably the MON

of the gasoline will be at least 80, for instance in the range of from 80 to 100, most preferably the MON of the gasoline will be at least 82, for instance in the range of from 82 to 95 (EN 25163).

5 Typically, gasolines comprise components selected from one or more of the following groups; saturated hydrocarbons, olefinic hydrocarbons, aromatic hydrocarbons, and oxygenated hydrocarbons. Conveniently, the gasoline may comprise a mixture of saturated
10 hydrocarbons, olefinic hydrocarbons, aromatic hydrocarbons, and, optionally, oxygenated hydrocarbons.

 Typically, the olefinic hydrocarbon content of the gasoline is in the range of from 0 to 40 percent by volume based on the gasoline (ASTM D1319); preferably,
15 the olefinic hydrocarbon content of the gasoline is in the range of from 0 to 30 percent by volume based on the gasoline, more preferably, the olefinic hydrocarbon content of the gasoline is in the range of from 0 to 20 percent by volume based on the gasoline.

20 Typically, the aromatic hydrocarbon content of the gasoline is in the range of from 0 to 70 percent by volume based on the gasoline (ASTM D1319), for instance the aromatic hydrocarbon content of the gasoline is in the range of from 10 to 60 percent by volume based on the
25 gasoline; preferably, the aromatic hydrocarbon content of the gasoline is in the range of from 0 to 50 percent by volume based on the gasoline, for instance the aromatic hydrocarbon content of the gasoline is in the range of from 10 to 50 percent by volume based on the gasoline.

30 The benzene content of the gasoline is at most 10 percent by volume, more preferably at most 5 percent by volume, especially at most 1 percent by volume based on the gasoline.

The gasoline preferably has a low or ultra low sulphur content, for instance at most 1000 ppmw (parts per million by weight), preferably no more than 500 ppmw, more preferably no more than 100, even more preferably no more than 50 and most preferably no more than even 10 ppmw.

The gasoline also preferably has a low total lead content, such as at most 0.005 g/l, most preferably being lead free - having no lead compounds added thereto (i.e. unleaded).

When the gasoline comprises oxygenated hydrocarbons, at least a portion of non-oxygenated hydrocarbons will be substituted for oxygenated hydrocarbons. The oxygen content of the gasoline may be up to 35 percent by weight (EN 1601) (e.g. ethanol per se) based on the gasoline. For example, the oxygen content of the gasoline may be up to 25 percent by weight, preferably up to 10 percent by weight. Conveniently, the oxygenate concentration will have a minimum concentration selected from any one of 0, 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 percent by weight, and a maximum concentration selected from any one of 5, 4.5, 4.0, 3.5, 3.0, and 2.7 percent by weight.

Examples of oxygenated hydrocarbons that may be incorporated into the gasoline include alcohols, ethers, esters, ketones, aldehydes, carboxylic acids and their derivatives, and oxygen containing heterocyclic compounds. Preferably, the oxygenated hydrocarbons that may be incorporated into the gasoline are selected from alcohols (such as methanol, ethanol, propanol, iso-propanol, butanol, tert-butanol and iso-butanol), ethers (preferably ethers containing 5 or more carbon atoms per molecule, e.g., methyl tert-butyl ether) and esters (preferably esters containing 5 or more carbon atoms per

molecule); a particularly preferred oxygenated hydrocarbon is ethanol.

When oxygenated hydrocarbons are present in the gasoline, the amount of oxygenated hydrocarbons in the gasoline may vary over a wide range. For example, gasolines comprising a major proportion of oxygenated hydrocarbons are currently commercially available in countries such as Brazil and U.S.A, e.g. ethanol per se and E85, as well as gasolines comprising a minor proportion of oxygenated hydrocarbons, e.g. E10 and E5. Therefore, the gasoline may contain up to 100 percent by volume oxygenated hydrocarbons. Preferably, the amount of oxygenated hydrocarbons present in the gasoline is selected from one of the following amounts: up to 85 percent by volume; up to 65 percent by volume; up to 30 percent by volume; up to 20 percent by volume; up to 15 percent by volume; and, up to 10 percent by volume, depending upon the desired final formulation of the gasoline. Conveniently, the gasoline may contain at least 0.5, 1.0 or 2.0 percent by volume oxygenated hydrocarbons.

Examples of suitable gasolines include gasolines which have an olefinic hydrocarbon content of from 0 to 20 percent by volume (ASTM D1319), an oxygen content of from 0 to 5 percent by weight (EN 1601), an aromatic hydrocarbon content of from 0 to 50 percent by volume (ASTM D1319) and a benzene content of at most 1 percent by volume.

Whilst not critical to the present invention, the base gasoline or the gasoline composition of the present invention may conveniently additionally include one or more fuel additive. The concentration and nature of the fuel additive(s) that may be included in the base

gasoline or the gasoline composition of the present invention is not critical. Non-limiting examples of suitable types of fuel additives that can be included in the base gasoline or the gasoline composition of the present invention include anti-oxidants, corrosion inhibitors, detergents, dehazers, antiknock additives, metal deactivators, valve-seat recession protectant compounds, dyes, friction modifiers, carrier fluids, diluents and markers. Examples of suitable such additives are described generally in US Patent No. 5,855,629.

Conveniently, the fuel additives can be blended with one or more diluents or carrier fluids, to form an additive concentrate, the additive concentrate can then be admixed with the base gasoline or the gasoline composition of the present invention.

The (active matter) concentration of any additives present in the base gasoline or the gasoline composition of the present invention is preferably up to 1 percent by weight, more preferably in the range from 5 to 1000 ppmw, advantageously in the range of from 75 to 300 ppmw, such as from 95 to 150 ppmw.

In the liquid fuel compositions of the present invention, if the base fuel used is a diesel fuel, then the diesel fuel used as the base fuel in the present invention includes diesel fuels for use in automotive compression ignition engines, as well as in other types of engine such as for example marine, railroad and stationary engines. The diesel fuel used as the base fuel in the liquid fuel composition of the present invention may conveniently also be referred to as 'diesel base fuel'.

The diesel base fuel may itself comprise a mixture of two or more different diesel fuel components, and/or be additivated as described below.

Such diesel fuels will contain one or more base fuels which may typically comprise liquid hydrocarbon middle distillate gas oil(s), for instance petroleum derived gas oils. Such fuels will typically have boiling points within the usual diesel range of 150 to 400°C, depending on grade and use. They will typically have a density from 750 to 1000 kg/m³, preferably from 780 to 860 kg/m³, at 15°C (e.g. ASTM D4502 or IP 365) and a cetane number (ASTM D613) of from 35 to 120, more preferably from 40 to 85. They will typically have an initial boiling point in the range 150 to 230°C and a final boiling point in the range 290 to 400°C. Their kinematic viscosity at 40°C (ASTM D445) might suitably be from 1.2 to 4.5 mm²/s.

An example of a petroleum derived gas oil is a Swedish Class 1 base fuel, which will have a density from 800 to 820 kg/m³ at 15°C (SS-EN ISO 3675, SS-EN ISO 12185), a T95 of 320°C or less (SS-EN ISO 3405) and a kinematic viscosity at 40°C (SS-EN ISO 3104) from 1.4 to 4.0 mm²/s, as defined by the Swedish national specification EC1.

Optionally, non-mineral oil based fuels, such as biofuels or Fischer-Tropsch derived fuels, may also form or be present in the diesel fuel. Such Fischer-Tropsch fuels may for example be derived from natural gas, natural gas liquids, petroleum or shale oil, petroleum or shale oil processing residues, coal or biomass.

The amount of Fischer-Tropsch derived fuel used in the diesel fuel may be from 0% to 100%v of the overall diesel fuel, preferably from 5% to 100%v, more preferably

from 5% to 75%v. It may be desirable for such a diesel fuel to contain 10%v or greater, more preferably 20%v or greater, still more preferably 30%v or greater, of the Fischer-Tropsch derived fuel. It is particularly preferred for such diesel fuels to contain 30 to 75%v, and particularly 30 or 70%v, of the Fischer-Tropsch derived fuel. The balance of the diesel fuel is made up of one or more other diesel fuel components.

Such a Fischer-Tropsch derived fuel component is any fraction of the middle distillate fuel range, which can be isolated from the (optionally hydrocracked) Fischer-Tropsch synthesis product. Typical fractions will boil in the naphtha, kerosene or gas oil range. Preferably, a Fischer-Tropsch product boiling in the kerosene or gas oil range is used because these products are easier to handle in for example domestic environments. Such products will suitably comprise a fraction larger than 90 wt% which boils between 160 and 400°C, preferably to about 370°C. Examples of Fischer-Tropsch derived kerosene and gas oils are described in EP-A-0583836, WO-A-97/14768, WO-A-97/14769, WO-A-00/11116, WO-A-00/11117, WO-A-01/83406, WO-A-01/83648, WO-A-01/83647, WO-A-01/83641, WO-A-00/20535, WO-A-00/20534, EP-A-1101813, US-A-5766274, US-A-5378348, US-A-5888376 and US-A-6204426.

The Fischer-Tropsch product will suitably contain more than 80 wt% and more suitably more than 95 wt% iso and normal paraffins and less than 1 wt% aromatics, the balance being naphthenics compounds. The content of sulphur and nitrogen will be very low and normally below the detection limits for such compounds. For this reason the sulphur content of a diesel fuel composition containing a Fischer-Tropsch product may be very low.

The diesel fuel composition preferably contains no more than 5000ppmw sulphur, more preferably no more than 500ppmw, or no more than 350ppmw, or no more than 150ppmw, or no more than 100ppmw, or no more than 70ppmw, or no more than 50ppmw, or no more than 30ppmw, or no more than 20ppmw, or most preferably no more than 15ppmw sulphur.

The diesel base fuel may itself be additivated (additive-containing) or unadditivated (additive-free). If additivated, e.g. at the refinery, it will contain minor amounts of one or more additives selected for example from anti-static agents, pipeline drag reducers, flow improvers (e.g. ethylene/vinyl acetate copolymers or acrylate/maleic anhydride copolymers), lubricity additives, antioxidants and wax anti-settling agents.

Detergent-containing diesel fuel additives are known and commercially available. Such additives may be added to diesel fuels at levels intended to reduce, remove, or slow the build up of engine deposits.

Examples of detergents suitable for use in diesel fuel additives for the present purpose include polyolefin substituted succinimides or succinamides of polyamines, for instance polyisobutylene succinimides or polyisobutylene amine succinamides, aliphatic amines, Mannich bases or amines and polyolefin (e.g. polyisobutylene) maleic anhydrides. Succinimide dispersant additives are described for example in GB-A-960493, EP-A-0147240, EP-A-0482253, EP-A-0613938, EP-A-0557516 and WO-A-98/42808. Particularly preferred are polyolefin substituted succinimides such as polyisobutylene succinimides.

The diesel fuel additive mixture may contain other components in addition to the detergent. Examples are

lubricity enhancers; dehazers, e.g. alkoxyated phenol
formaldehyde polymers; anti-foaming agents (e.g.
polyether-modified polysiloxanes); ignition improvers
(cetane improvers) (e.g. 2-ethylhexyl nitrate (EHN),
5 cyclohexyl nitrate, di-tert-butyl peroxide and those
disclosed in US-A-4208190 at column 2, line 27 to column
3, line 21); anti-rust agents (e.g. a propane-1,2-diol
semi-ester of tetrapropenyl succinic acid, or polyhydric
alcohol esters of a succinic acid derivative, the
10 succinic acid derivative having on at least one of its
alpha-carbon atoms an unsubstituted or substituted
aliphatic hydrocarbon group containing from 20 to 500
carbon atoms, e.g. the pentaerythritol diester of
polyisobutylene-substituted succinic acid); corrosion
15 inhibitors; reodorants; anti-wear additives;
anti-oxidants (e.g. phenolics such as
2,6-di-tert-butylphenol, or phenylenediamines such as
N,N'-di-sec-butyl-p-phenylenediamine); metal
deactivators; combustion improvers; static dissipator
20 additives; cold flow improvers; and wax anti-settling
agents.

The diesel fuel additive mixture may contain a
lubricity enhancer, especially when the diesel fuel
composition has a low (e.g. 500 ppmw or less) sulphur
25 content. In the additivated diesel fuel composition, the
lubricity enhancer is conveniently present at a
concentration of less than 1000 ppmw, preferably between
50 and 1000 ppmw, more preferably between 70 and 1000
ppmw. Suitable commercially available lubricity
30 enhancers include ester- and acid-based additives. Other
lubricity enhancers are described in the patent
literature, in particular in connection with their use in
low sulphur content diesel fuels, for example in:

- the paper by Danping Wei and H.A. Spikes, "The Lubricity of Diesel Fuels", Wear, III (1986) 217-235;

- WO-A-95/33805 - cold flow improvers to enhance lubricity of low sulphur fuels;

5 - WO-A-94/17160 - certain esters of a carboxylic acid and an alcohol wherein the acid has from 2 to 50 carbon atoms and the alcohol has 1 or more carbon atoms, particularly glycerol monooleate and di-isodecyl adipate, as fuel additives for wear reduction in a diesel engine injection system;

10 - US-A-5490864 - certain dithiophosphoric diester-dialcohols as anti-wear lubricity additives for low sulphur diesel fuels; and

15 - WO-A-98/01516 - certain alkyl aromatic compounds having at least one carboxyl group attached to their aromatic nuclei, to confer anti-wear lubricity effects particularly in low sulphur diesel fuels.

20 It may also be preferred for the diesel fuel composition to contain an anti-foaming agent, more preferably in combination with an anti-rust agent and/or a corrosion inhibitor and/or a lubricity enhancing additive.

25 Unless otherwise stated, the (active matter) concentration of each such additive component in the additivated diesel fuel composition is preferably up to 10000 ppmw, more preferably in the range from 0.1 to 1000 ppmw, advantageously from 0.1 to 300 ppmw, such as from 0.1 to 150 ppmw.

30 The (active matter) concentration of any dehazer in the diesel fuel composition will preferably be in the range from 0.1 to 20 ppmw, more preferably from 1 to 15 ppmw, still more preferably from 1 to 10 ppmw, advantageously from 1 to 5 ppmw. The (active matter)

concentration of any ignition improver present will preferably be 2600 ppmw or less, more preferably 2000 ppmw or less, conveniently from 300 to 1500 ppmw. The (active matter) concentration of any detergent in the diesel fuel composition will preferably be in the range from 5 to 1500 ppmw, more preferably from 10 to 750 ppmw, most preferably from 20 to 500 ppmw.

In the case of a diesel fuel composition, for example, the fuel additive mixture will typically contain a detergent, optionally together with other components as described above, and a diesel fuel-compatible diluent, which may be a mineral oil, a solvent such as those sold by Shell companies under the trade mark "SHELLSOL", a polar solvent such as an ester and, in particular, an alcohol, e.g. hexanol, 2-ethylhexanol, decanol, isotridecanol and alcohol mixtures such as those sold by Shell companies under the trade mark "LINEVOL", especially LINEVOL 79 alcohol which is a mixture of C7-9 primary alcohols, or a C₁₂₋₁₄ alcohol mixture which is commercially available.

The total content of the additives in the diesel fuel composition may be suitably between 0 and 10000 ppmw and preferably below 5000 ppmw.

In the above, amounts (concentrations, % vol, ppmw, % wt) of components are of active matter, i.e. exclusive of volatile solvents/diluent materials.

The liquid fuel composition of the present invention is produced by admixing the one or more poly(hydroxycarboxylic acid) amide salt derivatives with a base fuel suitable for use in an internal combustion engine. If the base fuel to which the one or more poly(hydroxycarboxylic acid) amide salt derivatives is admixed is a gasoline, then the liquid fuel composition

produced is a gasoline composition; likewise, if the base fuel to which the one or more poly(hydroxycarboxylic acid) amide salt derivatives is admixed is a diesel fuel, then the liquid fuel composition produced is a diesel fuel composition.

Preferably, the amount of the one or more poly(hydroxycarboxylic acid) amide salt derivatives present in the liquid fuel composition of the present invention is at least 1 ppmw (part per million by weight), based on the overall weight of the liquid fuel composition. More preferably, the amount of the one or more poly(hydroxycarboxylic acid) amide salt derivatives present in the liquid fuel composition of the present invention additionally accords with one or more of the parameters (i) to (xx) listed below:

- (i) at least 10 ppmw
- (ii) at least 20 ppmw
- (iii) at least 30 ppmw
- (iv) at least 40 ppmw
- (v) at least 50 ppmw
- (vi) at least 60 ppmw
- (vii) at least 70 ppmw
- (viii) at least 80 ppmw
- (ix) at least 90 ppmw
- (x) at least 100 ppmw
- (xi) at most 20 %wt.
- (xii) at most 18 %wt.
- (xiii) at most 16 %wt.
- (xiv) at most 14 %wt.
- (xv) at most 12 %wt.
- (xvi) at most 10 %wt.
- (xvii) at most 8 %wt.
- (xviii) at most 6 %wt.

(xix) at most 4 %wt.

(xx) at most 2 %wt.

Conveniently, the amount of the one or more poly(hydroxycarboxylic acid) amide salt derivatives present in the liquid fuel composition of the present invention may also be at least 200 ppmw, at least 300 ppmw, at least 400 ppmw, at least 500 ppmw, or even at least 1000 ppmw.

Surprisingly, it has been found that the use of the one or more poly(hydroxycarboxylic acid) amide salt derivatives in the liquid fuel compositions can provide significant benefits in terms of improved lubricity of the liquid fuel composition, in particular when the liquid fuel composition is gasoline, relative to the liquid base fuel.

By the term "improved/improving lubricity" used herein, it is meant that the wear scar produced using a high frequency reciprocating rig (HFRR) is reduced.

It has additionally been found that the use of the one or more poly(hydroxycarboxylic acid) amide salt derivatives in liquid fuel compositions can also provide benefits in terms of engine cleanliness, in particular in terms of improved inlet valve deposit keep clean and/or injector nozzle keep clean performance, of an internal combustion engine being fuelled by the liquid fuel composition of the present invention relative to the internal combustion engine being fuelled by the liquid base fuel.

By the term "improved/improving inlet valve deposit keep clean performance", it is meant that the weight of deposit formed on the inlet valve of the engine is reduced relative to the base fuel not containing the one

or more poly(hydroxycarboxylic acid) amide salt derivatives.

By the term "improved/improving injector nozzle keep clean performance", it is meant that the amount of deposit formed on the injector nozzle of the engine is reduced as measured by the loss of engine torque.

It has additionally been found that the use of the one or more poly(hydroxycarboxylic acid) amide salt derivatives in liquid fuel compositions can also provide benefits in terms improved fuel economy of an internal combustion engine being fuelled by the liquid fuel composition of the present invention relative to the internal combustion engine being fuelled by the liquid base fuel.

The present invention therefore also provides a method of improving the lubricity of a liquid base fuel suitable for use in an internal combustion engine, comprising admixing one or more poly(hydroxycarboxylic acid) amide salt derivatives with a major portion of the liquid base fuel suitable for use in an internal combustion engine; a method of improving the inlet valve deposit clean up performance of a liquid base fuel suitable for use in an internal combustion engine, comprising admixing one or more poly(hydroxycarboxylic acid) amide salt derivatives with a major portion of the liquid base fuel suitable for use in an internal combustion engine; a method of improving the injector nozzle keep clean performance of a liquid base fuel suitable for use in an internal combustion engine, comprising admixing one or more poly(hydroxycarboxylic acid) amide salt derivatives with a major portion of the liquid base fuel suitable for use in an internal combustion engine; and, a method of improving the fuel

economy performance of a liquid base fuel suitable for use in an internal combustion engine, comprising admixing one or more poly(hydroxycarboxylic acid) amide salt derivatives with a major portion of the liquid base fuel suitable for use in an internal combustion engine.

It has additionally been found that the use of the one or more poly(hydroxycarboxylic acid) amide salt derivatives in liquid fuel compositions can also provide benefits in terms improving the lubricant performance of an internal combustion engine being fuelled by the liquid fuel composition of the present invention relative to the internal combustion engine being fuelled by the liquid base fuel.

In particular, the improvement in the lubricant performance of the internal combustion engine fuelled by a liquid fuel composition according to the present invention can be observed by the a reduction in the levels of sludge and varnish on specific engine parts, such as sludge on rocker arm covers, cam baffles, timing chain covers, oil pans, oil pan baffles, and valve decks, and varnish on piston skirts and cam baffles.

In particular, it has been found that the use of the one or more poly(hydroxycarboxylic acid) amide salt derivatives in a gasoline compositions can provide benefits in terms inhibiting specific sludge and varnish deposit formation, as measured by ASTM D 6593-07, of an internal combustion engine being fuelled by the gasoline composition of the present invention relative to the internal combustion engine being fuelled by the gasoline base fuel.

Therefore, the present invention also provides a method of improving the performance of the lubricant of an internal combustion engine, said method comprising

fuelling an internal combustion engine containing the engine lubricant with a liquid fuel composition according to the present invention.

It has also been observed that the use of one or more poly(hydroxycarboxylic acid) amide salt derivatives wherein the anion is a non-sulfur-containing anion in a liquid fuel composition can have the additional advantage of improved phosphorus volatility properties of the engine lubricant of an internal combustion engine fuelled by the liquid fuel composition compared to the phosphorus volatility properties of the engine lubricant when one or more poly(hydroxycarboxylic acid) amide salt derivatives wherein the anion is a sulfur-containing anion is used in the liquid fuel composition.

The phosphorus volatility properties of the engine lubricant can conveniently be measured according to the phosphorus emission index (PEI) test, which is also known as the "Selby-Noack PEI test". This test has been described in T.W. Selby, R.J. Bosch and D.C. Fee, "Continued Studies of the Causes of Engine Oil, Phosphorus Volatility - Part 2". SAE 2007-01-1073, the teaching of which is hereby incorporated by specific reference. The "Selby-Noack PEI test" is similar to the "Noack procedure" as described in ASTM D 5800, procedure C, but deviates in duration (16 hours instead of 24 hours for the Noack procedure) and temperature (250°C for the Noack procedure). As the PEI is an approximation of the quantity of phosphorus (mg) obtained from 1 kg of fluid, it has no unit. By the term "improved phosphorus volatility properties", it is meant that the PEI is lower than the PEI result it is being compared to.

Therefore, the present invention also provides the use of one or more poly(hydroxycarboxylic acid) amide

salt derivatives wherein the anion is a non-sulfur-containing anion in a liquid fuel composition according to the present invention for improving the phosphorus volatility properties of an engine lubricant of an internal combustion engine fuelled by the liquid fuel composition compared to the phosphorus volatility properties of the engine lubricant when one or more poly(hydroxycarboxylic acid) amide salt derivatives wherein the anion is a sulfur-containing anion is used in the liquid fuel composition.

The present invention further provides a method of operating an internal combustion engine, which method involves introducing into a combustion chamber of the engine a liquid fuel composition according to the present invention.

The one or more poly(hydroxycarboxylic acid) amide salt derivatives of the present invention may also be conveniently incorporated into lubricant formulations, especially engine crank case lubricant formulations.

The present invention will be further understood from the following examples. Unless otherwise stated, all amounts and concentrations disclosed in the examples are based on weight of the fully formulated fuel composition.

Examples

In examples 1 to 41, two different commercially available hyperdispersants have been used, the hyperdispersants were poly(hydroxycarboxylic acid) amide salt derivatives, wherein the anion is a methyl sulphate anion, according to the present invention were products available commercially from Shanghai Sanzheng Polymer Company under the trade designations "CH-5" and "CH-7".

Certain measured properties of both CH-5 and CH-7 are given in Table 1 below:

	MW	TBN (mgKOH/g)	(ASTM D 4739)	N (%w)	S (%w)
CH-5 ~	1130		1.9	0.89	0.95
CH-7 ~	1050		1.9	0.82	0.86

Table 1: Measure properties of CH-5 and CH-7

Examples 1 to 39 and Comparative Examples A to D

5 The CH-5 and CH-7 hyperdispersants described above were blended into a base fuel selected from the gasoline, diesel, GTL diesel and Swedish Class I diesel base fuels described in Tables 2 and 3 below, in various amounts.

Parameter	Diesel A	Diesel B ^a	Diesel C ^b
Cetane No. (ASTM D613)	52.80	>76	53.10
Density at 15 °C (IP365)	0.84 g/cm ³	0.78 g/cm ³	0.82 g/cm ³
Flash Point (IP34)	62.0 °C	104.0 °C	72.5 °C
IBP (IP123)	168.6 °C	211.0 °C	190.3 °C
10 % rec. (IP123)	201.3 °C	251.3 °C	203.4 °C
20 % rec. (IP123)	223.9 °C	262.4 °C	211.1 °C
30 % rec. (IP123)	246.3 °C	273.3 °C	225.9 °C
40 % rec. (IP123)	266.7 °C	285.6 °C	225.9 °C
50 % rec. (IP123)	281.8 °C	297.3 °C	234.2 °C
60 % rec. (IP123)	293.9 °C	307.6 °C	242.2 °C
70 % rec. (IP123)	306.0 °C	316.9 °C	250.6 °C
80 % rec. (IP123)	319.7 °C	326.9 °C	259.4 °C
90 % rec. (IP123)	337.2 °C	339.1 °C	270.5 °C
95 % rec. (IP123)	350.8 °C	348.6 °C	279.5 °C
FBP (IP123)	362.3 °C	355.3 °C	291.6 °C
Viscosity at 40 °C (IP71)	2.74 mm ² /s	3.54 mm ² /s	1.94 mm ² /s
Sulphur content	8.4 mg/kg ^c	<3 mg/kg ^c	<3 mg/kg ^d
Total Aromatics (IP391/01 / IP548/07)	40.5 %m/m	0.4 %m/m	13.3 %m/m

a - Fischer-Tropsch (GTL) derived diesel fuel

b - Swedish Class I diesel fuel

c - ISO 20884

d - ISO 20846

Table 2. Diesel base fuels.

Parameter	"Gasoline"
RON (ASTM D2699)	96.00
MON (ASTM D2700)	85.10
Density at 15 °C (IP365)	0.73 g/cm ³
IBP (IP123)	26.5 °C
10 % rec. (IP123)	37.9 °C
20 % rec. (IP123)	48.9 °C
30 % rec. (IP123)	61.0 °C
40 % rec. (IP123)	74.4 °C
50 % rec. (IP123)	88.2 °C
60 % rec. (IP123)	101.4 °C
70 % rec. (IP123)	113.3 °C
80 % rec. (IP123)	127.9 °C
90 % rec. (IP123)	149.2 °C
95 % rec. (IP123)	164.7 °C
FBP (IP123)	191.2 °C
RVP *(IP394)	87.8 kPa
Olefins (inc. dienes)	16.40 %vol.
Aromatics	28.88 %vol.

Table 3. Gasoline base fuel.

To assess the lubricity of the liquid fuel compositions described above, the following test procedures were used.

The lubricity of the diesel fuel compositions was determined using the HFRR test used described in ISO 12156-1.

The lubricity of the gasoline compositions was determined by using a modified HFRR test. The modified HFRR test is based on ISO 12156-1 using a PCS Instruments HFRR supplemented with the PCS Instruments Gasoline Conversion Kit, and using a fluid volume of 15.0 ml (+/- 0.2 ml), a fluid temperature of 25.0 °C (+/- 1 °C), and

wherein a PTFE cover is used to cover the test sample in order to minimise evaporation.

The results of the lubricity tests are given below in Table 4.

Example	Base Fuel	Hyperdispersant (concentration)	Average HFRR Wear Scar (μm)
A*	Diesel A	-	366.5
1	Diesel A	CH-5 (100 ppmw)	344.5
2	Diesel A	CH-5 (500 ppmw)	341.5
3	Diesel A	CH-5 (1000 ppmw)	332
4	Diesel A	CH-5 (1 %wt)	254
5	Diesel A	CH-5 (10 %wt.)	224.5
6	Diesel A	CH-7 (50 ppmw)	319.5
7	Diesel A	CH-7 (100 ppmw)	321.5
8	Diesel A	CH-7 (500 ppmw)	327.5
9	Diesel A	CH-7 (1000 ppmw)	322
10	Diesel A	CH-7 (1 %wt)	228.5
11	Diesel A	CH-7 (10 %wt.)	214.5
B*	Diesel B	-	624
12	Diesel B	CH-5 (500 ppmw)	335
13	Diesel B	CH-5 (1000 ppmw)	365
14	Diesel B	CH-5 (1 %wt)	281.5
15	Diesel B	CH-5 (10 %wt.)	246.5
16	Diesel B	CH-7 (500 ppmw)	427.5
17	Diesel B	CH-7 (1000 ppmw)	386.5
18	Diesel B	CH-7 (1 %wt)	304
19	Diesel B	CH-7 (10 %wt.)	216
C*	Diesel C	-	624.5
20	Diesel c	CH-5 (100 ppmw)	442.5
21	Diesel C	CH-5 (1000 ppmw)	376.5
22	Diesel c	CH-5 (1 %wt)	289.5

23	Diesel C	CH-5 (10 %wt.)	228.5
24	Diesel c	CH-7 (500 ppmw)	471
25	Diesel C	CH-7 (1000 ppmw)	335
26	Diesel c	CH-7 (1 %wt)	255.5
27	Diesel C	CH-7 (10 %wt.)	209
D*	Gasoline	-	907
28	Gasoline	CH-5 (50 ppmw)	630.5
29	Gasoline	CH-5 (100 ppmw)	412.5
30	Gasoline	CH-5 (500 ppmw)	308.5
31	Gasoline	CH-5 (1000 ppmw)	346
32	Gasoline	CH-5 (1 %wt)	229.5
33	Gasoline	CH-5 (10 %wt.)	202.5
34	Gasoline	CH-7 (50 ppmw)	861.5
35	Gasoline	CH-7 (100 ppmw)	639
36	Gasoline	CH-7 (500 ppmw)	358
37	Gasoline	CH-7 (1000 ppmw)	347
38	Gasoline	CH-7 (1 %wt)	206.5
39	Gasoline	CH-7 (10 %wt.)	206.5

* - Not according to the present invention.

Table 4. HFRR Results for base fuel and fuel compositions according to the present invention.

As can be seen from the results in Table 4, a reduced wear scar is observed in the HFRR test for the fuel compositions (both gasoline and diesel fuel compositions) containing the CH-5 and CH-7 hyperdispersants compared to the base fuel, which represents an improvement in lubricity of the fuels containing the hyperdispersant compared to the base fuel.

Example 40

Inlet valve deposit (IVD) keep clean tests were performed for two gasoline compositions prepared by

blending a base gasoline as described in Table 5 below with 400 ppmw and 1000 ppmw of the CH-5 hyperdispersant.

Parameter	
RON (ASTM D2699)	98.9
MON (ASTM D2700)	87.3
Density at 15 °C (IP365)	0.7758 g/cm ³
IBP (IP123)	33.3 °C
10 % rec. (IP123)	56.4 °C
20 % rec. (IP123)	78.2 °C
30 % rec. (IP123)	96.8 °C
40 % rec. (IP123)	109.3 °C
50 % rec. (IP123)	118.6 °C
60 % rec. (IP123)	127.0 °C
70 % rec. (IP123)	136.4 °C
80 % rec. (IP123)	147.5 °C
90 % rec. (IP123)	161.4 °C
95 % rec. (IP123)	171.8 °C
FBP (IP123)	202.9 °C
RVP (IP394)	62.2 kPa
Olefins (inc. dienes)	7.44 %vol.
Aromatics	49.78 %vol.

Table 5. Gasoline base fuel.

The IVD test was performed in a Toyota 2.0 L 3S-FE bench engine using the CEC-F-05-A-93 M102E operating cycle modified by BMEP to the torque conditions detailed in Table 6 below. The Toyota engine has been modified to concurrently run two fuel systems, one fuelling cylinders 1 and 2 and a second fuelling cylinders 3 and 4. The engine starts with clean valves and combustion chamber and is run for 69hr on the test fuels. At the end of the

69 hours the engine is stripped, the valves weighed to determine the level of deposits.

Stage No	Stage time (s)	Engine speed (rpm)	Torque (Nm)	Coolant out temp (°C)	Oil out temp (°C)
1	30	800	0	90	97
2	60	1300	26	90	97
3	120	1850	28	90	97
4	60	3000	30	90	97

Table 6: Engine test cycle details for Toyota DF engine

The gasoline containing 400 and 1000 ppmw respectively of CH-5 was tested in the Toyota 3S-FE dual fuelled engine with the 400 ppmw CH-5 gasoline test blend in cylinders 1 and 2 and the 1000 ppmw CH-5 gasoline test blend in cylinders 3 and 4.

The average weight of the inlet valve deposits for cylinders 1 and 2 was 194.6 mg and for cylinders 3 and 4 was 130.0 mg. An average level of deposit observed with a gasoline containing no additives in a 69 hour test is typically about 200 mg.

Example 41

The injector nozzle keep clean performance of the CH-5 hyperdispersant in diesel fuel was assessed using the CEC SG-F-098 test procedure. The diesel fuel used in the test procedure contained 300 ppmw of the CH-5 hyperdispersant. In the test, up until 24 hours no power loss was observed and at 32 hours a power loss equating to 3 % was observed. At this point the equivalent power loss for the reference fuel was 9 %.

Preparation of non-sulfur-containing
poly(hydroxycarboxylic acid) amide salt derivatives

Example E

8 gram of the poly(hydroxycarboxylic acid) amide
salt derivative commercially available from Shanghai
Sanzheng Polymer Company under the trade designation "CH-
5" was dissolved in 140 ml of dichloromethane (DCM)
whilst stirring. The resultant mixture was further
diluted with 110 ml DCM and added to a separation funnel
containing 250 ml of 1M KOH solution.

The funnel was shaken and allowed to stand until
there was clear separation between the two layers. The
organic bottom layer was collected and added to 250 ml of
fresh 1M KOH in a separation funnel. Again, the organic
bottom layer was collected, dried over MgSO_4 and
concentrated in vacuo. About 6 gram of
poly(hydroxycarboxylic acid) amide salt derivative
wherein the anion $\text{X}^{\text{q-}}$ is OH was obtained.

The obtained poly(hydroxycarboxylic acid) amide salt
derivative had a TBN content of 7.4 mg.KOH/g (according
to ASTM D 4739).

Example F

The "CH-5" product (see Example E) was ion-exchanged
with a sodium salicylate (available from Sigma-Aldrich
Chemical Company, Gillingham, United Kingdom) in a ion-
exchange column, whilst using 1:3 MeOH: CHCl_3 as an
eluent.

To this end, a column was prepared using 500 gram
Dowex 1x8 ion-exchange resin (200-400 mesh, strongly
basic Cl^- form; CAS nr [69011-19-4]) which was washed in
1 l of deionised water. The washed Dowex resin was then
loaded as a suspension onto a column using 1 l of 1:1
MeOH:de-ionised water. The resin was then washed with 4

bed volumes of 1:1 methanol/de-ionised water and loaded with a 30 wt.% solution of the sodium salicylate salt of in a small amount of MeOH.

Subsequent polarity change of the resin was done in the following order: 2x 4 bed volumes of 1:1 MeOH/de-ionised water; 1x 4 bed volumes of MeOH; 4 bed volumes of 3:1, then 1:1, then 1:3 of MeOH:chloroform.

220 gram of the "CH-5" product was dissolved in a minimum amount of eluent (1:3 MeOH:chloroform) and loaded onto the column. The column was eluted, whilst following the elution by means of thin layer chromatography using appropriate staining techniques. The eluent was collected and concentrated in vacuo to dryness to yield about 200 gram of poly(hydroxycarboxylic acid) amide salt derivative wherein the anion X^{q-} is salicylate.

The obtained poly(hydroxycarboxylic acid) amide salt derivative had a TBN content of 8.2 mg.KOH/g (according to ASTM D 4739).

Example G

Similar to Example F, a poly(hydroxycarboxylic acid) amide salt derivative was obtained wherein the anion X^{q-} is a phenate. To this end sodium phenoate (available from Sigma-Aldrich Chemical Company, Gillingham, United Kingdom) was used.

The obtained poly(hydroxycarboxylic acid) amide salt derivative had a TBN content of 8.5 mg.KOH/g (according to ASTM D 4739).

Example H

Similar to Example F, a poly(hydroxycarboxylic acid) amide salt derivative was obtained wherein the anion X^{q-} is an oleate. To this end sodium oleate (available from Sigma-Aldrich Chemical Company, Gillingham, United Kingdom) was used.

The obtained poly(hydroxycarboxylic acid) amide salt derivative had a TBN content of 7.9 mg.KOH/g (according to ASTM D 4739).

Example I

5 Similar to Example F, a poly(hydroxycarboxylic acid) amide salt derivative was obtained wherein the anion X^{q-} is an acetate. To this end sodium acetate (available from Sigma-Aldrich Chemical Company, Gillingham, United Kingdom) was used.

10 The obtained poly(hydroxycarboxylic acid) amide salt derivative had a TBN content of 8.5 mg.KOH/g (according to ASTM D 4739).

Engine Lubricant Performance

15 The performance of the crankcase lubricant of an engine fuelled using a liquid fuel composition according to the present invention was assessed using the Sequence VG test, ASTM D 6593-07.

20 Two separate poly(hydroxycarboxylic acid) amide salt derivatives were assessed using in the Sequence VG tests. The base fuel used for both poly(hydroxycarboxylic acid) amide salt derivatives was an ASTM VG base fuel.

- Fuel "Base" is ASTM VG base fuel.
- Fuel "F-A" is "Base" + 500 ppmw of "CH-5".
- Fuel "F-B" is "Base" + 200 ppmw of Example F.
- 25 • Lubricant "L-A" is an SF grade lubricant.
- Lubricant "L-B" is a SL/CF grade lubricant.

30 The results of the Sequence VG tests are provided in Table 7 below. The "merit" rating used in the results is on a scale of 0 to 10, with 10 representing the rating of the condition of the component when new, and a single number increase in the "merit" rating represents a reduction in the sludge or varnish by half.

Example	Fuel	Lubricant	Final Original Unit Results			
			Average Engine Sludge (merits)	Rocker Cover Sludge (merits)	Average Engine Varnish (merits)	Average Piston Skirt Varnish
42	F-A	L-A	9.71	9.79	9.82	9.69
J*	Base	L-A	7.88	9.42	8.99	7.60
43	F-B	L-B	9.78	9.74	9.92	9.99
K*	Base	L-B	9.28	9.41	9.28	8.26
44	F-B	L-B	9.80	9.73	9.98	10.00

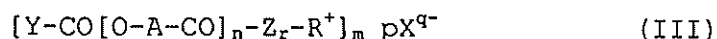
* - Comparative

Table 7. Sequence VG test results

As can clearly be seen from the results given in Table 7 above, the use of poly(hydroxycarboxylic acid) amide salt derivatives in the gasoline compositions results in a significant improvement in the performance of the lubricant in terms of inhibition of sludge and varnish deposit formation.

C L A I M S

1. A liquid fuel composition comprising:
- a gasoline suitable for use in a spark-ignition internal combustion engine; and
 - one or more poly(hydroxycarboxylic acid) amide salt derivatives having formula (III):



wherein Y is hydrogen or an optionally substituted hydrocarbyl group, A is a divalent optionally substituted hydrocarbyl group, n is from 1 to 100, 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 0 or 1, R^+ is an ammonium group and X^{q-} is an anion.

2. A liquid fuel composition according to claim 1, wherein the amount of the one or more poly(hydroxycarboxylic acid) amide salt derivatives present in the liquid fuel composition of the present invention is at least 1 ppmw, based on the overall weight of the liquid fuel composition.

3. A liquid fuel composition according to claim 2, wherein the amount of the one or more poly(hydroxycarboxylic acid) amide salt derivatives present in the liquid fuel composition of the present invention is in the range of from 10 ppmw to 20 %wt, based on the overall weight of the liquid fuel composition.

4. A liquid fuel composition according to any one of claims 1 to 3, wherein the anion, X^{q-} , is a non-sulphur-containing anion, preferably the anion, X^{q-} , is selected

from anions derived from compounds containing a carboxylic acid group, anions derived from compounds containing a hydroxyl group, nitrogen based anions, phosphorus based anions, and mixtures thereof.

5 5. A liquid fuel composition according to any one of claims 1 to 3, wherein the anion, X^{q-} , is a sulphur-based anion, preferably the anion, X^{q-} , is selected from sulphate, sulphonate and mixtures thereof.

10 6. A liquid fuel composition according to claim 5, wherein the one or more of the poly(hydroxycarboxylic acid) amide salt derivatives have a sulphur content in the range of from 0.1 to 2.0 wt. %, based on the total weight of said poly(hydroxycarboxylic acid) amide salt derivatives.

15 7. A liquid fuel composition according to any one of claims 1 to 6, wherein the 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.

20 8. A method of operating a spark-ignition internal combustion engine, which method involves introducing into a combustion chamber of the engine a liquid fuel composition according to any one of claims 1 to 7.

25 9. Use of a liquid fuel composition as claimed in any one of claims 1 to 7 for improving the lubricity of said liquid fuel composition, relative to the gasoline.

30 10. Use of a liquid fuel composition as claimed in any one of claims 1 to 7 for improving engine cleanliness of a spark ignition internal combustion engine being fuelled by said liquid fuel composition, relative to said engine being fuelled by the gasoline.

11. Use as claimed in claim 10 for improving inlet valve deposit keep clean performance.

12. Use of a liquid fuel composition as claimed in any one of claims 1 to 7 for improving fuel economy of a spark-ignition internal combustion engine being fuelled by said liquid fuel composition, relative to said engine being fuelled by the gasoline.

13. Use of a liquid fuel composition as claimed in any one of claims 1 to 7 for improving the performance of the lubricant of a spark-ignition internal combustion engine being fuelled by said liquid fuel composition, relative to said engine being fuelled by the gasoline.

14. Use as claimed in claim 13 of a liquid fuel composition as claimed in claim 4 for improving the phosphorus volatility properties of said lubricant compared to that when said engine is fuelled by a composition of claim 5.