

COMPOSITION, METHOD AND USE FOR REDUCING EMISSIONS OF A DIESEL ENGINE

The present invention relates to fuel compositions, and to methods and uses relating thereto. In particular, the invention relates to additives for reducing particulate emissions in diesel engines, especially direct injection diesel engines having a high pressure fuel system.

Due to consumer demand and legislation, diesel engines have in recent years become much more energy efficient, show improved performance and have reduced emissions.

These improvements in performance and emissions have been brought about by improvements in the combustion process. To achieve the fuel atomisation necessary for this improved combustion, fuel injection equipment has been developed which uses higher injection pressures and reduced fuel injector nozzle hole diameters.

Diesel engines having high pressure fuel systems can include but are not limited to heavy duty diesel engines and smaller passenger car type diesel engines. Heavy duty diesel engines can include very powerful engines such as the MTU series 4000 diesel having 20 cylinder variants designed primarily for ships and power generation with power output up to 4300 kW or engines such as the Renault dXi 7 having 6 cylinders and a power output around 240kW. A typical passenger car diesel engine is the Peugeot DW10 having 4 cylinders and power output of 100 kW or less depending on the variant.

In all of the diesel engines relating to this invention, a common feature is a high pressure fuel system. Typically pressures in excess of 1350 bar (1.35×10^8 Pa) are used but often pressures of up to 2000 bar (2×10^8 Pa) or more may exist.

Two non-limiting examples of such high pressure fuel systems are: the common rail injection system, in which the fuel is compressed utilizing a high-pressure pump that supplies it to the fuel injection valves through a common rail; and the unit injection system which integrates the high-pressure pump and fuel injection valve in one assembly, achieving the highest possible injection pressures exceeding 2000 bar (2×10^8 Pa). In both systems, in pressurizing the fuel, the fuel gets hot, often to temperatures around 100°C, or above.

A common problem with diesel engines is fouling of the injector, particularly the injector body, and the injector nozzle. Fouling may also occur in the fuel filter. Deposits increase with degradation of the fuel. In recent years the need to reduce emissions has led to the continual redesign of injection systems to help meet lower targets. This has led to increasingly complex injectors and lower tolerance to deposits.

Various additives have been developed for such engines to reduce wear and for deposit control. Considerable work has also been carried out to control emissions from such engines, especially carbon monoxide and NO_x in exhaust gases.

It is common to include catalytic converters in the exhaust system of a direct injection diesel engine. These typically include three way catalytic converters which reduce the concentrations of hydrocarbons, carbon monoxide and NO_x species released into the atmosphere.

Direct injection diesel engines are also fitted with particulate filters. However current guidelines only require the emissions of particulates having a diameter of at least 2.5 microns to be measured. However it is known that particulates having a smaller diameter are also emitted, and some of these may pass through particulate filters (when fitted) on exhaust systems.

Particulates having a diameter of less than 2.5 microns, for example ultrafine particles, can be highly damaging to human health. Fine particulate matter can accumulate in the lungs causing increasing damage over time. Ultrafine particles are also able to enter the bloodstream. Additionally particulates having a diameter of less than 2.5 microns are very damaging to the environment.

It is therefore desirable to provide additives which cause a reduction in particulate emissions, such as particulates having a diameter of less than 2.5 microns, from direct injection diesel engines.

According to a first aspect of the present invention there is provided a method of reducing the emission of particulates having a diameter of less than 2.5 microns from a direct injection diesel engine, the method comprising combusting in the engine a diesel fuel composition comprising as an additive one or more quaternary ammonium compounds.

According to a second aspect of the present invention there is provided the use of one or more quaternary ammonium compounds as an additive in a diesel fuel composition to reduce the emission of particulates having a diameter of less than 2.5 microns from a direct injection diesel engine.

Preferred features of the first and second aspects of the invention will now be described. Any feature of any aspect may be combined with any feature of any other aspect as appropriate.

The present invention relates to a method and a use involving one or more quaternary ammonium compounds as a fuel additive. The additive may be referred to herein as "the additive

of the present invention”, “the quaternary ammonium compound” or as “the quaternary ammonium salt additive”.

The quaternary ammonium salt additive may comprise a single compound. In some embodiments mixtures containing more than one quaternary ammonium compound may be used. Thus the present invention may involve the use of one quaternary ammonium compound, or a mixture of two or more quaternary ammonium compounds. References herein to “an additive” of the invention or “the additive” include embodiments in which mixtures of two or more quaternary ammonium compounds are used.

The or each quaternary ammonium compound is suitably the reaction product of a nitrogen-containing species having at least one tertiary amine group and a quaternising agent.

The nitrogen-containing species having at least one tertiary amine group may be selected from any compound including a tertiary amine functional group.

Suitably the nitrogen-containing species having at least one tertiary amine group may be selected from:

- (i) the reaction product of a hydrocarbyl-substituted acylating agent and a compound having at least one tertiary amine group and a primary amine, secondary amine or alcohol group;
- (ii) a Mannich reaction product comprising a tertiary amine group;
- (iii) a polyalkylene substituted amine having at least one tertiary amine group;
- (iv) a tertiary amine of formula $R^5R^6R^7N$, wherein each of R^5 , R^6 and R^7 is independently an optionally substituted alkyl, alkenyl, aryl, alkaryl or aralkyl group;
- (v) a cyclic tertiary amine; and
- (vi) a polyetheramine compound.

The nitrogen-containing species having at least one tertiary amine group is reacted with a quaternising agent. Any suitable quaternising agent may be used.

In some embodiments the nitrogen-containing species having at least one tertiary amine group is (i) the reaction product of a hydrocarbyl-substituted acylating agent and a compound

comprising at least one tertiary amine group and a primary amine, secondary amine or alcohol group.

Suitable hydrocarbyl substituted acylating agents for use herein include fatty acids, i.e. compounds of formula RCOOH in which R is an alkyl or alkenyl group having 6 to 36 carbon atoms, preferably 8 to 30 carbon atoms or 12 to 24 carbon atoms. One preferred fatty acid is oleic acid.

The hydrocarbyl substituted acylating agent may be based on a hydrocarbyl substituted mono- di- or polycarboxylic acid or a reactive equivalent thereof. In some preferred embodiments the hydrocarbyl substituted acylating agent is a hydrocarbyl substituted succinic acid compound, for example a hydrocarbyl substituted succinic acid or succinic anhydride.

The hydrocarbyl substituent preferably comprises at least 10, more preferably at least 12, for example 30 or 50 carbon atoms. It may comprise up to about 200 carbon atoms. Preferably the hydrocarbyl substituent has a number average molecular weight (M_n) of between 170 to 2800, for example from 250 to 1500, preferably from 450 to 1500 and more preferably 450 to 1100. An M_n of 700 to 1300 is especially preferred.

The hydrocarbyl based substituents may be made from homo- or interpolymers (e.g. copolymers, terpolymers) of mono- and di-olefins having 2 to 10 carbon atoms, for example ethylene, propylene, but-1-ene, isobutene, butadiene, isoprene, 1-hexene, 1-octene, etc. Preferably these olefins are 1-monoolefins. The hydrocarbyl substituent may also be derived from the halogenated (e.g. chlorinated or brominated) analogs of such homo- or interpolymers. Alternatively the substituent may be made from other sources, for example monomeric high molecular weight alkenes (e.g. 1-tetra-contene) and chlorinated analogs and hydrochlorinated analogs thereof, aliphatic petroleum fractions, for example paraffin waxes and cracked and chlorinated analogs and hydrochlorinated analogs thereof, white oils, synthetic alkenes for example produced by the Ziegler-Natta process (e.g. poly(ethylene) greases) and other sources known to those skilled in the art. Any unsaturation in the substituent may if desired be reduced or eliminated by hydrogenation according to procedures known in the art.

In some preferred embodiments component (i) comprises the reaction product of a hydrocarbyl-substituted succinic acid derivative and an alcohol or amine also including a tertiary amine group.

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:

(i) hydrocarbon groups, that is, aliphatic (which may be saturated or unsaturated, linear or branched, e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form a ring);

(ii) substituted hydrocarbon groups, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent (e.g., halo (e.g. chloro, fluoro or bromo), hydroxy, alkoxy (e.g. C₁ to C₄ alkoxy), keto, acyl, cyano, mercapto, amino, amido, nitro, nitroso, sulfoxy, nitril and carboxy);

(iii) hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms include sulphur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, preferably no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

In this specification, unless otherwise stated references to optionally substituted alkyl groups may include aryl-substituted alkyl groups and references to optionally-substituted aryl groups may include alkyl-substituted or alkenyl-substituted aryl groups.

Preferred hydrocarbyl-based substituents are poly-(isobutene)s. Such compounds are known in the art. Thus in some especially preferred embodiments the hydrocarbyl substituted acylating agent is a polyisobutenyl substituted succinic acid or succinic anhydride.

Polyisobutenyl substituted succinic anhydrides are especially preferred.

The preparation of polyisobutenyl substituted succinic anhydrides (PIBSA) is documented in the art. Suitable processes include thermally reacting polyisobutenes with maleic anhydride (see for example US-A-3,361,673 and US-A-3,018,250), or reacting a halogenated, in particular a chlorinated, polyisobutene (PIB) with maleic anhydride (see for example US-A-3,172,892). Alternatively, the polyisobutenyl succinic anhydride can be prepared by mixing the polyolefin with maleic anhydride and passing chlorine through the mixture (see for example GB-A-949,981).

Conventional polyisobutenes and so-called "highly-reactive" polyisobutenes are suitable for use in the invention. Highly reactive polyisobutenes in this context are defined as polyisobutenes wherein at least 50%, preferably 70% or more, of the terminal olefinic double bonds are of the vinylidene type as described in EP0565285. Particularly preferred polyisobutenes are those having more than 80 mol% and up to 100% of terminal vinylidene groups such as those described in EP1344785.

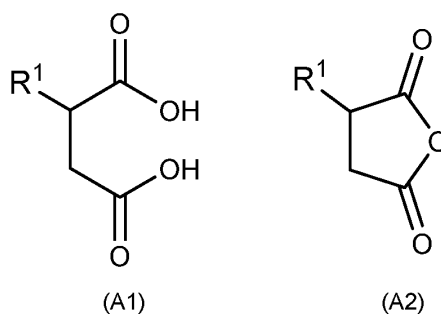
The person skilled in the art will appreciate that in the preparation of PIBSAs from the reaction of PIB with maleic acid (MA), a mixture of products will result. Typically reaction mixtures include some unreacted PIB, some PIBSA from the reaction of PIB with one MA (monomaleated PIBSA) and some PIBSA from the reaction of PIB with two MA (bismaleated PIBSA). The fraction of bismaleated product as a proportion of the total PIBSA product may be referred to as the bismaleation level (BML). Suitable PIBSAs for use in preparing additive (i) may have a BML of up to 90%, suitably up to 70%, for example 1 to 50% or 2 to 30%.

Other preferred hydrocarbyl groups include those having an internal olefin for example as described in the applicant's published application WO2007/015080.

An internal olefin as used herein means any olefin containing predominantly a non-alpha double bond, that is a beta or higher olefin. Preferably such materials are substantially completely beta or higher olefins, for example containing less than 10% by weight alpha olefin, more preferably less than 5% by weight or less than 2% by weight. Typical internal olefins include Neodene 1518 IO available from Shell.

Internal olefins are sometimes known as isomerised olefins and can be prepared from alpha olefins by a process of isomerisation known in the art, or are available from other sources. The fact that they are also known as internal olefins reflects that they do not necessarily have to be prepared by isomerisation.

In some preferred embodiments the additive of the present invention comprises the quaternised reaction product of an alcohol or amine including a tertiary amino group and an optionally substituted succinic acid or anhydride thereof of formula (A1) or (A2):



wherein R^1 is an optionally substituted hydrocarbyl group. Preferably R^1 is an optionally substituted alkyl or alkenyl group.

R^1 may be substituted with one or more groups selected from halo (e.g. chloro, fluoro or bromo), nitro, hydroxy, mercapto, sulfoxy, amino, nitril, acyl, carboxy, alkyl (e.g. C_1 to C_4 alkyl), alkoxy (e.g. C_1 to C_4 alkoxy), amido, keto, sulfoxy and cyano.

Preferably R^1 is an unsubstituted alkyl or alkenyl group. The substituted succinic acid or anhydrides may suitably be prepared by reacting maleic anhydride with an alkene.

In some preferred embodiments R^1 has a number average molecular weight of from 100 to 5000, preferably from 300 to 4000, suitably from 450 to 2500, for example from 450 to 2000 or from 450 to 1500.

In especially preferred embodiments the additive of the present invention comprises a quaternary ammonium compound prepared from the reaction product of a hydrocarbyl substituted succinic acid or an anhydride thereof substituted with a polyisobutenyl group having a number average molecular weight of 450 to 1500 and an alcohol or amine which further includes a tertiary amino group.

In some embodiments the substituted succinic acid or anhydride thereof may comprise a mixture of compounds including groups R^1 of different lengths. In such embodiments any reference to the molecular weight of the group R^1 relates to the number average molecular weight of all of that group for all compounds in the composition.

In preferred embodiments R^1 is a polyisobutenyl group, preferably having a number average molecular weight of from 100 to 5000, preferably from 200 to 2400, suitably from 450 to 1500.

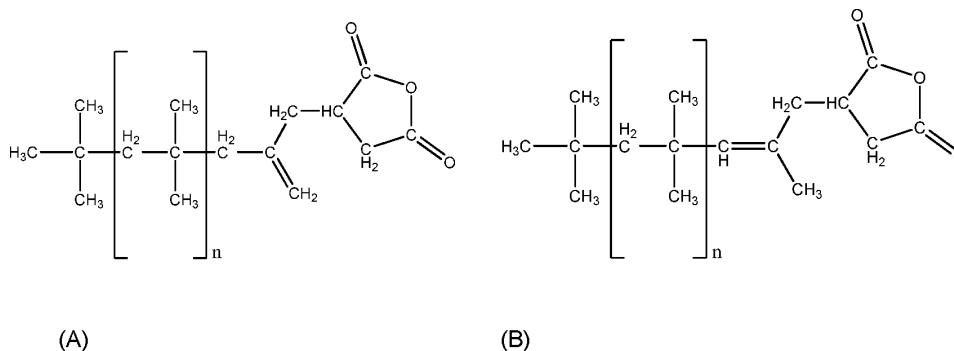
In some embodiments R^1 is an optionally substituted C_1 to C_{500} alkyl or alkenyl group, for example a C_8 to C_{40} alkyl or alkenyl group, suitably C_{16} to C_{36} alkyl or alkenyl group.

In some embodiments the additive of the present invention comprises a quaternary ammonium compound prepared from the reaction product of a succinic acid or anhydride having a C₁₀ to C₃₀, preferably a C₂₀ to C₂₄ alkyl or alkenyl group and an amine or alcohol which further includes a tertiary amino group.

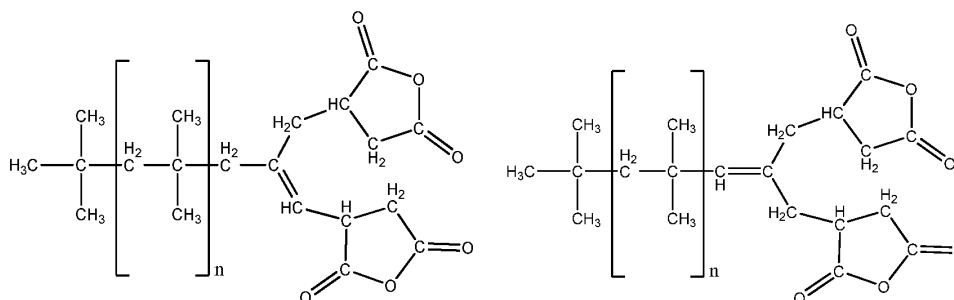
Preferred hydrocarbyl substituted acylating agents for use herein are polyisobutenyl substituted succinic anhydrides or PIBSAs. Preferably the succinic acid or anhydride thereof is substituted with a polyisobutenyl group having a number average molecular weight of from 170 to 2800, preferably 450 to 1500. Especially preferred PIBSAs are those having a PIB molecular weight (M_n) of from 300 to 2800, preferably from 450 to 2300, more preferably from 500 to 1300.

The hydrocarbyl substituted succinic acid derived acylating agent is suitably prepared by reacting maleic anhydride with an alkene, for example a polyisobutene. The product obtained (such as a PIBSA) still includes a double bond. The maleic anhydride is present in the resultant molecule as a succinic acid moiety. This initial product is a monomaleated PIBSA.

The monomaleated PIBSA may have the structure (A) or (B):



The double bond in the monomaleated product can react with a further molecule of maleic anhydride to form a bismaleated PIBSA having the structure (C) or (D):



(C)

(D)

Thus it is possible to provide a hydrocarbyl group which is substituted with more than one succinic acid moiety.

The skilled person will appreciate that the hydrocarbyl substituted succinic acid derived acylating agents used in the invention typically comprise mixtures of compounds, for example mixtures of monomaleated and bismaleated PIBSAs. The PIBSAs may be defined in terms of their level of bismaleation.

One way in which this may be determined is by calculating the average number of succinic acid moieties per molecule of acylating agent.

A monomaleated PIBSA has one succinic acid moiety per module.

A bismaleated PIBSA has two succinic acid moieties per molecule.

A mixture comprising monomaleated PIBSA and bismaleated PIBSA in a 1:1 molar ratio would comprise an average of 1.5 succinic acid moieties per molecule of PIBSA.

The average number of succinic acid moieties per molecule of acylating agent is sometimes referred to in the art as the "P value".

Suitably the or each quaternary ammonium compound is prepared from a hydrocarbyl substituted succinic acid derived acylating agent comprising on average from 1 to 2 succinic acid moieties per molecule.

In some preferred embodiments the present invention may involve the use of quaternary ammonium compounds derived from hydrocarbyl substituted acylating agents which include an average of at least 1.2 succinic acid moieties per molecule.

As the skilled person will appreciate, a single molecule cannot have 1.2 succinic acid moieties. What is meant by at least 1.2 succinic acid moieties is the mean number of succinic acid moieties per molecule of acylating agent as the sum of all the succinic acid moieties present in a sample divided by the total number of molecules of acylating agent having one or more succinic acid moieties present in the sample.

Preferably the hydrocarbyl substituted succinic acid derived acylating agent comprises on average at least 1.21 succinic acid moieties per molecule, more preferably at least 1.22 succinic acid moieties per molecule.

In some embodiments the hydrocarbyl substituted succinic acid derived acylating agent may comprise at least 1.23 or at least 1.24 succinic acid moieties per molecule.

In some embodiments the hydrocarbyl substituted succinic acid derived acylating agent may comprise at least 1.25, at least 1.26 or at least 1.27 succinic acid moieties per molecule.

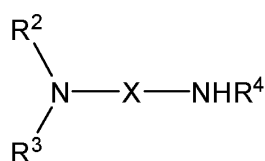
In some embodiments the hydrocarbyl substituted succinic acid derived acylating agent may comprise at least 1.28, at least 1.29 or at least 1.30 succinic acid moieties per molecule.

By succinic acid moiety we mean to include residues of succinic acid present in diacid or anhydride form.

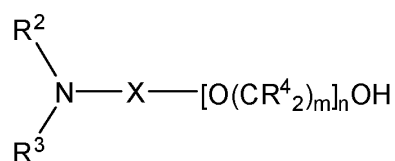
The hydrocarbyl substituted acylating agent is reacted with a compound able to react with said acylating agent and which includes a tertiary amine group. The tertiary amine group is quaternised to provide the quaternary ammonium salt.

Examples of suitable compounds able to react with the hydrocarbyl substituted succinic acid derived acylating agent and which include a tertiary amine group can include but are not limited to: N,N-dimethylaminopropylamine, N,N-diethylaminopropylamine, N,N-dimethylaminoethylamine. The nitrogen or oxygen containing compounds capable of condensing with the acylating agent and further having a tertiary amino group can further include amino alkyl substituted heterocyclic compounds such as 1-(3-aminopropyl)imidazole and 4-(3-aminopropyl)morpholine, 1-(2-aminoethyl)piperidine, 3,3-diamino-N-methyldipropylamine, and 3'3'-aminobis(N,N-dimethylpropylamine). Other types of nitrogen or oxygen containing compounds capable of condensing with the acylating agent and having a tertiary amino group include alkanolamines including but not limited to triethanolamine, trimethanolamine, N,N-dimethylaminopropanol, N,N-dimethylaminoethanol, N,N-diethylaminopropanol, N,N-diethylaminoethanol, N,N-diethylaminobutanol, N,N,N-tris(hydroxyethyl)amine, N,N,N-tris(hydroxymethyl)amine, N,N,N-tris(aminoethyl)amine, N,N-dibutylaminopropylamine and N,N,N'-trimethyl-N'-hydroxyethyl-bisaminoethylether; N,N-bis(3-dimethylaminopropyl)-N-isopropanolamine ; N-(3-dimethylaminopropyl)-N,N-diisopropanolamine; N'-(3-(dimethylamino)propyl)-N,N-dimethyl 1,3-propanediamine; 2-(2-dimethylaminoethoxy)ethanol, N,N,N'-trimethylaminoethylethanolamine and 3-(2-(dimethylamino)ethoxy) propylamine.

Preferred nitrogen-containing species having at least one tertiary amino group of type (i) are formed by the reaction of a hydrocarbyl-substituted acylating agent and an amine of formula (B1) or (B2):



(B1)



(B2)

wherein R^2 and R^3 are the same or different alkyl groups having from 1 to 36 carbon atoms; X is an alkylene group having from 1 to 20 carbon atoms; n is from 0 to 20; m is from 1 to 5; and R^4 is hydrogen or a C_1 to C_{36} alkyl group.

To form the quaternary ammonium salt additives of the present invention a quaternising agent may be reacted with a compound formed by the reaction of a hydrocarbyl substituted acylating agent and an amine of formula (B1) or (B2).

When a compound of formula (B1) is used, R^4 is preferably hydrogen or a C_1 to C_{16} alkyl group, preferably a C_1 to C_{10} alkyl group, more preferably a C_1 to C_6 alkyl group. When R^4 is alkyl it may be straight chained or branched. It may be substituted for example with a hydroxy or alkoxy substituent. Preferably R^4 is not a substituted alkyl group. More preferably R^4 is selected from hydrogen, methyl, ethyl, propyl, butyl and isomers thereof. Most preferably R^4 is hydrogen.

When a compound of formula (B2) is used, each R^4 is preferably hydrogen or a C_1 to C_6 alkyl group. More preferably each R^4 is selected from hydrogen, methyl, ethyl, propyl, butyl and isomers thereof. Most preferably each R^4 is hydrogen or methyl.

When a compound of formula (B2) is used, m is preferably 2 or 3, most preferably 2; n is preferably from 0 to 15, preferably 0 to 10, more preferably from 0 to 5. Most preferably n is 0 and the compound of formula (B2) is an alcohol.

In some preferred embodiments the hydrocarbyl substituted acylating agent is reacted with a diamine compound of formula (B1).

R^2 and R^3 are the same or different alkyl, alkenyl or aryl groups having from 1 to 22 carbon atoms. In some embodiments R^2 and R^3 may be joined together to form a ring structure, for

example a piperidine or imidazole moiety. R^2 and R^3 may be branched alkyl or alkenyl groups. Each may be substituted, for example with a hydroxy or alkoxy substituent.

R^2 and R^3 may each independently be a C_1 to C_{16} alkyl group, preferably a C_1 to C_{10} alkyl group. R^2 and R^3 may independently be methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, or an isomer of any of these. Preferably R^2 and R^3 is each independently C_1 to C_4 alkyl. Preferably R^2 is methyl. Preferably R^3 is methyl.

X is a bond or alkylene group having from 1 to 20 carbon atoms. In preferred embodiments when X is an alkylene group this group may be straight chained or branched. The alkylene group may include a cyclic structure therein. It may be optionally substituted, for example with a hydroxy or alkoxy substituent. In some embodiments the alkylene group may be optionally interrupted with one or more heteroatoms, for example O, NH or N-alkyl.

X is preferably an alkylene group having 1 to 16 carbon atoms, preferably 1 to 12 carbon atoms, more preferably 1 to 8 carbon atoms, for example 2 to 6 carbon atoms or 2 to 5 carbon atoms. Most preferably X is an ethylene, propylene or butylene group, especially a propylene group.

Examples of compounds of formula (B1) suitable for use herein 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-dimethylaminopropylamine, 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), 1-(3-aminopropyl)imidazole and 4-(3-aminopropyl)morpholine, 1-(2-aminoethyl)piperidine, 3,3-diamino-N-methyldipropylamine, 3,3-aminobis(N,N-dimethylpropylamine), N'-(3-(dimethylamino)propyl)-N,N-dimethyl 1,3-propanediamine, 3-(2-(dimethylamino)ethoxy)propylamine or combinations thereof.

In some preferred embodiments the compound of formula (B1) is selected from N,N-dimethyl-1,3-diaminopropane, N,N-diethyl-1,3-diaminopropane, N,N-dimethylethylenediamine, N,N-diethylethylenediamine, N,N-dibutylethylenediamine, or combinations thereof.

An especially preferred compound of formula (B1) is dimethylaminopropylamine.

Examples of compounds of formula (B2) suitable for use herein include alkanolamines including but not limited to triethanolamine, N,N-dimethylaminopropanol, N,N-diethylaminopropanol, N,N-diethylaminobutanol, triisopropanolamine, 1-[2-hydroxyethyl]piperidine, 2-[2-(dimethylamine)ethoxy]-ethanol, N-ethyl-diethanolamine, N-methyl-diethanolamine, N-butyl-diethanolamine, N,N-diethylaminoethanol, N,N-dimethyl amino-ethanol, 2-dimethylamino-2-methyl-1-propanol; trimethanolamine, N,N,N-tris(hydroxymethyl)amine, N,N,N-tris(aminoethyl)amine, N,N-bis(3-dimethylaminopropyl)-N-isopropanolamine and N-(3-dimethylaminopropyl)-N,N-diisopropanolamine.

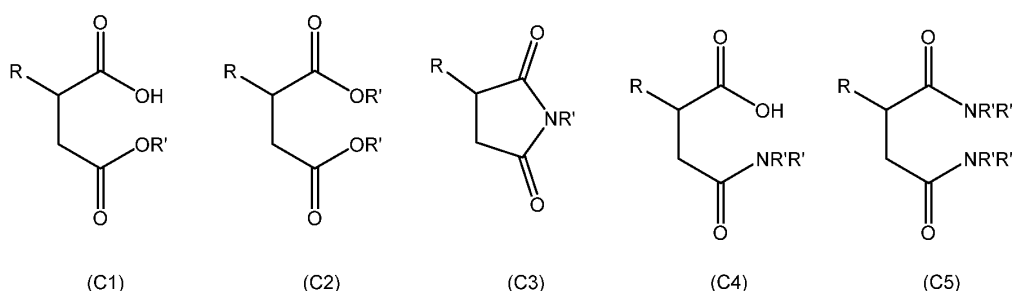
In some preferred embodiments the compound of formula (B2) is selected from N,N-dimethylaminopropanol, triisopropanolamine, 1-[2-hydroxyethyl]piperidine, 2-[2-(dimethylamine)ethoxy]-ethanol, N-ethyl-diethanolamine, N-methyl-diethanolamine, N-butyl-diethanolamine, N,N-diethylaminoethanol, N,N-dimethylaminoethanol, 2-dimethylamino-2-methyl-1-propanol, or combinations thereof.

An especially preferred compound of formula (B2) is dimethylaminopropanol.

Some preferred acylating agents for use in the preparation of the quaternary ammonium salt additives of the present invention are polyisobutene-substituted succinic acids or succinic anhydrides. When a compound of formula (B2) is reacted with a succinic acylating agent the resulting product is a succinic ester. When a succinic acylating agent is reacted with a compound of formula (B1) in which R⁴ is hydrogen the resulting product may be a succinimide or a succinamide. When a succinic acylating agent is reacted with a compound of formula (B1) in which R⁴ is not hydrogen the resulting product is an amide.

Thus in some embodiments component (i) may be the reaction product of a succinic acid derivative and an amine or alcohol which is an ester or an amide and which also includes a further unreacted carboxylic acid group. This further carboxylic acid functional group can react with another amine or alcohol when an excess is used to form a diester or the diamide.

For the avoidance of doubt, succinic esters include the monoester compounds having the general formula (C1) and the diester compounds having the general formula (C2); succinimides have the general formula (C3); and succinamides include the monoamide compounds having the general formula (C4) and the diamide compounds having the general formula (C5):



It will be appreciated isomers of (C1) and (C4) may be formed in which the other carboxylic acid group is esterified/amidated.

The groups R' shown in figures (C1) to (C5) include a tertiary amino group. This group may be quaternised by reaction with a quaternising agent. For compounds of formula (C2) or (C5) which include two tertiary amino groups, each of these may be reacted with a quaternising agent to provide a diquaternary ammonium compound including two cationic moieties. Compounds of this type to provide a diquaternary ammonium compound including two cationic moieties. Compounds of this type are described (for use as diesel detergents) in US9365787.

In some embodiments mixtures of compounds having formula (C1) and (C2) or mixtures containing compounds (C3) and/or (C4) and/or (C5) may be used.

In preferred embodiments a succinic acid derivative is reacted with an amine (also including a tertiary amine group) under conditions to form a succinimide.

In some embodiments the acid/anhydride and the alcohol/amine are reacted in a molar ratio of from 10:1 to 1:10, preferably from 5:1 to 1:5, more preferably from 2:1 to 1:2, for example from 1.5:1 to 1:1.5.

Preferably the acid/anhydride and the alcohol/amine are reacted in an approximately 1:1 molar ratio, for example from 1.2:1 to 1:1.2.

Suitably the quaternary ammonium salt additive of the present invention comprises a compound prepared from the reaction product of an optionally substituted succinic acid or anhydride thereof, preferably a hydrocarbyl substituted succinic acid or anhydride thereof, and an alcohol or amine selected from dimethylaminopropanol, dimethylaminopropylamine, N,N-diethyl-1,3-diaminopropane, N,N-dimethylethylenediamine, N,N-diethylethylenediamine, N,N-dibutylethylenediamine, 3-(2-(dimethylamino)ethoxy)propylamine or combinations thereof.

In some especially preferred embodiments the quaternary ammonium salt additives of the present invention comprise quaternary ammonium compounds prepared from tertiary amines (i) wherein the tertiary amine is prepared from an amine which includes a tertiary amino group (for example dimethylamino propylamine) and a polyisobutylene-substituted succinic anhydride. The number average molecular weight of the polyisobutylene substituent is preferably from 450 to 1300, more preferably from 900 to 1100.

The quaternary ammonium salt additives of the present invention comprising compounds derived from tertiary amines (i) may be prepared by any suitable method. Such methods will be known to the person skilled in the art and are exemplified herein. Typically the quaternary ammonium compounds will be prepared by heating the quaternising agent and a compound prepared by the reaction of a hydrocarbyl substituted acylating agent with an amine of formula (B1) or (B2) in an approximate 1:1 molar ratio, optionally in the presence of a solvent. The resulting crude reaction mixture may be added directly to a diesel fuel, optionally following removal of solvent. Any by-products or residual starting materials still present in the mixture have not been found to cause any detriment to the performance of the additive. Thus the present invention may provide a diesel fuel composition comprising the reaction product of a quaternising agent and the reaction product of a hydrocarbyl substituted acylating agent and an amine formula (B1) or (B2).

In some embodiments the quaternary ammonium compounds for use in the present invention are the quaternised reaction product of a fatty acid (for example oleic acid) and a compound of formula (B1) or (B2) (for example dimethylaminopropyl amine).

In some embodiments the nitrogen-containing species having at least one tertiary amine group may be (ii) a Mannich reaction product including a tertiary amine. The preparation of quaternary ammonium salts formed from nitrogen-containing species including component (ii) is described in US2008/0052985.

The Mannich reaction product having a tertiary amine group is prepared from the reaction of a hydrocarbyl-substituted phenol, an aldehyde and an amine.

The hydrocarbyl substituent of the hydrocarbyl substituted phenol can have 6 to 400 carbon atoms, suitably 30 to 180 carbon atoms, for example 10 or 40 to 110 carbon atoms. This hydrocarbyl substituent can be derived from an olefin or a polyolefin. Useful olefins include alpha-olefins, such as 1-decene, which are commercially available.

The polyolefins which can form the hydrocarbyl substituent can be prepared by polymerizing olefin monomers by well known polymerization methods and are also commercially available.

Some preferred polyolefins include polyisobutylenes having a number average molecular weight of 400 to 3000, in another instance of 400 to 2500, and in a further instance of 400 or 450 to 1500.

The hydrocarbyl-substituted phenol can be prepared by alkylating a phenol with an olefin or polyolefin described above, such as, a polyisobutylene or polypropylene, using well-known alkylation methods.

In some embodiments the phenol may include a lower molecular weight alkyl substituent for example a phenol which carries one or more alkyl chains having a total of less than 28 carbon atoms, preferably less than 24 carbon atoms, more preferably less than 20 carbon atoms, preferably less than 18 carbon atoms, preferably less than 16 carbon atoms and most preferably less than 14 carbon atoms.

A monoalkyl phenol may be preferred, suitably having from 4 to 20 carbons atoms, preferably 6 to 18, more preferably 8 to 16, especially 10 to 14 carbon atoms, for example a phenol having a C₁₂ alkyl substituent.

The aldehyde used to form the Mannich detergent can have 1 to 10 carbon atoms, and is generally formaldehyde or a reactive equivalent thereof such as formalin or paraformaldehyde.

The amine used to form the Mannich detergent can be a monoamine or a polyamine.

Examples of monoamines include but are not limited to ethylamine, dimethylamine, diethylamine, n-butylamine, dibutylamine, allylamine, isobutylamine, cocoamine, stearylamine, laurylamine, methyllaurylamine, oleylamine, N-methyl-octylamine, dodecylamine, diethanolamine, morpholine, and octadecylamine.

Suitable polyamines may be selected from any compound including two or more amine groups. Suitable polyamines include polyalkylene polyamines, for example in which the alkylene component has 1 to 6, preferably 1 to 4, most preferably 2 to 3 carbon atoms. Preferred polyamines are polyethylene polyamines.

The polyamine has 2 to 15 nitrogen atoms, preferably 2 to 10 nitrogen atoms, more preferably 2 to 8 nitrogen atoms.

In especially preferred embodiments the amine used to form the Mannich detergent comprises a diamine. Suitably it includes a primary or secondary amine which takes part in the Mannich reaction and in addition a tertiary amine.

In preferred embodiments component (ii) comprises the product directly obtained from a Mannich reaction and comprising a tertiary amine. For example the amine may comprise a single primary or secondary amine which when reacted in the Mannich reaction forms a tertiary amine which is capable of being quaternised. Alternatively the amine may comprise a primary or secondary amine capable of taking part in the Mannich reaction and also a tertiary amine capable of being quaternised. However component (ii) may comprise a compound which has been obtained from a Mannich reaction and subsequently reacted to form a tertiary amine, for example a Mannich reaction may yield a secondary amine which is then alkylated to a tertiary amine.

In some embodiments the nitrogen-containing species comprising at least one tertiary amine group is (iii) a polyalkylene substituted amine having at least one tertiary amine group.

The preparation of quaternary ammonium salt additives in which the nitrogen-containing species includes component (iii) is described for example in US2008/0113890.

The polyalkene-substituted amines having at least one tertiary amino group of the present invention may be derived from an olefin polymer and an amine, for example ammonia, monoamines, polyamines or mixtures thereof. They may be prepared by a variety of methods such as those described and referred to in US2008/0113890.

Suitable preparation methods include, but are not limited to: reacting a halogenated olefin polymer with an amine; reacting a hydroformylated olefin with a polyamine and hydrogenating the reaction product; converting a polyalkene into the corresponding epoxide and converting the epoxide into the polyalkene substituted amine by reductive amination; and hydrogenation of a β -aminonitrile.

The olefin monomers from which the olefin polymers are derived include polymerizable olefin monomers characterised by the presence of one or more ethylenically unsaturated groups for example ethylene, propylene, 1-butene, isobutene, 1-octene, 1,3-butadiene and isoprene.

The olefin monomers are usually polymerizable terminal olefins. However, polymerizable internal olefin monomers can also be used to form the polyalkenes.

Examples of terminal and internal olefin monomers, which can be used to prepare the polyalkenes according to conventional, well-known polymerization techniques include: ethylene; propylene; butenes, including 1-butene, 2-butene and isobutylene; 1-pentene; 1-hexene; 1-heptene; 1-octene; 1-nonene; 1-decene; 2-pentene; propylene-tetramer; diisobutylene; isobutylene trimer; 1,2-butadiene; 1,3-butadiene; 1,2-pentadiene; 1,3-pentadiene; 1,4-pentadiene; isoprene; 1,5-hexadiene; 2-methyl-5-propyl-1-hexene; 3-pentene; 4-octene; and 3,3-dimethyl-1-pentene.

Suitably the polyalkene substituent of the polyalkene-substituted amine is derived from a polyisobutylene.

The amines that can be used to make the polyalkene-substituted amine include ammonia, monoamines, polyamines, or mixtures thereof, including mixtures of different monoamines, mixtures of different polyamines, and mixtures of monoamines and polyamines (which include diamines). The amines include aliphatic, aromatic, heterocyclic and carbocyclic amines.

The monomers and polyamines suitably include at least one primary or secondary amine group.

Suitable monoamines are generally substituted with a hydrocarbyl group having 1 to about 50 carbon atoms, preferably 1 to 30 carbon atoms. Saturated aliphatic hydrocarbon radicals are particularly preferred.

Examples of suitable monoamines include methylamine, ethylamine, diethylamine, 2-ethylhexylamine, di-(2-ethylhexyl)amine, n-butylamine, di-n-butylamine, allylamine, isobutylamine, cocoamine, stearylamine, laurylamine, methyl laurylamine and oleylamine.

Aromatic monoamines include those monoamines wherein a carbon atom of the aromatic ring structure is attached directly to the amine nitrogen. Examples of aromatic monoamines include aniline, di(para-methylphenyl)amine, naphthylamine, and N-(n-butyl)aniline.

Examples of aliphatic substituted, cycloaliphatic-substituted, and heterocyclic-substituted aromatic monoamines include: para-dodecylaniline, cyclohexyl-substituted naphthylamine, and thienyl-substituted aniline respectively.

Hydroxy amines are also included in the class of useful monoamines. Examples of hydroxyl-substituted monoamines include ethanolamine, di-3-propanolamine, 4-hydroxybutylamine; diethanolamine, and N-methyl-2-hydroxypropylamine.

The amine of the polyalkene-substituted amine can be a polyamine. The polyamine may be aliphatic, cycloaliphatic, heterocyclic or aromatic.

Examples of suitable polyamines include alkylene polyamines, hydroxy containing polyamines, arylpolyamines, and heterocyclic polyamines.

Ethylene polyamines, are especially useful for reasons of cost and effectiveness. Suitable ethylene polyamines are described in relation to the first aspect.

Suitable hydroxy containing polyamines include hydroxyalkyl alkylene polyamines having one or more hydroxyalkyl substituents on the nitrogen atoms and can be prepared by reacting alkylene polyamines with one or more alkylene oxides. Examples of suitable hydroxyalkyl-substituted polyamines include: N-(2-hydroxyethyl)ethylene diamine, N,N-bis(2-hydroxyethyl)ethylene diamine, 1-(2-hydroxyethyl) piperazine, monohydroxypropyl-substituted diethylene triamine, dihydroxypropyl-substituted tetraethylene pentamine, propyl and N-(3-hydroxybutyl)tetramethylene diamine.

Suitable arylpolyamines are analogous to the aromatic monoamines mentioned above except for the presence within their structure of another amino nitrogen. Some examples of arylpolyamines include N,N'-di-n-butyl-para-phenylene diamine and bis-(para-aminophenyl)methane.

Suitable heterocyclic mono- and polyamines will be known to the person skilled in the art. Specific examples of such heterocyclic amines include N-aminopropylmorpholine, N-aminoethylpiperazine, and N,N'-diaminoethylpiperazine. Hydroxy heterocyclic polyamines may also be used for example N-(2-hydroxyethyl)cyclohexylamine, 3-hydroxycyclopentylamine, parahydroxy-aniline and N-hydroxyethylpiperazine.

Examples of polyalkene-substituted amines can include: poly(propylene)amine, poly(butene)amine, N,N-dimethylpolyisobutyleneamine; N-polybutenemorpholine, N-poly(butene)ethylenediamine, N-poly(propylene) trimethylenediamine, N-poly(butene)diethylenetriamine, N',N'-poly(butene)tetraethylenepentamine, and N,N-dimethyl-N'poly(propylene)-1,3 propylenediamine.

The number average molecular weight of the polyalkene-substituted amines can range from 500 to 5000, or from 500 to 3000, for example from 1000 to 1500.

In some embodiments the nitrogen-containing species having at least one tertiary amine group is (iv) a tertiary amine of formula $R^5R^6R^7N$, wherein each of R^5 , R^6 and R^7 is independently an optionally substituted alkyl, alkenyl, aryl, alkaryl or aralkyl group.

In some embodiments of the present invention the tertiary amine of formula $R^5R^6R^7N$ may be a small compound of low complexity and low molecular weight. In some embodiments the tertiary amine may be a complex molecule and/or a molecule of high molecular weight which includes a tertiary amine group.

The tertiary amine compounds of formula $R^5R^6R^7N$ preferably do not include any primary or secondary amine groups. In some embodiments they may be derived from compounds including these groups but preferably these have been subsequently reacted to form additional tertiary amine species. The tertiary amine compound formula $R^5R^6R^7N$ may contain more than one tertiary amine group. However tertiary amine compounds including primary or secondary amine groups are within the scope of the invention provided these groups do not prevent quaternisation of the tertiary amine species.

Tertiary amines (iv) for use herein are preferably compounds of formula $R^5R^6R^7N$, wherein each of R^5 , R^6 and R^7 is independently an optionally substituted alkyl, alkenyl, aryl, alkaryl or alkaryl group.

R^5 , R^6 and R^7 may be the same or different. In some preferred embodiments R^5 and R^6 are the same and R^7 is different.

Preferably each of R^5 and R^6 is independently an optionally substituted alkyl, alkenyl, aryl, alkaryl or alkaryl group having from 1 to 50 carbon atoms, preferably from 1 to 40 carbon atoms, more preferably from 1 to 30 carbon atoms.

Each of R^5 and R^6 may be optionally substituted with one or more groups selected from halo (especially chloro and fluoro), hydroxy, alkoxy, keto, acyl, cyano, mercapto, alkylmercapto, dialkylamino, nitro, nitroso, and sulphonyl. The alkyl groups of these substituents may be further substituted.

Preferably each of R^5 and R^6 is independently an optionally substituted alkyl or alkenyl group. Preferably each of R^5 and R^6 is independently an optionally substituted alkyl group. In some embodiments each of R^5 and R^6 is independently an optionally substituted alkyl or alkenyl group having from 1 to 50 carbon atoms, preferably from 1 to 40 carbon atoms, more preferably from 1 to 30 carbon atoms, suitably from 1 to 20 carbon atoms, preferably from 1 to 12 carbon atoms,

more preferably from 1 to 10 carbon atoms, suitably from 1 to 8 carbon atoms, for example from 1 to 6 carbon atoms.

In some preferred embodiments R^5 is an optionally substituted alkyl or alkenyl group, preferably having from 1 to 10, preferably from 1 to 4 carbon atoms. Preferably R^5 is an alkyl group. It may be a substituted alkyl group, for example a hydroxy substituted alkyl group. Preferably R^5 is an unsubstituted alkyl group. The alkyl chain may be straight-chained or branched. Preferably R^5 is selected from methyl, ethyl, propyl and butyl, including isomers thereof. Most preferably R^5 is methyl.

In some preferred embodiments R^6 is an optionally substituted alkyl or alkenyl group, preferably having from 1 to 10, preferably from 1 to 4 carbon atoms. Preferably R^6 is an alkyl group. It may be a substituted alkyl group, for example a hydroxy substituted alkyl group. Preferably R^6 is an unsubstituted alkyl group. The alkyl chain may be straight-chained or branched. Preferably R^6 is selected from methyl, ethyl, propyl and butyl, including isomers thereof. Most preferably R^6 is methyl.

In some embodiments R^7 is an optionally substituted alkyl or alkenyl group having from 1 to 50 carbon atoms, preferably from 1 to 40 carbon atoms, more preferably from 1 to 30 carbon atoms, suitably from 1 to 20 carbon atoms, preferably from 1 to 12 carbon atoms, more preferably from 1 to 10 carbon atoms, suitably from 1 to 8 carbon atoms, for example from 1 to 6 carbon atoms. Suitable substituents include halo (especially chloro and fluoro), hydroxy, alkoxy, keto, acyl, cyano, mercapto, alkylmercapto, amino, alkylamino, nitro, nitroso, sulphony, amido, alkylamido, imido and alkylimido. The alkyl groups of these substituents may be further substituted.

In some embodiments R^7 is an optionally substituted alkyl or alkenyl group, preferably having from 1 to 10, preferably from 1 to 4 carbon atoms. Suitably R^7 is an optionally substituted alkyl group. Preferably R^7 is a substituted alkyl group. Preferred substituents include alkoxy and hydroxyl groups.

In some preferred embodiments R^7 is a hydroxyl-substituted alkyl group. The alkyl chain may be straight-chained or branched. Most preferably R^7 is a hydroxyethyl group.

Suitable tertiary amine compounds of formula $R^5R^6R^7N$ include simple alkylamino and hydroxyalkylamino compounds; trialkylamino compounds having a high molecular weight substituent; Mannich reaction products including a tertiary amine and substituted acylated amines or alcohols including a tertiary amine.

Simple alkylamino and hydroxyalkyl amino compounds are preferably compounds of formula $R^5R^6R^7N$, wherein each of R^5 , R^6 and R^7 is an alkyl group or a hydroxyalkyl group. Each of R^5 , R^6 and R^7 may be the same or different. In some embodiments each of R^5 , R^6 and R^7 is independently selected from an alkyl or hydroxyalkyl group having 1 to 10, preferably 1 to 6 carbon atoms, for example 1 to 4 carbon atoms. Each of R^5 , R^6 and R^7 may be independently selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, hydroxymethyl, hydroxyethyl, hydroxypropyl, hydroxybutyl, hydroxypentyl and hydroxyhexyl. The amine of formula $R^5R^6R^7N$ may be a trialkylamine, a dialkylhydroxyalkylamine, a dihydroxyalkylalkylamine or a trihydroxyalkylamine. There are many different compounds of this type and these will be known to the person skilled in the art.

In some embodiments one or two of the groups R^5 , R^6 and R^7 is a short chain alkyl group having 1 to 6, preferably 1 to 4 carbon atoms and the other one or two groups is a longer chain alkyl or group having 6 to 30, preferably 10 to 24 carbon atoms.

In some embodiments each of R^5 and R^6 is C_1 to C_4 alkyl, preferably methyl and R^7 is an alkyl or alkenyl group having 6 to 36, preferably 10 to 30, for example 12 to 24 carbon atoms.

Compounds of this type include, for example, dimethyloctadecylamine and hexadecyl dimethyl amine.

In order to provide a quaternary ammonium compound, the hexadecyl dimethyl amine may be quaternised by reaction with propylene oxide (for example 1 to 3 molar equivalent of propylene oxide) and polyisobutylene succinic acid (for example 1 molar equivalent of polyisobutylene succinic acid).

For example in some embodiments R^5 is C_1 to C_4 alkyl, preferably methyl and each R^6 and R^7 is an alkyl or alkenyl having 6 to 36, preferably 8 to 30, for example 10 to 24 carbon atoms.

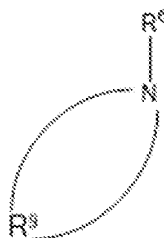
Compounds of this type include, for example, hexadecyl dimethyl amine, N-methyl N,N-ditallowamine and dicocomethyl amine.

Especially preferred tertiary amine compounds of formula $R^5R^6R^7N$ include N,N-dimethyl ethanolamine, dimethyloctadecylamine and N-methyl-N,N-ditallowamine.

In some embodiments the nitrogen-containing species having at least one tertiary amine group is (v) a cyclic tertiary amine.

Suitable cyclic amines have the formula (D1):

23



(D1)

wherein R^6 is an optionally substituted alkyl, alkenyl, aryl, aralkyl or alkaryl group, and R^9 together with N forms a heterocycle.

Preferably heterocycle has less than 12 carbon atoms. Preferably R^6 has less than 8 carbon atoms.

Preferably R^6 is an optionally substituted alkyl, alkenyl or aryl group having from 1 to 7 carbon atoms, preferably from 1 to 5 carbon atoms, more preferably from 1 to 4 carbon atoms.

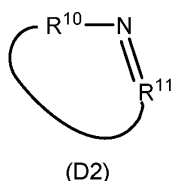
R^6 may be optionally substituted with one or more groups selected from halo (especially chloro and fluoro), hydroxy, alkoxy, keto, acyl, cyano, mercapto, alkylmercapto, dialkylamino, nitro, nitroso, and sulphony. The alkyl groups of these substituents may be further substituted.

Preferably R^6 is an optionally substituted alkyl or alkenyl group. Preferably R^6 is an optionally substituted alkyl group. Preferably R^6 is an optionally substituted alkyl or alkenyl group having from 1 to 7 carbon atoms, preferably from 1 to 6 carbon atoms, more preferably from 1 to 5 carbon atoms, suitably from 1 to 4 carbon atoms, preferably from 1 to 3 carbon atoms, more preferably from 1 to 2 carbon atoms.

Preferably R^6 is an optionally substituted alkyl or alkenyl group, preferably having from 1 to 6, preferably from 1 to 4 carbon atoms. Preferably R^6 is an alkyl group. It may be a substituted alkyl group, for example a hydroxy substituted alkyl group. Preferably R^6 is an unsubstituted alkyl group or a hydroxy alkyl group. More preferably R^6 is an unsubstituted alkyl group. The alkyl chain may be straight-chained or branched. Preferably R^6 is selected from methyl, ethyl, propyl and butyl, including isomers thereof. Most preferably R^6 is methyl.

In some embodiments R^{10} , R^{11} and N together form an aromatic ring and the cyclic amine may have the structure (D2):

24



In such embodiments the total number of carbon atoms in groups R^{10} and R^{11} is preferably less than 19.

R^9 together with N may form an aliphatic heterocyclic group or an aromatic heterocyclic group. Thus they form a heterocyclic ring. There may be one or more further heteroatoms in the ring. Suitably the ring may include one or more further atoms selected from N, O and S.

The heterocyclic group formed by R^9 and N may be substituted or unsubstituted; i.e. there may be one or more substituents bonded to atoms that form the ring. Suitable substituents include halo (especially chloro and fluoro); hydroxy, alkoxy, keto, acyl, cyano, mercapto, alkylmercapto, alkyl, alkenyl, aryl, dialkylamino, alkylamino, nitro, nitroso, and sulphony. The alkyl, alkenyl and aryl groups of these substituents may be further substituted.

The heterocyclic group may be substituted with a further cyclic group i.e. it may be part of a bicyclic heterocyclic group.

In some preferred embodiments the heterocyclic group formed by N and R^9 is not substituted.

Preferably the group formed by R^9 and N is a heterocyclic group having from 3 to 12 atoms in the ring. The atoms in the ring include carbon atoms and other atoms. Preferably the heterocyclic ring includes 3 to 10 atoms, preferably 4 to 8, more preferably 5 to 7 atoms.

In some preferred embodiments the heterocyclic group contains only carbon and nitrogen atoms within the ring.

The heterocyclic group formed by R^9 and N may be aliphatic or aromatic.

In some preferred embodiments R^9 and N together form an aliphatic or aromatic heterocycle having 5 to 7 atoms in the ring.

Suitable aliphatic heterocyclic groups include those based on pyrrolidine, piperidine, morpholine and piperazine.

Suitable aliphatic heterocyclic groups include unsaturated heterocycles that are not aromatic. i.e. they may contain one or more double bonds, for example those based on dihydropyrrole.

Suitable aromatic heterocyclic groups including those based on pyrrole, pyridine, imidazole, pyrimidine, isoxazole, quinolone, oxazole, and pyrazole.

In especially preferred embodiments R^9 and N together form an imidazole moiety or a pyrrolidine moiety.

Suitably R^9 contains 3 to 11 carbon atoms (and optional heteroatoms with the ring), preferably 3 to 10 carbon atoms, preferably 3 to 9 carbon atoms, suitably 3 to 8 carbon atoms, preferably 3 to 7 carbon atoms, more preferably 3 to 6 carbon atoms, for example 3 to 5 or 3 to 4 carbon atoms.

Preferably R^9 contains less than 8 carbon atoms.

The compound of formula (D1) or (D2) is a cyclic tertiary amine. By this we mean to refer to an amine group in which the nitrogen atom is part of a heterocyclic ring and is preferably further bonded to another group.

Suitably the compound of formula (D1) or (D2) is a cyclic tertiary amine having less than 18 carbon atoms. Preferably it has less than 16 carbon atoms, suitably less than 14 carbon atoms, preferably less than 12 carbon atoms, for example less than 10 carbon atoms, less than 8 carbon atoms or less than 6 carbon atoms.

Suitably the cyclic amine compound is a compound of formula (D1) and is an N-substituted heterocyclic amine. Preferably it is an N-alkyl heterocyclic amine having 5 to 7 atoms in the heterocyclic ring.

In some preferred embodiments the tertiary amine is an N-methyl cyclic amine wherein the heterocyclic ring moiety may include one or more further heteroatoms such as O, N or S and may be aliphatic or non-aromatic.

There are many different compounds of this type and these will be known to the person skilled in the art.

Some suitable cyclic amines for use herein are based on N-alkyl heterocycles, for example N-methyl heterocycles, selected from pyrrolidine, piperidine, morpholine, piperazine, pyrrole, imidazole and dihydropyrrole.

Other suitable amines include those based on the above in which the heterocyclic ring includes one or more further alkyl, alkenyl or aryl substituents, provided the total number of carbon atoms in the tertiary amine is less than 19. For example compounds which include one, two or three methyl groups bonded to carbon atoms within the heterocyclic ring are within the scope of the invention.

Some suitable cyclic amines for use herein include those based on heterocycles in which R¹⁰, R¹¹ and N together form an aromatic ring, for example those based on piperidine, pyrimidine, isoxazole and oxazole.

Other suitable amines include those based on the above in which the heterocyclic ring includes one or more further alkyl, alkenyl or aryl substituents, provided the total number of carbon atoms in the tertiary amine is less than 19.

Tertiary amine compounds including primary or secondary amine groups are within the scope of the invention provided these groups do not prevent quaternisation of the tertiary amine species.

The cyclic tertiary amine compounds preferably do not include any free primary or secondary amine groups. The tertiary amine compound of formula R⁹==NR⁶ may contain more than one tertiary amine group.

Some preferred cyclic amine compounds include 1-methyl pyrrolidine, 1-methylimidazole, 1,2-dimethyl-1H-imidazole, pyridine and mixtures and isomers thereof. 8-hydroxyquinoline could also be used.

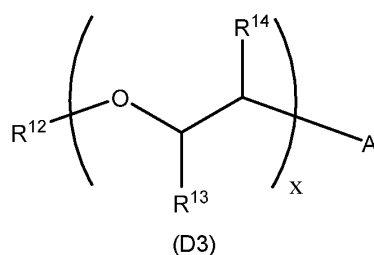
Especially preferred tertiary amine compounds include methyl pyrrolidine and methyl imidazole.

In some embodiments the nitrogen-containing species having at least one tertiary amine group is (vi) a polyetheramine compound.

Some preferred polyetheramine compounds are polyoxyalkylene amines.

In some preferred embodiments the polyetheramine compound has the general formula (D3):

27



wherein R^{12} is H or a hydrocarbonyl group having from 1 to 30 carbon atoms; R^{13} and R^{14} are each independently hydrogen or lower alkyl having from about 1 to about 6 carbon atoms and each R^{13} and R^{14} is independently selected in each $--O--CH(R^{13})--CH(R^{14})--$ unit; and x is an integer of from 1 to 100, preferably 5 to 50; A is $NR^{15}R^{16}$, $NR^{17}NR^{15}R^{16}$, $OR^{17}NR^{15}R^{16}$, $OCONR^{15}R^{16}$ or a polyamine moiety having about 2 to about 12 nitrogen atoms, about 4 to about 40 carbon atoms and including at least one tertiary amine group; wherein each of R^{15} and R^{16} is independently an alkyl group having about 1 to about 20 carbon atoms in each alkyl group, and R^{17} is an alkylene group having 1 to 20 carbon atoms.

In a preferred embodiment R^{12} is H or a C_1 - C_{30} alkyl preferably a C_4 - C_{20} alkyl.

In another preferred embodiment R^{12} is an alkylphenyl group, wherein the alkyl group has from about 1 to about 24 carbon atoms.

Preferably, one of R^{13} and R^{14} is lower alkyl of 1 to 4 carbon atoms, and the other is hydrogen. More preferably, one of R^{13} and R^{14} is methyl or ethyl, and the other is hydrogen.

Preferably each of R^{15} and R^{16} is an alkyl group having from about 1 to about 20 carbon atoms in each alkyl group, preferably about 1 to about 6 carbon atoms, more preferably about 1 to about 4 carbon atoms. Suitably R^{17} is an alkyl group having from about 1 to about 20 carbon atoms in each alkyl group, preferably about 1 to about 6 carbon atoms, more preferably about 1 to about 4 carbon atoms.

In some embodiments A is a polyamine moiety comprising a tertiary amine group and having from about 2 to about 12 nitrogen atoms and from about 4 to about 40 carbon atoms.

In some embodiments, the compound of formula (D3) may be derived by alkoxylation of an N,N-dialkyl hydroxyalkylamine such as N,N-dimethylaminoethanol or N,N-dimethylaminopropanol. In other embodiments the compound of formula D4 may be derived by alkoxylation of a C_1 - C_{30} alcohol preferably a C_4 - C_{20} alcohol followed by amination with ammonia further followed by alkylation of the amine. Such processes are described in US2013225463.

Other preferred features of the polyetheramine compound are also described in US2013225463.

In especially preferred embodiments, the quaternary ammonium salt additive of the present invention comprises compounds prepared by the reaction of a quaternising agent and (i) the reaction product of a hydrocarbyl-substituted acylating agent and a compound comprising at least one tertiary amine group and a primary amine, secondary amine or alcohol group.

The quaternary ammonium salt compounds used in the present invention are prepared by the reaction of a nitrogen-containing species having at least one tertiary amine group and a quaternising agent.

Any compound capable of reacting with the tertiary amine group to form a quaternary ammonium cation may be used as the quaternising agent.

In some embodiments following reaction with a quaternising agent an ion exchange reaction may be carried out to provide a quaternary ammonium compound having a different anion.

The quaternary ammonium compounds used in the present invention may be prepared by reaction of a tertiary amine with a quaternising agent selected from an ester of a carboxylic acid, epoxides optionally in combination with an acid, dialkyl sulfates, benzyl halides, hydrocarbyl substituted carbonates, alkyl halides, alkyl sulfonates, sultones, hydrocarbyl substituted phosphates, hydrocarbyl substituted borates, alkyl nitrites, alkyl nitrates, hydroxides, N-oxides or mixtures thereof.

In fuel applications it is often desirable to reduce the levels of halogen-, sulfur-, and phosphorus-containing species. Thus if a quaternising agent containing such an element is used it may be advantageous to carry out a subsequent reaction to exchange the counterion. For example a quaternary ammonium salt formed by reaction with an alkyl halide could be subsequently reacted with sodium hydroxide and the sodium halide salt removed by filtration.

The quaternising agent can include halides, such as chloride, iodide or bromide; hydroxides; sulphonates; bisulphites, alkyl sulphates, such as dimethyl sulphate; sulphones; phosphates; C1-12 alkylphosphates; di C1-12 alkylphosphates; borates; C1-12 alkylborates; nitrites; nitrates; carbonates; bicarbonates; alkanoates; O,O-di C1-12 alkyldithiophosphates; or mixtures thereof.

Preferably the quaternising agent is selected from esters of a carboxylic acid, dialkyl sulfates, benzyl halides, hydrocarbyl substituted carbonates, hydrocarbyl substituted epoxides optionally in combination with an acid, alkyl halides, alkyl sulfonates, sultones, hydrocarbyl substituted

phosphates, hydrocarbyl substituted borates, alkyl nitrites, alkyl nitrates, hydroxides, N-oxides, chloroacetic acid or salts thereof, or mixtures thereof.

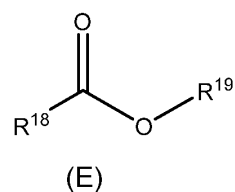
In one embodiment the quaternising agent may be derived from dialkyl sulphates such as dimethyl sulphate, N-oxides, sulphones such as propane and butane sulphone; alkyl, acyl or aralkyl halides such as methyl and ethyl chloride, bromide or iodide or benzyl chloride, and a hydrocarbyl (or alkyl) substituted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

Preferred quaternising agents for use herein are esters of a carboxylic acid or an epoxide, optionally in combination with an acid.

In one preferred embodiment the quaternising agent is an ester of formula $R^{18}COOR^{19}$.

In such embodiments R^{19} is a C_1 to C_7 alkyl group and $R^{18}COO$ is preferably the residue of a carboxylic acid selected from a substituted aromatic carboxylic acid, an α -hydroxycarboxylic acid and a polycarboxylic acid.

Preferred ester quaternising agents are compounds of formula (E):



in which R^{18} is an optionally substituted alkyl, alkenyl, aryl or alkylaryl group which may comprise a further carboxy derived functional group; and R^{19} is a C_1 to C_{22} alkyl, aryl or alkylaryl group.

The compound of formula (E) is suitably an ester of a carboxylic acid capable of reacting with a tertiary amine to form a quaternary ammonium compound.

Suitable quaternising agents include esters of carboxylic acids having a pK_a of 3.5 or less.

The compound of formula (E) is preferably an ester of a carboxylic acid selected from a substituted aromatic carboxylic acid, an α -hydroxycarboxylic acid and a polycarboxylic acid.

In some preferred embodiments the compound of formula (E) is an ester of a substituted aromatic carboxylic acid and thus R^{18} is a substituted aryl group.

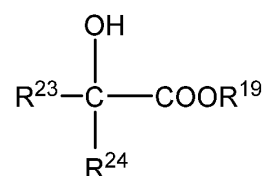
In such embodiments R^{18} is suitably a substituted aryl group having 6 to 10 carbon atoms, preferably a phenyl or naphthyl group, most preferably a phenyl group. R^{18} is suitably substituted with one or more groups selected from carboalkoxy, nitro, cyano, hydroxy, SR^{20} or $NR^{21}R^{22}$. Each of R^{21} and R^{22} may be hydrogen or optionally substituted alkyl, alkenyl, aryl or carboalkoxy groups. Preferably each of R^{21} and R^{22} is hydrogen or an optionally substituted C_1 to C_{22} alkyl group, preferably hydrogen or a C_1 to C_{16} alkyl group, preferably hydrogen or a C_1 to C_{10} alkyl group, more preferably hydrogen or a C_1 to C_4 alkyl group. Preferably R^{21} is hydrogen and R^{22} is hydrogen or a C_1 to C_4 alkyl group. Most preferably R^{21} and R^{22} are both hydrogen. Preferably R^{18} is an aryl group substituted with one or more groups selected from hydroxyl, carboalkoxy, nitro, cyano and NH_2 . R^{18} may be a poly-substituted aryl group, for example trihydroxyphenyl. Preferably R^{18} is a mono-substituted aryl group. Preferably R^{18} is an ortho substituted aryl group. Suitably R^{18} is substituted with a group selected from OH, NH_2 , NO_2 or COOMe. Preferably R^{18} is substituted with an OH or NO_2 group. Suitably R^{18} is a hydroxy substituted aryl group. Most preferably R^{18} is a 2-hydroxyphenyl group.

Preferably R^{19} is an alkyl or alkaryl group. R^{19} may be a C_1 to C_{16} alkyl group, preferably a C_1 to C_{10} alkyl group, suitably a C_1 to C_8 alkyl group. R^{19} may be C_1 to C_{16} alkaryl group, preferably a C_1 to C_{10} alkaryl group, suitably a C_1 to C_8 alkaryl group. R^{19} may be methyl, ethyl, propyl, butyl, pentyl, benzyl or an isomer thereof. Preferably R^{19} is benzyl or methyl. Most preferably R^{19} is methyl.

Some especially preferred compounds of formula (E) are esters of salicylic acid such as benzyl salicylate, methyl salicylate, ethyl salicylate, *n* and *i*-propyl salicylate, and butyl salicylate.

An especially preferred compound of formula (E) is methyl salicylate.

In some embodiments the compound of formula (E) is an ester of an α -hydroxycarboxylic acid. In such embodiments R^{18} is $R^{23}CR^{24}OH$ and the compound of formula (E) has the structure:



wherein R²³ and R²⁴ are the same or different and each is selected from hydrogen, alkyl, alkenyl, aralkyl or aryl. Compounds of this type suitable for use herein are described in EP1254889.

Examples of compounds of formula (E) in which R¹⁸COO is the residue of an α -hydroxycarboxylic acid include methyl-, ethyl-, propyl-, butyl-, pentyl-, hexyl-, benzyl-, phenyl-, and allyl esters of 2-hydroxyisobutyric acid; methyl-, ethyl-, propyl-, butyl-, pentyl-, hexyl-, benzyl-, phenyl-, and allyl esters of 2-hydroxy-2-methylbutyric acid; methyl-, ethyl-, propyl-, butyl-, pentyl-, hexyl-, benzyl-, phenyl-, and allyl esters of 2-hydroxy-2-ethylbutyric acid; methyl-, ethyl-, propyl-, butyl-, pentyl-, hexyl-, benzyl-, phenyl-, and allyl esters of lactic acid; and methyl-, ethyl-, propyl-, butyl-, pentyl-, hexyl-, allyl-, benzyl-, and phenyl esters of glycolic acid. Of the above, a preferred compound is methyl 2-hydroxyisobutyrate.

In some embodiments the compound of formula (E) is an ester of a polycarboxylic acid. In this definition we mean to include dicarboxylic acids and carboxylic acids having more than 2 acidic moieties.

In such embodiments R¹⁸ includes a carboxy derived functional group. This is preferably present in the form of an ester, that is the one or more further acid groups present in the group R¹⁸ are in esterified form. Preferred esters are C₁ to C₄ alkyl esters.

Compound (E) may be selected from the diester of oxalic acid, the diester of phthalic acid, the diester of maleic acid, the diester of malonic acid or the diester of citric acid. One especially preferred compound of formula (E) is dimethyl oxalate.

In preferred embodiments the compound of formula (E) 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.

Compound (E) 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.

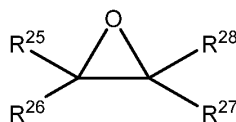
Suitably the compound of formula (E) may be selected from dimethyl oxalate, methyl 2-nitrobenzoate, dimethylphthalate, dimethyltartrate and methyl salicylate

Preferred compounds of formula (E) include dimethyl oxalate, methyl 2-nitrobenzoate and methyl salicylate.

Most preferred ester quaternising agents are dimethyl oxalate and methyl salicylate.

In some preferred embodiments the quaternising agent is an epoxide, optionally in combination with an acid.

Any suitable epoxide compound may be used. Suitable epoxide compounds are those of formula:



wherein each of R^{25} , R^{26} , R^{27} , R^{28} is independently selected from hydrogen or an optionally substituted alkyl, alkenyl or aryl group, provided at least one of R^{25} , R^{26} , R^{27} and R^{28} is hydrogen.

Preferably at least two of R^{25} , R^{26} , R^{27} and R^{28} are hydrogen. Most preferably three of R^{25} , R^{26} , R^{27} and R^{28} are hydrogen. R^{25} , R^{26} , R^{27} and R^{28} may be all hydrogen.

In the structure above and the definitions which follow R^{25} and R^{26} are interchangeable and thus when these groups are different either enantiomer or diastereomer may be used as component (b).

In the structure above and the definitions which follow R^{27} and R^{28} are interchangeable and thus when these groups are different either enantiomer or diastereomer may be used as component (b).

Preferably R^{25} is hydrogen or an optionally substituted alkyl, alkenyl, aryl, alkaryl or aralkyl group. R^{25} may suitably be selected from hydrogen and phenyl. Most preferably R^{25} is hydrogen.

Preferably R^{26} is hydrogen or an optionally substituted alkyl, alkenyl, aryl, alkaryl or aralkyl group. Most preferably R^{26} is hydrogen.

Preferably R^{27} is hydrogen or an optionally substituted alkyl, alkenyl, aryl, alkaryl or aralkyl group. Most preferably R^{27} is hydrogen.

Preferably R^{28} is hydrogen or an optionally substituted alkyl, alkenyl, aryl, alkaryl or aralkyl group.

In some preferred embodiments R^{28} is an optionally substituted aryl group. For example R^{28} may be phenyl.

In some preferred embodiments R^{28} is an optionally substituted alkyl or alkenyl group. R^{28} may be an alkyl group, for example an unsubstituted alkyl group. R^{28} may be an alkyl group having 1 to 50 carbon atoms, preferably from 1 to 30 carbon atoms, suitably 1 to 20 carbon atoms, preferably from 1 to 12 carbon atoms, for example from 1 to 8 or from 1 to 4 carbon atoms.

In some embodiments R^{28} is hydrogen.

In some embodiments R^{28} is the moiety $\text{CH}_2\text{OR}^{29}$ or $\text{CH}_2\text{OCOR}^{30}$ wherein each of R^{29} and R^{30} may be an optionally substituted alkyl, alkenyl, aryl, alkaryl or aralkyl group.

Preferably R^{25} , R^{26} and R^{27} are hydrogen and R^{28} is selected from phenyl, an optionally substituted alkyl or alkenyl group having 1 to 20 carbon atoms, hydrogen, $\text{CH}_2\text{OR}^{29}$ or $\text{CH}_2\text{OCOR}^{30}$ wherein each of R^{29} and R^{30} is an optionally substituted alkyl or aryl group having from 1 to 20 carbon atoms.

R^{29} is preferably an optionally substituted alkyl or aryl group, preferably having from 1 to 30 carbon atoms, preferably from 1 to 20 carbon atoms, suitably from 1 to 12 carbon atoms. When R^{29} is an alkyl group it may be straight-chained or branched. In some embodiments it is branched. R^{29} may be an optionally substituted phenyl group.

In one embodiment R^{29} is a 2-methyl phenyl group. In another embodiment R^{29} is $\text{CH}_2\text{C}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$.

R^{30} may be an optionally substituted alkyl, alkenyl, aryl, alkaryl or aralkyl group.

R^{30} is preferably an optionally substituted alkyl or aryl group, preferably having from 1 to 30 carbon atoms, preferably from 1 to 20 carbon atoms, suitably from 1 to 12 carbon atoms. When R^{30} is an alkyl group it may be straight-chained or branched. In some preferred embodiments it is branched. R^{30} may be an optionally substituted phenyl group.

In one embodiment R^{30} is $C(CH_3)R_2$ wherein each R is an alkyl group. The R groups may be the same or different.

Preferably R^{30} is an alkyl group having 1 to 5 carbon atoms. In some embodiments R^{30} may include an oxygen atom in the carbon chain, i.e. R^{30} may include an ether functional group.

Suitable epoxide compounds for use herein as quaternising agents include ethylene oxide, propylene oxide, butylene oxide, pentylene oxide, hexylene oxide, heptylene oxide, dodecylene oxide, alkyl glycidyl ethers, for example 2-ethylhexyl glycidyl ether or isopropyl glycidyl ether, alkyl glycidyl esters styrene oxide, stilbene oxide and other C2 to C30 hydrocarbyl groups.

Some preferred epoxide compounds for use herein as quaternising agents include styrene oxide, ethylene oxide, propylene oxide, butylene oxide, stilbene oxide, dodecylene oxide 2-ethylhexyl glycidyl ether and isopropyl glycidyl ether. Styrene oxide, butylene oxide, 2-ethylhexyl glycidyl ether and propylene oxide are especially preferred.

Typically epoxide quaternising agents are used in combination with an acid. However in embodiments in which the nitrogen-containing species having at least one tertiary amine group includes (i) the reaction product of a substituted succinic acid which is an ester or an amide and which also includes a further unreacted carboxylic acid group, an additional acid may be omitted and the hydrocarbyl epoxide may be used alone as the quaternising agent. It is believed that formation of the quaternary ammonium salt is promoted by protonation by the carboxylic acid group also present in the molecule.

In such embodiments in which a further acid is not used, the quaternary ammonium compound is suitably prepared in a protic solvent. Suitable protic solvents include water, alcohols (including polyhydric alcohols) and mixtures thereof. Preferred protic solvents have a dielectric constant of greater than 9.

In preferred embodiments the epoxide quaternising agent is used in combination with an acid. Any suitable acid may be used. In preferred embodiments the acid is an organic acid, preferably a carboxylic acid. Suitable carboxylic acids include monocarboxylic acids and polycarboxylic acids. Preferably the acid is a monocarboxylic acid or a dicarboxylic acid.

For the avoidance of doubt the acid suitably activates the epoxide and forms the anionic counterion of the quaternary ammonium compound. In some embodiments a subsequent ion exchange reaction may be carried out but this is not preferred.

Any compound which includes a carboxylic acid functional group may be used. In some embodiments the acid may be a very small simple molecule. Examples of suitable small simple acids include formic acid, acetic acid, propionic acid and butyric acid.

In some embodiments the acid may be a simple fatty acid compound. However the acid may also be a more complex molecule including additional acid functional groups.

Suitable fatty acids include caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid, lignoceric acid, cerotic acid, myristoleic acid, palmitoleic acid, sapienic acid, oleic acid, elaidic acid, vaccenic acid, linoleic acid, linoelaidic acid, arachidonic acid, eicosapentaenoic acid, erucic acid, undecylenic acid and docosahexenoic acid.

Suitable complex acids include optionally substituted phthalic acids and succinic acid derivatives.

Some preferred species of this type are hydrocarbyl substituted phthalic acid or succinic acid derivatives. Hydrocarbyl substituted succinic acid derivatives are especially preferred.

In one embodiment the hydrocarbyl group is preferably a polyisobutenyl group, preferably having a molecular weight of from 100 to 5000, preferably from 300 to 4000, suitably from 450 to 2500, for example from 450 to 2000 or from 450 to 1500.

In one embodiment the hydrocarbyl group is an alkyl or alkenyl group having 6 to 30 carbon atoms, preferably 10 to 26 carbon atoms, more preferably 12 to 24 carbon atoms, suitably 16 to 20 carbon atoms, for example 18 carbon atoms.

In one embodiment the hydrocarbyl group is an alkyl or alkenyl group having 6 to 50 carbon atoms, preferably 12 to 40 carbon atoms, more preferably 18 to 36 carbon atoms, suitably 24 to 36 carbon atoms, for example 30 carbon atoms.

The succinic acid derivative may be polyisobutylene succinic acid (for example which may be used with an epoxide quaternising agent such as propylene oxide). The polyisobutylene succinic acid may form a salt via one or both of its acid groups. When only one of its acid groups is used to form a salt it may maintain a free acid group.

In embodiments in which the acid has more than one acid functional group the further groups may be present as the free acid or the ester. Where there is more than one free acid group there may be an equivalent number of cations. For example in some embodiments the quaternary

ammonium compound may comprise a dicarboxylate dianion and two quaternary ammonium ions. Compounds of this type are described in EP3024913.

Some preferred epoxide quaternising agents for use herein include styrene oxide, butylene oxide, propylene oxide or 2-ethylhexyl glycidyl ether in combination with a monocarboxylic acid, suitably acetic acid.

Some preferred epoxide quaternising agents for use herein include styrene oxide, butylene oxide, propylene oxide or 2-ethylhexyl glycidyl ether in combination with a polycarboxylic acid, suitably a polyisobutenyl substituted succinic acid.

In some preferred embodiments the quaternising agent is selected from an ester of a carboxylic acid, a quaternising agent optionally in combination with an acid and chloroacetic acid or a salt thereof.

In some preferred embodiments the quaternary ammonium compound is the reaction product of a tertiary amine of a tertiary amine of formula $R^5R^6R^7N$, wherein each of R^5 , R^6 and R^7 is independently an optionally substituted alkyl or alkenyl group having 1 to 40 carbon atoms; an epoxide; and a monocarboxylic acid or a dicarboxylic acid.

In some embodiments the quaternary ammonium compound is the reaction product of a tertiary amine of a tertiary amine of formula $R^5R^6R^7N$, wherein each of R^5 , R^6 and R^7 is an alkyl group or a hydroxyalkyl group having 1 to 10 carbon atoms; an epoxide; and a monocarboxylic acid or a dicarboxylic acid.

In some embodiments the quaternary ammonium compound is the reaction product of a tertiary amine of a tertiary amine of formula $R^5R^6R^7N$, wherein one or two of the groups R^5 , R^6 and R^7 is a short chain alkyl group having 1 to 6, preferably 1 to 4 carbon atoms and the other one or two groups is a longer chain alkyl or group having 6 to 30, preferably 10 to 24 carbon atoms; an epoxide; and a monocarboxylic acid or a dicarboxylic acid.

In some embodiments the quaternary ammonium compound is the reaction product of a tertiary amine; an epoxide, preferably propylene oxide; and an optionally substituted succinic acid, preferably a polyisobutenyl substituted succinic acid wherein the tertiary amine has the formula $R^5R^6R^7N$, wherein one or two of the groups R^5 , R^6 and R^7 is a short chain alkyl group having 1 to 6, preferably 1 to 4 carbon atoms and the other one or two groups is a longer chain alkyl or group having 6 to 30, preferably 10 to 24 carbon atoms.

Preferred quaternary ammonium salt additives for use in the present invention include at least one reaction product of:

- (x) the reaction product of a hydrocarbyl-substituted acylating agent and a compound having at least one tertiary amine group and a primary amine, secondary amine or alcohol group; and
- (y) a quaternising agent selected from: an ester of a carboxylic acid; and an epoxide, optionally in combination with an acid.

Preferred quaternary ammonium salt additives for use in the present invention include at least one reaction product of:

- (x) the reaction product of a hydrocarbyl-substituted succinic acid derived acylating agent including an average of at least 1.2 succinic acid moieties per molecule and a compound having at least one tertiary amine group and a primary amine, secondary amine or alcohol group; and
- (y) a quaternising agent selected from: an ester of a carboxylic acid; and an epoxide, optionally in combination with an acid.

More preferred quaternary ammonium salt additives of the present invention include at least one reaction product of:

- (x) a polyisobutenyl substituted succinic acid or anhydride thereof and an amine or alcohol which further includes a tertiary amine group; and
- (y) a quaternising agent 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; and an epoxide selected from one or more of ethylene oxide, propylene oxide, butylene oxide, pentylene oxide, hexylene oxide, heptylene oxide, isopropyl glycidyl ether, styrene oxide, stilbene oxide and other C2 to C30 hydrocarbyl groups, optionally in combination with an acid.

Some especially preferred quaternary ammonium salt additives of the present invention include at least one reaction product of:

- (x) a polyisobutenyl substituted succinic acid or anhydride thereof having a PIB molecular weight of 170 to 2800, preferably 450 to 1500 and an amine or alcohol selected from dimethylaminopropanol, dimethylaminopropylamine, N,N-diethyl-1,3-diaminopropane, N,N-dimethylethylenediamine, N,N-diethylethylenediamine, N,N-dibutylethylenediamine, or combinations thereof; and
- (y) a quaternising agent selected from dimethyl oxalate, methyl 2-nitrobenzoate, dimethylphthalate, dimethyltartrate, methyl salicylate; and an epoxide selected from styrene oxide, 2-ethylhexyl glycidyl ether, ethylene oxide, propylene oxide, butylene oxide, 2-ethylhexyl glycidyl ether, stilbene oxide and isopropyl glycidyl ether, in combination with an acid.

Some especially preferred quaternary ammonium salt additives of the present invention include at least one reaction product of:

- (x) a polyisobutenyl substituted succinic acid or anhydride thereof having a PIB molecular weight of 170 to 2800, preferably 450 to 1500 and an amine or alcohol selected from dimethylaminopropanol and dimethylaminopropylamine; and
- (y) a quaternising agent selected from dimethyl oxalate; methyl salicylate; and an epoxide selected from styrene oxide, propylene oxide and butylene oxide, in combination with an acid.

Some especially preferred quaternary ammonium salt additives of the present invention include at least one reaction product of:

- (x) a polyisobutenyl substituted succinic acid or anhydride thereof having a PIB molecular weight of 170 to 2800, preferably 450 to 1500 and including an average of at least 1.2 succinic acid moieties per molecule, and an amine or alcohol selected from dimethylaminopropanol and dimethylaminopropylamine; and
- (y) a quaternising agent selected from dimethyl oxalate; methyl salicylate; and an epoxide selected from styrene oxide, propylene oxide and butylene oxide, in combination with an acid.

In some embodiments the quaternary ammonium salt additives for use in the present invention are the quaternised reaction product of a fatty acid (for example oleic acid) and dimethylaminopropyl amine.

The present invention relates to uses of a diesel fuel composition.

By diesel fuel we include any fuel suitable for use in a diesel engine, either for road use or non-road use. This includes, but is not limited to, fuels described as diesel, marine diesel, heavy fuel oil, industrial fuel oil etc.

The diesel fuel composition of the present invention may comprise a petroleum-based fuel oil, especially a middle distillate fuel oil. Such distillate fuel oils generally boil within the range of from 110°C to 500°C, e.g. 150°C to 400°C. The diesel fuel may comprise atmospheric distillate or vacuum distillate, cracked gas oil, or a blend in any proportion of straight run and refinery streams such as thermally and/or catalytically cracked and hydro-cracked distillates.

The diesel fuel composition used in the present invention may comprise non-renewable Fischer-Tropsch fuels such as those described as GTL (gas-to-liquid) fuels, CTL (coal-to-liquid) fuels and OTL (oil sands-to-liquid).

The diesel fuel composition used in the present invention may comprise a renewable fuel such as a biofuel composition or biodiesel composition.

The diesel fuel composition may comprise 1st generation biodiesel. First generation biodiesel contains esters of, for example, vegetable oils, animal fats and used cooking fats. This form of biodiesel may be obtained by transesterification of oils, for example rapeseed oil, soybean oil, safflower oil, palm oil, corn oil, peanut oil, cotton seed oil, tallow, coconut oil, physic nut oil (*Jatropha*), sunflower seed oil, used cooking oils, hydrogenated vegetable oils or any mixture thereof, with an alcohol, usually a monoalcohol, in the presence of a catalyst.

The diesel fuel composition may comprise second generation biodiesel. Second generation biodiesel is derived from renewable resources such as vegetable oils and animal fats and processed, often in the refinery, often using hydroprocessing such as the H-Bio process developed by Petrobras. Second generation biodiesel may be similar in properties and quality to petroleum based fuel oil streams, for example renewable diesel produced from vegetable oils, animal fats etc. and marketed by ConocoPhillips as Renewable Diesel and by Neste as NExBTL.

The diesel fuel composition used in the present invention may comprise third generation biodiesel. Third generation biodiesel utilises gasification and Fischer-Tropsch technology including those described as BTL (biomass-to-liquid) fuels. Third generation biodiesel does not differ widely from some second generation biodiesel, but aims to exploit the whole plant (biomass) and thereby widens the feedstock base.

The diesel fuel composition may contain blends of any or all of the above diesel fuel compositions.

In some embodiments the diesel fuel composition used in the present invention may be a blended diesel fuel comprising bio-diesel. In such blends the bio-diesel may be present in an amount of, for example up to 0.5%, up to 1%, up to 2%, up to 3%, up to 4%, up to 5%, up to 10%, up to 20%, up to 30%, up to 40%, up to 50%, up to 60%, up to 70%, up to 80%, up to 90%, up to 95% or up to 99%.

In some embodiments the diesel fuel composition may comprise a secondary fuel, for example ethanol. Preferably however the diesel fuel composition does not contain ethanol.

The diesel fuel composition of the present invention may contain a relatively high sulphur content, for example greater than 0.05% by weight, such as 0.1% or 0.2%.

However in preferred embodiments the diesel fuel has a sulphur content of at most 0.05% by weight, more preferably of at most 0.035% by weight, especially of at most 0.015%. Fuels with

even lower levels of sulphur are also suitable such as, fuels with less than 50 ppm sulphur by weight, preferably less than 20 ppm, for example 10 ppm or less.

The present inventors have surprisingly found that even very low concentrations of the quaternary ammonium compound provide a significant reduction in the emission of particulates having a diameter of less than 2.5 microns from a direct injection diesel engine.

Suitably the quaternary ammonium salt additive is present in the diesel fuel composition in an amount of less than 300 ppm, suitably less than 100 ppm, preferably less than 50 ppm, preferably less than 30 ppm. In some embodiments the quaternary ammonium compound is present in the diesel fuel composition in an amount of less than 20 ppm, preferably less than 15 ppm, preferably less than 10 ppm, for example less than 8 ppm or even less than 5 ppm.

Suitably the quaternary ammonium salt additive is present in the diesel fuel in an amount of from 0.1 to 100 ppm, preferably 0.5 to 50 ppm, preferably 1 to 25 ppm or 1 to 10 ppm.

In this specification any reference to ppm is to parts per million by weight.

The diesel fuel compositions used in the present invention may comprise a mixture of two or more quaternary ammonium compounds. In such embodiments the above amounts refer to the total amounts of all such compounds present in the composition.

The skilled person will appreciate that commercial sources of additive may be provided with a diluent or carrier. All amounts mentioned therein relate to the amount of active quaternary ammonium compound.

The quaternary ammonium salt additive comprises one or more quaternary ammonium compounds.

The amounts of quaternary ammonium salt additive referred to herein refer to the total amount of active quaternary ammonium compounds present in the composition. The amounts referred to herein do not include any diluent or carrier and do not include any unreacted starting materials or byproducts. Such components may however be present in the additive composition dosed into a fuel. The crude reaction mixture following the quaternisation reaction may be used as an additive without purification but the amounts referred to herein relate to the active quaternary ammonium compound or compounds.

The use of mixtures may arise due to the availability of starting materials or a particular mixture may be deliberately selected to use in order to achieve a benefit. For example a particular

mixture may lead to improvements in handling, a general improvement in performance or a synergistic improvement in performance.

In some embodiments the diesel fuel composition used in the present invention may comprise one or more further nitrogen containing detergents.

In such embodiments the one or more further nitrogen containing detergents may be selected from:

- (i) the product of a Mannich reaction between an aldehyde, an amine and an optionally substituted phenol;
- (ii) the reaction product of a carboxylic acid-derived acylating agent and an amine;
- (iii) the reaction product of a carboxylic acid-derived acylating agent and hydrazine;
- (iv) a salt formed by the reaction of a carboxylic acid with di-n-butylamine or tri-n-butylamine; and
- (v) the reaction product of a hydrocarbyl-substituted dicarboxylic acid or anhydride and an amine compound or salt which product comprises at least one amino triazole group.

Preferably the one or more the further nitrogen containing detergents is selected from:

- (i) the product of a Mannich reaction between an aldehyde, an amine and an optionally substituted phenol;
- (ii) the reaction product of a carboxylic acid-derived acylating agent and an amine; and
- (v) the reaction product of a hydrocarbyl-substituted dicarboxylic acid or anhydride and an amine compound or salt which product comprises at least one amino triazole group;

and mixtures thereof.

In some preferred embodiments the further nitrogen containing detergent comprises:

- (i) the product of a Mannich reaction between an aldehyde, an amine and an optionally substituted phenol.

In some preferred embodiments the further nitrogen containing detergent comprises:

- (ii) the reaction product of a carboxylic acid-derived acylating agent and an amine.

In some preferred embodiments the further nitrogen containing detergent comprises:

- (v) the reaction product of a hydrocarbyl-substituted dicarboxylic acid or anhydride and an amine compound or salt which product comprises at least one amino triazole group.

In some preferred embodiments the further nitrogen containing detergent comprises:

- (i) the product of a Mannich reaction between an aldehyde, an amine and an optionally substituted phenol; and
- (ii) the reaction product of a carboxylic acid-derived acylating agent and an amine.

The one or more the further nitrogen containing detergents may comprise (i) the product of a Mannich reaction between an aldehyde, an amine and an optionally substituted phenol.

Preferably component (i) comprises the product of a Mannich reaction between:

- (x) an aldehyde;
- (y) an amine; and
- (z) an optionally substituted phenol.

Preferably the aldehyde component used to prepare the Mannich additive is an aliphatic aldehyde. Preferably the aldehyde has 1 to 10 carbon atoms. Most preferably the aldehyde is formaldehyde.

Suitable amines for use in preparing the Mannich additive include monoamines and polyamines. One suitable monoamine is butylamine.

The amine used to prepare the Mannich additive is preferably a polyamine. This may be selected from any compound including two or more amine groups. Preferably the polyamine is a

polyalkylene polyamine, preferably a polyethylene polyamine. Most preferably the polyamine comprises tetraethylenepentamine or ethylenediamine.

The optionally substituted phenol component used to prepare the Mannich additive may be substituted with 0 to 4 groups on the aromatic ring (in addition to the phenol OH). For example it may be a hydrocarbyl-substituted cresol. Most preferably the phenol component is a mono-substituted phenol. Preferably it is a hydrocarbyl substituted phenol. Preferred hydrocarbyl substituents are alkyl substituents having 4 to 28 carbon atoms, especially 10 to 14 carbon atoms. Other preferred hydrocarbyl substituents are polyalkenyl substituents. Such polyisobutenyl substituents having a number average molecular weight of from 400 to 2500, for example from 500 to 1500.

Suitable Mannich reaction products and the methods of preparing such additives will be known to the person skilled in the art and include the compounds described, for example, in the applicant's publications WO2009040582 and WO2013017887.

Preferred Mannich reaction product additives are the reaction product of formaldehyde, polyethylene polyamine; and a para-substituted monoalkyl phenol.

An especially preferred Mannich reaction product additive for use herein is the reaction product of dodecyl phenol, formaldehyde and ethylene diamine.

The one or more the further nitrogen containing detergents may comprise (ii) the reaction product of a carboxylic acid-derived acylating agent and an amine.

These may also be referred to herein in general as acylated nitrogen-containing compounds.

Suitable acylated nitrogen-containing compounds may be made by reacting a carboxylic acid acylating agent with an amine and are known to those skilled in the art.

Preferred hydrocarbyl substituted acylating agents are polyisobutenyl succinic anhydrides. These compounds are commonly referred to as "PIBSAs" and are known to the person skilled in the art.

Conventional polyisobutenes and so-called "highly-reactive" polyisobutenes are suitable for use in the invention.

Especially preferred PIBSAs are those having a PIB molecular weight (M_n) of from 300 to 2800, preferably from 450 to 2300, more preferably from 500 to 1300.

In preferred embodiments the reaction product of the carboxylic acid derived acylating agent and an amine includes at least one primary or secondary amine group.

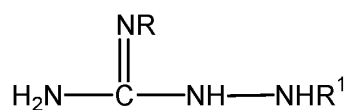
A preferred acylated nitrogen-containing compound for use herein is prepared by reacting a poly(isobutene)-substituted succinic acid-derived acylating agent (e.g., anhydride, acid, ester, etc.) wherein the poly(isobutene) substituent has a number average molecular weight (M_n) of between 170 to 2800 with a mixture of ethylene polyamines having 2 to about 9 amino nitrogen atoms, preferably about 2 to about 8 nitrogen atoms, per ethylene polyamine and about 1 to about 8 ethylene groups. These acylated nitrogen compounds are suitably formed by the reaction of a molar ratio of acylating agent:amino compound of from 10:1 to 1:10, preferably from 5:1 to 1:5, more preferably from 2:1 to 1:2 and most preferably from 2:1 to 1:1. In especially preferred embodiments, the acylated nitrogen compounds are formed by the reaction of acylating agent to amino compound in a molar ratio of from 1.8:1 to 1:1.2, preferably from 1.6:1 to 1:1.2, more preferably from 1.4:1 to 1:1.1 and most preferably from 1.2:1 to 1:1. Acylated amino compounds of this type and their preparation are well known to those skilled in the art and are described in for example EP0565285 and US5925151.

In some preferred embodiments the composition comprises a detergent of the type formed by the reaction of a polyisobutene-substituted succinic acid-derived acylating agent and a polyethylene polyamine. Suitable compounds are, for example, described in WO2009/040583.

In a preferred embodiment the reaction product of a carboxylic acid-derived acylating agent and an amine (ii) comprises the reaction product of a polyisobutene-substituted succinic acid or succinic anhydride and a polyethylene polyamine selected from ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenhexamine, hexaethylene-heptamine and mixtures and isomers thereof; wherein polyisobutene substituent has a number average molecular weight of between 500 and 2000, preferably between 600 and 1000.

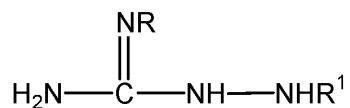
The one or more the further nitrogen containing detergents may comprise (v) the reaction product of a hydrocarbyl-substituted dicarboxylic acid or anhydride and an amine compound or salt which product comprises at least one amino triazole group.

Detergent additive (v) is suitably reaction product of a hydrocarbyl substituted dicarboxylic acid or anhydride and an amine compound having the formula:

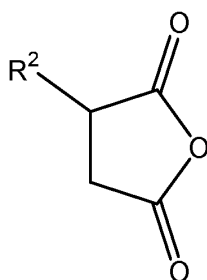


wherein R is selected from the group consisting of a hydrogen and a hydrocarbyl group containing from about 1 to about 15 carbon atoms, and R¹ is selected from the group consisting of hydrogen and a hydrocarbyl group containing from about 1 to about 20 carbon atoms.

Detergent additive (v) suitably comprises the reaction product of an amine compound having the formula:

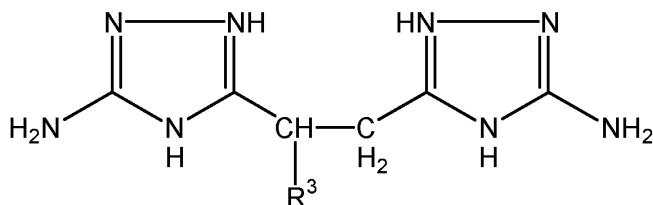


and a hydrocarbyl carbonyl compound of the formula:



wherein R² is a hydrocarbyl group having a number average molecular weight ranging from about 100 to about 5000, preferably from 200 to 3000.

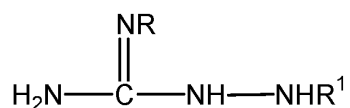
Without being bound by theory, it is believed that the reaction product of the amine and hydrocarbyl carbonyl compound is an aminotriazole, such as a bis-aminotriazole compound of the formula:



including tautomers having a number average molecular weight ranging from about 200 to about 3000 containing from about 40 to about 80 carbon atoms. The five-membered ring of the triazole is considered to be aromatic.

Non-limiting examples of suitable hydrocarbyl carbonyl compounds include, but are not limited to, hydrocarbyl substituted succinic anhydrides, hydrocarbyl substituted succinic acids, and esters of hydrocarbyl substituted succinic acids. In some preferred embodiments the hydrocarbyl carbonyl compounds may comprise a polyisobutenyl-substituted succinic acid or succinic anhydride. Such compounds are suitably as described in relation to the hydrocarbyl-substituted acylating agent of the nitrogen-containing species (i) above.

Suitable amine compounds of the formula:



may be chosen from guanidines and aminoguanidines or salts thereof wherein R and R¹ are as defined above. Accordingly, the amine compound may be chosen from the inorganic salts of guanidines, such as the halide, carbonate, nitrate, phosphate, and orthophosphate salts of guanidines. The term "guanidines" refers to guanidine and guanidine derivatives, such as aminoguanidine. In one embodiment, the guanidine compound for the preparation of the additive is aminoguanidine bicarbonate. Aminoguanidine bicarbonates are readily obtainable from commercial sources, or can be prepared in a well-known manner.

Further preferred features of embodiments in which the one or more the further nitrogen containing detergents comprises detergent additive (v) are as defined in US2009/0282731.

Preferably the weight ratio of the quaternary ammonium salt additive and the one or more further nitrogen containing detergents, when present, is from 1:100 to 100:1, preferably from 1:50 : 50:1, preferably 1:15 to 20:1 preferably from 1:15 to 10:1 preferably from 1:10 to 10:1 preferably from 1:5 to 5:1, preferably 1:2 to 2:1.

All ratios are weight ratios on an active basis. The total amount of active quaternary ammonium compound(s) and active amounts of the one or more further nitrogen containing detergents specified in the respective definition is to be taken into account. Any residual starting materials, byproducts, diluents or solvents are not included in the ratios referred to herein.

The diesel fuel composition used in the present invention may include one or more further additives such as those which are commonly found in diesel fuels. These include, for example, antioxidants, additional dispersants / detergents, metal deactivating compounds, wax anti-settling agents, cold flow improvers, cetane improvers, dehazers, stabilisers, demulsifiers, antifoams, corrosion inhibitors, lubricity improvers, dyes, markers, combustion improvers, metal deactivators, odour masks, drag reducers and conductivity improvers. Examples of suitable amounts of each of these types of additives will be known to the person skilled in the art.

Such further ingredients could in principle be added separately to the quaternary ammonium compound(s) but it is preferred for reasons of convenience and consistency of dosing to include all additives in a common additive composition.

The diesel fuel composition used in the present invention may include one or more additional components selected from:

- a) carrier oils;
- b) acylated nitrogen compounds which are the reaction product of a carboxylic acid-derived acylating agent and an amine;
- c) hydrocarbyl-substituted amines wherein the hydrocarbyl substituent is substantially aliphatic and contains at least 8 carbon atoms;
- d) Mannich base additives comprising nitrogen-containing condensates of a phenol, aldehyde and primary or secondary amine; and
- e) polyether amines.

Preferably the quaternary ammonium salt additive and further additives (when present) is/are present in the fuel in the fuel storage tank which supplies the engine. Although they could be mixed into the fuel in the storage tank, preferably they are present in bulk fuel which is pumped into the storage tank.

The quaternary ammonium salt additives may be added to diesel fuel at any convenient place in the supply chain. For example, the additives may be added to fuel at the refinery, at a distribution terminal or after the fuel has left the distribution terminal. If the additive is added to the fuel after it has left the distribution terminal, this is termed an aftermarket application. Aftermarket applications include such circumstances as adding the additive to the fuel in the delivery tanker, directly to a customer's bulk storage tank, or directly to the end user's vehicle tank. Aftermarket applications may include supplying the fuel additive in small bottles suitable for direct addition to fuel storage tanks or vehicle tanks.

The present invention relates to improving the reducing the emission of particulates having a diameter of less than 2.5 microns from a direct injection diesel engines by combusting diesel fuel compositions comprising a quaternary ammonium compound as an additive.

By reducing particulate emissions we mean that the level of particulates released via the exhaust stream of a direct injection diesel engine on combustion of a diesel fuel comprising the additive is lower than that achieved on combustion of the same fuel without the additive in the same engine.

The level of particulates, such as the level of particulates having a diameter of less than 2.5 microns, released via the exhaust stream may be measured by any suitable means and such means will be known to the person skilled in the art. Suitably the number of particulates, such as the number of particulates having a diameter of less than 2.5 microns, in a given volume of exhaust gas is counted.

One preferred method by which particulate emissions may be measured is described in the examples. The size, number and distribution of emitted particulates is suitably measured using a Cambustion® DMS500 exhaust gas analyser, equipped with a Catalytic Stripping Accessory (CSA), by an electrical mobility detection method.

As well as reducing the number of particulates having a diameter less than 2.5 microns emitted, the present invention preferably also reduces the total mass of particulates having a diameter less than 2 microns emitted.

In some embodiments the present invention reduces the number of particulates having a diameter less than 2.5 microns emitted per unit volume of exhaust gas.

In some embodiments the present invention reduces the total mass of particulates having a diameter less than 2.5 microns emitted per unit volume of exhaust gas.

In some embodiments the present invention reduces the total mass and the number of particulates having a diameter less than 2.5 microns emitted per unit volume of exhaust gas.

The present invention reduces particulate emissions from a direct injection diesel engine. In some embodiments the exhaust gases from the engine may be directed through a particulate filter. In such embodiments the present invention may advantageously reduce the level of particulates in the exhaust gases which pass through the filter. As a result this may extend the life of the particulate filter and/or increase the maintenance intervals and/or increase regeneration intervals.

Thus the present invention may provide the use of a quaternary ammonium compound as an additive in a diesel fuel composition to improve the performance of a particulate filter fitted to the exhaust of a direct injection diesel engine wherein the improvement in performance is selected from:

- increased longevity;
- an increase in maintenance intervals; and
- an increase in regeneration intervals.

A particular advantage of the present invention is that the emission of very small particulates is reduced, including particulates that may be small enough to pass through exhaust filters.

Preferably the method and use of the present invention reduce the emission of particulates having a diameter of less than 2 microns from a direct injection diesel engine.

Preferably the method and use of the present invention reduce the emission of particulates having a diameter of less than 1 micron from a direct injection diesel engine.

Preferably the method and use of the present invention reduce the emission of particulates having a diameter of less than 0.5 microns from a direct injection diesel engine.

Preferably the method and use of the present invention reduce the emission of particulates having a diameter of less than 0.3 microns from a direct injection diesel engine.

Preferably the method and use of the present invention reduce the emission of nanoparticles from a direct injection diesel engine.

Nanoparticles are particles which have one or more dimensions of the order of 100 nm or less. The size of the nanoparticles may be measured by any suitable method. For example, any of the methods described in PAS 71:2005 published by British Standards could be used. Preferred methods for the determination of particle size include TEM (Transmission Electron Microscopy, when particles are made of a material that has high contrast with a carbon TEM grid), SEM (Scanning Electron Microscopy) and AFM (Atomic Force Microscopy). If the particles show plasmon resonance then the size can also be determined from the peak in the UV-VIS spectrum. For larger particles having a size of order of magnitude of 10^{-8} m or greater, light scattering can be used.

In some embodiments method and use of the present invention reduce the emission of particulates having a particle size (as defined above) of between 5 nm and 100 nm, for example between 10 nm and 80 nm.

Preferably the method and use of the present invention reduces the number of particulates emitted per unit volume of exhaust gas and /or the total mass of particulates emitted per unit volume of exhaust gas by at least 50%, wherein the particulates are as defined herein.

Preferably the method and use of the present invention reduce the emission of particulates having a diameter of less than 2.5 microns from a direct injection diesel engine by at least 50%. Preferably the method and use of the present invention reduce the emission of particulates having a diameter of less than 2.5 microns from a direct injection diesel engine by at least one order of magnitude. Preferably there is at least a ten-fold reduction in the concentration of particulates having a diameter of less than 2.5 microns emitted from the direct injection diesel engine.

Preferably the method and use of the present invention reduce the emission of particulates having a diameter of less than 2 microns from a direct injection diesel engine by at least 50%. Preferably the method and use of the present invention reduce the emission of particulates having a diameter of less than 2 microns from a direct injection diesel engine by at least one order of magnitude. Preferably there is at least a ten-fold reduction in the concentration of particulates having a diameter of less than 2 microns emitted from the direct injection diesel engine.

Preferably the method and use of the present invention reduce the emission of particulates having a diameter of less than 1 micron from a direct injection diesel by at least 50%. Preferably the method and use of the present invention reduce the emission of particulates having a diameter of less than 1 micron from a direct injection diesel engine by at least one order of magnitude. Preferably there is at least a ten-fold reduction in the concentration of particulates having a diameter of less than 1 micron emitted from the direct injection diesel engine.

Preferably the method and use of the present invention reduce the emission of particulates having a diameter of less than 0.5 microns from a direct injection diesel engine by at least 50%. Preferably the method and use of the present invention reduce the emission of particulates having a diameter of less than 0.5 microns from a direct injection diesel engine by at least one order of magnitude. Preferably there is at least a ten-fold reduction in the concentration of particulates having a diameter of less than 0.5 microns emitted from the direct injection diesel engine.

Preferably the method and use of the present invention reduce the emission of particulates having a diameter of less than 0.3 microns from a direct injection diesel engine by at least 50%. Preferably the method and use of the present invention reduce the emission of particulates having a diameter of less than 0.3 microns from a direct injection diesel engine by at least one order of magnitude. Preferably there is at least a ten-fold reduction in the concentration of particulates having a diameter of less than 0.3 microns emitted from the direct injection diesel engine.

Preferably the method and use of the present invention reduce the emission of nanoparticles from a direct injection diesel engine by at least 50%. Preferably the method and use of the present invention reduce the emission of nanoparticles, preferably having a diameter of 1 to 100 nm from a direct injection diesel engine by at least one order of magnitude. Preferably there is at least a ten-fold reduction in the concentration of nanoparticles, preferably having a diameter of 1 to 100 nm emitted from the direct injection diesel engine.

In some embodiments the present invention may provide a method of reducing the emission of particulates having a diameter of less than 2.5 microns from a direct injection diesel engine, the method comprising the steps of:

- preparing a diesel fuel composition comprising as an additive a quaternary ammonium compound;
- combusting the diesel fuel composition in a direct injection diesel engine; and
- measuring the concentration of particulates having a diameter of less than 2.5 microns emitted from the exhaust of the engine during combustion of the diesel fuel composition comprising the quaternary ammonium compound.

In such embodiments the method may further comprise comparing the concentration of particulates having a diameter of less than 2.5 microns emitted from the exhaust of the engine during combustion of the diesel fuel composition comprising the quaternary ammonium compound with the concentration of particulates having a diameter of less than 2.5 microns emitted from the exhaust of the engine during combustion of the diesel fuel composition without the quaternary ammonium compound. The diesel fuel composition without the quaternary ammonium compound is suitably otherwise an identical diesel fuel composition.

In some embodiments the present invention may provide a method of reducing the emission of particulates having a diameter of less than 0.5 microns from a direct injection diesel engine, the method comprising the steps of:

- preparing a diesel fuel composition comprising as an additive a quaternary ammonium compound;
- combusting the diesel fuel composition in a direct injection diesel engine; and

- measuring the concentration of particulates having a diameter of less than 0.5 microns emitted from the exhaust of the engine during combustion of the diesel fuel composition comprising the quaternary ammonium compound.

In such embodiments the method may further comprise comparing the concentration of particulates having a diameter of less than 0.5 microns emitted from the exhaust of the engine during combustion of the diesel fuel composition comprising the quaternary ammonium compound with the concentration of particulates having a diameter of less than 0.5 microns emitted from the exhaust of the engine during combustion of the diesel fuel composition without the quaternary ammonium compound.

In some embodiments the present invention may provide a method of reducing the emission of particulates having a diameter of less than 100 nm from a direct injection diesel engine, the method comprising the steps of:

- preparing a diesel fuel composition comprising as an additive a quaternary ammonium compound;
- combusting the diesel fuel composition in a direct injection diesel engine; and
- measuring the concentration of particulates having a diameter of less than 0.5 microns emitted from the exhaust of the engine during combustion of the diesel fuel composition comprising the quaternary ammonium compound.

In such embodiments, the method may further comprise comparing the concentration of particulates having a diameter of less than 100 nm emitted from the exhaust of the engine during combustion of the diesel fuel composition comprising the quaternary ammonium compound with the concentration of particulates having a diameter of less than 100 nm emitted from the exhaust of the engine during combustion of the diesel fuel composition without the quaternary ammonium compound.

In one especially preferred embodiment the present invention the use of from 1 to 20 ppm of a quaternary ammonium compound as an additive in a diesel fuel composition to reduce the emission of particulates having a diameter of less than 0.5 microns from a direct injection diesel engine by at least 50%, preferably at least 90% wherein the quaternary ammonium compound is the quaternised reaction product of a hydrocarbyl substituted succinic acid derived acylating agent and a compound comprising at least one tertiary amine group and a primary amine, secondary amine or alcohol group wherein hydrocarbyl substituted acylating agent includes an average of at least 1.2 succinic acid moieties per molecule.

The invention will now be further described with reference to the following non-limiting examples. In the examples which follow the values given in parts per million (ppm) for treat rates denote

active agent amount, not the amount of a formulation as added, and containing an active agent. All parts per million are by weight.

Example 1

Intermediate Additive A, the reaction product of a hydrocarbyl substituted acylating agent and a compound of formula (B1) was prepared as follows:

554.36g (0.467 moles) PIBSA (made from 1000 MW PIB and maleic anhydride) was charged to 1 litre vessel. The mixture was stirred and heated, under nitrogen to 120°C. 47.72g (0.467 moles) DMAPA was added over 1 hour and the mixture heated to 140°C for 3 hours, with concurrent removal of water using a Dean-Stark apparatus.

[Note: PIB herein means polyisobutene; PIBSA means polyisobutenyl-substituted succinic anhydride; DMAPA means dimethylaminopropylamine]

Example 2

Additive B, an additive comprising a quaternary ammonium salt additive of the present invention was prepared as follows:

333.49g (0.262 moles) of Additive A mixed with 39.92g (0.262 moles) methyl salicylate under nitrogen. The mixture was stirred and heated to 140°C for 8 hours. The non-volatile content was adjusted to 60% w/w with Caromax 20. The product mixture of this reaction was used without further processing as additive B and contained the quaternary ammonium salt(s) additive of the present invention, together with any unreacted raw materials, other reaction products and solvent.

Example 3

Additive C, an additive comprising a quaternary ammonium salt additive of the present invention was prepared as follows:

700 g (0.7 mol) of polyisobutylene (M_n 1000) was charged to a nitrogen flushed, jacketed reactor fitted with an overhead stirrer. The starting material was heated to 120 °C with stirring and nitrogen inerting was repeated. The reaction temperature was increased to 190 °C and maleic anhydride (82.4g, 0.84 mol, 1.2 eq) was charged over 1 hour. After maintaining a temperature of 190 °C for a further 1 hour, the temperature was increased to 200 - 208 °C and held in this range for 8 hours. Vacuum (< 30 mbar) was then applied for 2.5 hrs, whilst maintaining the reaction temperature, which reduced the level of residual maleic anhydride to ≤ 0.05 wt%. The reaction mass was cooled to $\leq 80^\circ\text{C}$ then discharged from the reactor. The resulting PIBSA was

charged to a nitrogen flushed, jacketed reactor fitted with an overhead stirrer and heated to 120 °C. 3-(dimethylamino)propylamine (DMAPA) (1eq relative to anhydride groups) was charged slowly, maintaining the reaction temperature between 120 – 130 °C. After stirring at 120 °C for a further 1 hr, the reaction temperature was increased to 140 °C and held for 3 hrs with concurrent distillation of water. Methyl salicylate (2.1 eq relative to anhydride groups) was added in a single portion and heating was continued at 140 °C for 10 hours. The reaction mass was diluted with Aromatic 150 solvent to provide an overall solids content of 60 wt% prior to discharging from the reactor.

Example 4

Additive D is a comparative additive and is a 60 wt% active ingredient solution (in aromatic solvent) of a polyisobutenyl succinimide obtained from the condensation reaction of a polyisobutenyl succinic anhydride 25 (PIBSA) derived from polyisobutene of Mn approximately 750 with a polyethylene polyamine mixture of average composition approximating to tetraethylene pentamine. The product was obtained by mixing the PIBSA and polyethylene polyamine at 50°C under nitrogen and heating at 160°C for 5 hours with removal of water.

Example 5

Additive E, an oleyl amido propyl betaine quaternary ammonium additive of the invention, was prepared as follows:

A Lenz jacketed reactor was charged with 183.5 g (0.5 moles) oleyl amidopropyl dimethylamine (N-[3-(Dimethylamino)propyl]oleamide), 68 ml isopropyl alcohol, 25.5 g (1.42 moles) water and 56.5 g (0.48 moles) sodium chloroacetate. The reaction mixture was heated to 80°C and then heated for approx. 6 hrs at 80-85°C, before being cooled and allowed to stand under N₂ overnight. Following this the reaction mixture was re-heated to 60°C and charged with 300 ml of isopropylalcohol (IPA) and 67.5 g of 2-ethylhexanol. Then the heat was increased further to 90°C. This afforded the azeotropic removal of H₂O and IPA and precipitation of NaCl. A 100 mbar vacuum was applied to remove the remaining water and some solvent and the resulting suspension was filtered at 75-80°C through a glass microfibre filter. 275.6g of additive E was collected, which contained 53 wt% actives.

Example 6

Additive F, a quaternary ammonium additive of the invention, was prepared as follows:

A Lenz jacketed reactor equipped with a N₂ inlet, and reflux condenser was charged with 123.2 g (0.105 moles, 1.0 eq) of a polyisobutenyl substituted succinic anhydride (1000 MW PIB) and 123.0 g A150 solvent. 8.9 g (0.087 moles, 0.83 equivalents) N,N-dimethylaminopropylamine (DMAPA) was added via a dropping funnel over approx. 30 mins. During the addition the reaction was kept at 20°C – 25°C and following the addition the mixture was allowed to stir for 1hr. The reaction mixture temperature had subsided to 17°C and propylene oxide (12.2 g) was added over approx. 25 mins. Following the addition, the temperature was maintained at 20-22°C whilst stirring. This was maintained for 4 hrs. The reactor was opened and left stirring for 2 hrs to let excess propylene oxide gas off. 264.4g of a deep orange liquid of additive F was collected. The active content was 50 wt%.

Example 7

Diesel fuel compositions were prepared by dosing additives into aliquots all drawn from a common batch of base fuel. The base fuel was an RF-06-03, EN590 compliant B0 diesel fuel (Coryton Advanced Fuels, UK) having batch number G23/1462. The base fuel satisfied the RF06 specification given in table 1.

Table 1

Property	Units	Limits		Method
		Min	Max	
Cetane Number		52.0	54.0	EN ISO 5165
Density at 15°C	kg/m ³	833	837	EN ISO 3675
Distillation				
50% v/v Point	°C	245	-	
95% v/v Point	°C	345	350	
FBP	°C	-	370	
Flash Point	°C	55	-	EN 22719
Cold Filter Plugging Point	°C	-	-5	EN 116
Viscosity at 40°C	mm ² /sec	2.3	3.3	EN ISO 3104
Polycyclic Aromatic Hydrocarbons	% m/m	3.0	6.0	IP 391
Sulphur Content	mg/kg	-	10	ASTM D 5453
Copper Corrosion		-	1	EN ISO 2160
Conradson Carbon Residue on 10% Dist. Residue	% m/m	-	0.2	EN ISO 10370
Ash Content	% m/m	-	0.01	EN ISO 6245
Water Content	% m/m	-	0.02	EN ISO 12937

Neutralisation (Strong Acid) Number	mg KOH/g	-	0.02	ASTM D 974
Oxidation Stability	mg/mL	-	0.025	EN ISO 12205
HFRR (WSD1,4)	µm	-	400	CEC F-06-A-96
Fatty Acid Methyl Ester		prohibited		

The compositions prepared are detailed in table 2:

Table 2		
Fuel composition	Additive	Additive content (ppm active)
1	None	0
2	C	200
3	D	200

Example 8 - Measurement of Particulate Matter Emissions

A Euro 6 compliant 2.0 litre, HSDI engine was connected to a test automation system and test bed fitted with an engine dynamometer. The engine was controlled by an ECU supplied by the engine manufacturer. The engine had had over 1,837 hours of use prior to the first test. The engine oil was changed prior to performing the first test.

The engine configuration included a diesel particulate filter (DPF) and the size, number and distribution of emitted particulates were measured before and after the DPF using two DMS500 instruments.

The size, number and distribution of emitted particulates was measured using a Cambustion® DMS500 exhaust gas analyser, equipped with a Catalytic Stripping Accessory (CSA). The instrument measures particulate matter having sizes between 5 and 1000 nm using an electrical mobility detection method.

The engine operating conditions were as follows :

- Change to test fuel
- Engine start
- Warm-up cycle
- Active DPF regeneration cycle
- Passive DPF regeneration cycle
- Engine stop

- Data & instrumentation check/review
- Engine start
- Warm-up cycle
- 6-hour steady-state multi-point test cycle (49 sites)
- Engine stop

The fuel injectors were not cleaned between tests.

The 6-hour steady-state multi-point test cycle comprised the following speed and load points :

Engine Speed [RPM]	Pedal Demand [%]
3750	70
3750	60
3750	50
3750	40
3750	30
3750	20
3750	10
3500	70
3500	60
3500	50
3500	40
3500	30
3500	20
3500	10
3250	70
3250	60
3250	50
3250	40
3250	30
3250	20
3250	10
3000	70
3000	60
3000	50
3000	40
3000	30

3000	20
3000	10
2750	70
2750	60
2750	50
2750	40
2750	30
2750	20
2750	10
2500	70
2500	60
2500	50
2500	40
2500	30
2500	20
2500	10
2250	70
2250	60
2250	50
2250	40
2250	30
2250	20
2250	10

For each test point the total number of particulates in the range 5 to 1000 nm was recorded, before and after the DPF, and an average (mean) value was reported for each.

The results of initial engine tests for fuel compositions 1 to 3 are shown in table 3. The results in table are the average values over the number of test runs indicated.

Table 3

Composition	Number of runs	Average particulates before DPF (#/cm ³)	Average particulates after DPF (#/cm ³)
1	3	1.1×10^8	8.59×10^4
2	3	5.98×10^7	5.98×10^4
3	4	9.5×10^7	8.94×10^4

Example 9

To demonstrate the effectiveness of a range of quaternary ammonium compounds, further tests were carried out, using a method analogous to that described in example 8 but with the steady state multi-point test cycle consisting of 21 set engine speed and pedal demand points. Additives were dosed into a further batch of the same base fuel as detailed in table 4:

Table 4					
Composition	Additive	Treat rate (ppm active)	Number of runs	Average particulates before DPF (#/cm ³)	Average particulates after DPF (#/cm ³)
4	None	0	1	1.26 x 10 ⁸	9837.735
5	B	200	1	1.17 x 10 ⁸	1990.591
6	E	200	1	1.23 x 10 ⁸	1316.234
7	F	200	1	1.21 x 10 ⁸	5921.403

Example 10 – Particulate emissions from an agricultural vehicle

A fully formulated additive package including 33 ppm active of additive B was dosed into a B5 fuel.

The mineral diesel component was a No. 2-D S15 diesel fuel oil, compliant with ASTM D975-21.

The biodiesel component was a plant-based fatty acid methyl ester (FAME) meeting ASTM D6751 specifications.

The test vehicle was a John Deere 5100E tractor with the following specifications:
4 cylinder, 4.5 L direct injection diesel engine (100 hp)
Rated power 74.6 kW @ 2400 rpm
The vehicle aftertreatment system did not include a DPF.
The year of manufacture was 2016 and, prior to this testing, the tractor had 2,853 hours of working use.

The tractor was set up in an enclosed, ambient-controlled test facility with a motoring dynamometer connected to its power take-off (PTO) shaft. The tractor was configured to be loaded exclusively through its PTO shaft, such that the wheels could not be driven or loaded.

The test facility allowed for automated control of the PTO speed and torque, and measurement of engine parameters, fuel flow and exhaust emissions.

No cleaning of engine parts took place prior to starting the controlled test.

A drive cycle was selected to be representative of typical agricultural use and consisted of daily repeats of the following sequence:

- 4 hour “steady state” phase (continuous, high PTO speed and torque)
- 1 hour heat soak
- 4 hour “transient” phase (variable PTO speed and torque)
- Engine stop

Figures 1 and 2 illustrate the set values of speed and load (torque) across the PTO shaft during the test cycle.

This sequence was repeated daily until 100 hours of engine operation had been completed (~ 13 days).

Two 100 hour cycles were consecutively run, the first used unadditized base fuel and the second was with the same base fuel plus the additive package.

For two time periods during the experiment, engine exhaust particulate matter (PM) emissions in the size range 5.6 to 560 nm were measured.

The size, number and distribution of emitted particulates was measured using a Cambustion® DMS500 exhaust gas analyser, equipped with a Catalytic Stripping Accessory (CSA), in the manner of example 8. In this experiment, the particle count in the size range 5.6 to 560 nm was reported.

The results are given in table 5:

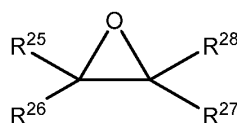
Fuel composition	Average particulates emitted (#/cm ³)
Base fuel	6.67×10^6
Additised fuel	5.27×10^6

Claims

1. A method of reducing the emission of particulates having a diameter of less than 2.5 microns from a direct injection diesel engine, the method comprising combusting in the engine a diesel fuel composition comprising as an additive one or more quaternary ammonium compounds.
2. The use of one or more quaternary ammonium compounds as an additive in a diesel fuel composition to reduce the emission of particulates having a diameter of less than 2.5 microns from a diesel ignition diesel engine.
3. A method or use according to claim 1 or 2 wherein the or each quaternary ammonium compound is the reaction product of a nitrogen-containing species having at least one tertiary amine group and a quaternising agent wherein the nitrogen-containing species having at least one tertiary amine group may be selected from:
 - (i) the reaction product of a hydrocarbyl-substituted acylating agent and a compound comprising at least one tertiary amine group and a primary amine, secondary amine or alcohol group;
 - (ii) a Mannich reaction product comprising a tertiary amine group;
 - (iii) a polyalkylene substituted amine having at least one tertiary amine group;
 - (iv) a tertiary amine of formula $R^5R^6R^7N$, wherein each of R^5 , R^6 and R^7 is independently an optionally substituted alkyl, alkenyl, aryl, alkaryl or aralkyl group;
 - (v) a cyclic tertiary amine; and
 - (vi) a polyetheramine compound.
4. A method or use according to claim 3 wherein the nitrogen-containing species having at least one tertiary amine group is the reaction product of an alcohol or amine including a tertiary amino group and an optionally substituted succinic acid or anhydride thereof.
5. A method or use according to claim 4 wherein the succinic acid or anhydride thereof is substituted with a hydrocarbyl group and the hydrocarbyl substituted acylating agent includes an average of at least 1.2 succinic acid moieties per molecule.

6. A method or use according to claim 4 or claim 5 wherein the succinic acid or anhydride thereof is substituted with a polyisobutenyl group having a number average molecular weight of from 170 to 2800, preferably 450 to 1500.
7. A method or use according to any of claims 3 to 6 wherein the alcohol or amine including a tertiary amino group is selected from dimethylaminopropanol, dimethylaminopropylamine, N,N-diethyl-1,3-diaminopropane, N,N-dimethylethylenediamine, N,N-diethylethylenediamine, N,N-dibutylethylenediamine, 3-(2-(dimethylamino)ethoxy)propylamine, or combinations thereof.
8. A method or use according to any of claims 3 to 7 wherein the quaternising agent is selected from esters of a carboxylic acid, dialkyl sulfates, benzyl halides, hydrocarbyl substituted carbonates, hydrocarbyl substituted epoxides optionally in combination with an acid, alkyl halides, alkyl sulfonates, sultones, hydrocarbyl substituted phosphates, hydrocarbyl substituted borates, alkyl nitrites, alkyl nitrates, hydroxides, N-oxides, chloroacetic acid or salts thereof, or mixtures thereof.
9. A method or use according to claim 8 wherein the quaternising agent is an ester of formula $R^{18}COOR^{19}$ wherein R^{19} is a C_1 to C_7 alkyl group and R^{18} is the residue of a carboxylic acid selected from a substituted aromatic carboxylic acid, an α -hydroxycarboxylic acid and a polycarboxylic acid.
10. A method or use according to claim 9 wherein the quaternising agent is 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.
11. A method or use according to claim 10 wherein the quaternising agent is selected from dimethyl oxalate, methyl 2-nitrobenzoate, dimethylphthalate, dimethyltartrate and methyl salicylate
12. A method or use according to claim 8 wherein the quaternising agent is selected from epoxides, optionally in combination with an acid, wherein the epoxide has the formula:

63



wherein each of R^{25} , R^{26} , R^{27} , R^{28} is independently selected from hydrogen or an optionally substituted alkyl, alkenyl or aryl group, provided at least one of R^{25} , R^{26} , R^{27} and R^{28} is hydrogen.

13. A method or use according to claim 12 wherein each of R^{25} , R^{26} and R^{27} are hydrogen and R^{28} is selected from phenyl, an optionally substituted alkyl or alkenyl group having 1 to 20 carbon atoms, hydrogen, $\text{CH}_2\text{OR}^{29}$ or $\text{CH}_2\text{OCOR}^{30}$ wherein each of R^{29} and R^{30} is an optionally substituted alkyl or aryl group having from 1 to 20 carbon atoms.
14. A method or use according to claim 13 or claim 14 wherein the epoxide is selected from styrene oxide, ethylene oxide, propylene oxide, butylene oxide, stilbene oxide, dodecylene oxide 2-ethylhexyl glycidyl ether and isopropyl glycidyl ether.
15. A method or use according to any of claims 8, 12, 13 or 14 wherein the epoxide quaternising agents are used in combination with an acid.
16. A method or use according to claim 15 wherein the acid is selected from:
 - a small simple acid selected from formic acid, acetic acid, propionic acid and butyric acid;
 - a fatty acid compound; and
 - a hydrocarbyl substituted phthalic acid or succinic acid derivative.
17. A method or use according to any preceding claim wherein the diesel fuel composition further comprises one or more additional components selected from:
 - a) carrier oils
 - b) acylated nitrogen compounds which are the reaction product of a carboxylic acid-derived acylating agent and an amine
 - c) hydrocarbyl-substituted amines wherein the hydrocarbyl substituent is substantially aliphatic and contains at least 8 carbon atoms
 - d) Mannich base additives comprising nitrogen-containing condensates of a phenol, aldehyde and primary or secondary amine; and
 - e) polyether amines.

18. A method or use according to any preceding claim which reduces the number of particulates emitted per unit volume of exhaust gas and /or the total mass of particulates emitted per unit volume of exhaust gas.
19. A method or use according to any preceding claim which reduces the number of particulates emitted per unit volume of exhaust gas and /or the total mass of particulates emitted per unit volume of exhaust gas by at least 50%.
20. A method or use according to any preceding claim which reduces the emission of particulates having a diameter of less than 0.3 microns.
21. A method or use according to any preceding claim wherein the quaternary ammonium compound is present in the diesel fuel composition in an amount of from 0.5 to 50 ppm.