

**METHODS AND USES RELATING TO FUEL COMPOSITIONS**

The present invention relates to methods and uses for improving the performance of diesel engines using fuel additives. In particular the invention relates to additives for diesel fuel compositions for use in indirect diesel engines.

Diesel engines have developed significantly over recent years and many new vehicles have high pressure direct injection diesel engines. Many new additives have been developed to improve the performance of these modern direct injection engines. However there are also a lot of vehicles on the road which have indirect injection diesel engines and it is therefore important that commercially available diesel fuels are able to provide good performance in such engines.

The provision of detergent additives to prevent and reduce the formation of deposits in indirect diesel engines is well known. However little work has been carried out to remove existing deposits in such engines. The formation of deposits in indirect injection engines, especially on the injectors, can significantly hinder the performance of the engine. This can lead to poor fuel atomisation resulting in inefficient combustion, increased emissions, smoke, and possible diesel knock or noise.

It is an aim of the present invention to provide a fuel composition which reduces the problems caused by such deposits.

According to a first aspect of the present invention there is provided a method of removing deposits in an indirect injection diesel engine, the method comprising combusting in the engine a diesel fuel composition comprising a quaternary ammonium salt additive; wherein the quaternary ammonium salt additive comprises the quaternised reaction product of a hydrocarbyl substituted succinic acid derived acylating agent and a compound able to react with said acylating agent and which includes a tertiary amine group; wherein each molecule of the hydrocarbyl substituted succinic acid derived acylating agent includes on average at least 1.2 succinic acid moieties.

According to a second aspect of the present invention there is provided the use of a quaternary ammonium salt additive in a diesel fuel composition to remove deposits in an indirect injection diesel engine; wherein the quaternary ammonium salt additive comprises the quaternised reaction product of a hydrocarbyl substituted succinic acid derived acylating agent and a compound able to react with said acylating agent and which includes a tertiary amine group; wherein each molecule of the hydrocarbyl substituted succinic acid derived acylating agent includes on average at least 1.2 succinic acid moieties.

Preferred features of the first and second aspects of the present invention will now be described.

The present invention involves the use of a quaternary ammonium salt which is the quaternised reaction product of a hydrocarbyl substituted succinic acid derived acylating agent and a  
5 compound able to react with said acylating agent and which includes a tertiary amine group.

For the avoidance of doubt reference to the quaternised reaction product is meant to refer to a reaction product which comprises the tertiary amine which has then been quaternised to form a quaternary ammonium group. The quaternary ammonium salt additive is formed by reacting a  
10 quaternising agent with the reaction product of a hydrocarbyl substituted succinic acid derived acylating agent and a compound able to react with said acylating agent and which includes a tertiary amine group.

As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary  
15 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  
20 branched, e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic (including 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. C<sub>1</sub> to C<sub>4</sub> 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  
30 hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.  
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Suitable hydrocarbyl substituted succinic acid derived acylating agents and means of preparing them are well known in the art. For example a common method of preparing a hydrocarbyl

substituted succinic acylating agent is by the reaction of maleic anhydride with an olefin using a chlorination route or a thermal route (the so-called "ene" reaction).

5 Illustrative of hydrocarbyl substituent based groups include n-octyl, n-decyl, n-dodecyl, tetrapropenyl, n-octadecyl, oleyl, chlorooctadecyl, tricontanyl, etc. 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, butane-1, isobutene, butadiene, isoprene, 1-hexene, 1-octene, etc. Preferably these olefins are 1-  
10 monoolefins. Alternatively the substituent may be made from other sources, for example monomeric high molecular weight alkenes (e.g. 1-tetra-contene), aliphatic petroleum fractions, for example paraffin waxes and cracked 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.

15 Preferably the hydrocarbyl substituents are predominantly saturated, that is, they contain no more than one carbon-to-carbon unsaturated bond for every ten carbon-to-carbon single bonds present. Most preferably they contain no more than one carbon-to-carbon non-aromatic unsaturated bond for every 50 carbon-to-carbon bonds present.

20 The hydrocarbyl substituent of the succinic acid derived acylating agent preferably comprises at least 10, more preferably at least 12, for example at least 30 or at least 40 carbon atoms. It may comprise up to about 200 carbon atoms. Preferably the hydrocarbyl substituent of the acylating agent has a number average molecular weight (Mn) of between 170 to 2800, for example from  
25 250 to 1500, preferably from 500 to 1500 and more preferably 500 to 1100. An Mn of 700 to 1300 is especially preferred.

The hydrocarbyl substituted succinic acid derived acylating agent may comprise a mixture of compounds. For example a mixture of compounds having different hydrocarbyl substituents may  
30 be used.

Preferred hydrocarbyl-based substituents are polyisobutenes. Such compounds are known to the person skilled in the art.

35 Preferred hydrocarbyl substituted succinic acid derived 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. 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  
5 having more than 80 mol% and up to 100 mol% of terminal vinylidene groups such as those described in US7291758. Preferred polyisobutenes have preferred molecular weight ranges as described above for hydrocarbyl substituents generally.

Other preferred hydrocarbyl groups include those having an internal olefin for example as  
10 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  
15 less than 5% by weight or less than 2% by weight. Typical internal olefins include Neodene 1518IO available from Shell.

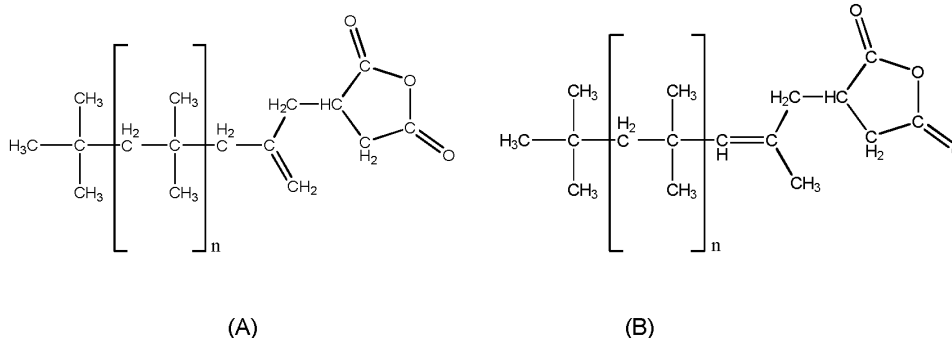
Internal olefins are sometimes known as isomerised olefins and can be prepared from alpha olefins by a process of isomerisation known in the art, or are available from other sources. The  
20 fact that they are also known as internal olefins reflects that they do not necessarily have to be prepared by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

Preferred hydrocarbyl substituted succinic acid derived acylating agents for use in preparing the quaternary ammonium salt additive of the present invention are polyisobutenyl substituted  
25 succinic anhydrides or PIBSAs. Especially preferred PIBSAs are those having a PIB molecular weight (Mn) of from 300 to 2800, preferably from 450 to 2300, more preferably from 500 to 1300.

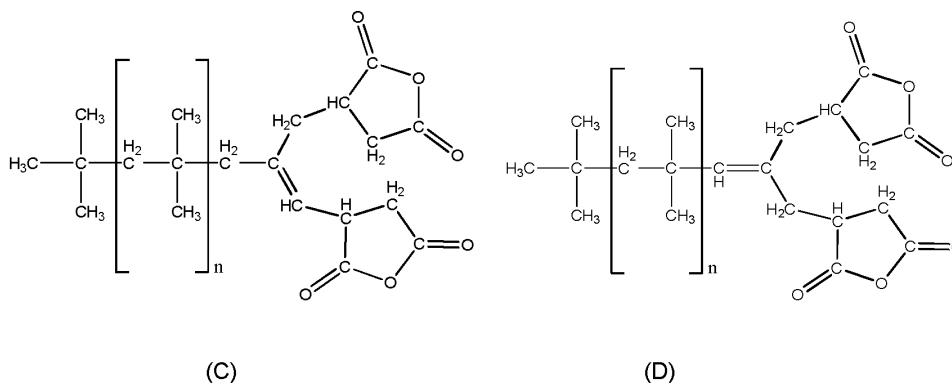
The hydrocarbyl substituted succinic acid derived acylating agent is suitably prepared by reacting maleic anhydride with an alkene, for example a polyisobutene. The product obtained  
30 (such as a PIBSA) still includes a double bond. The maleic anhydride is present in the resultant molecule as a succinic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

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

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- 5 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):



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Thus it is possible to provide a hydrocarbonyl group which is substituted with more than one succinic acid moiety. In such embodiments each molecule of the hydrocarbonyl substituted succinic acid derived acylating agent includes more than one succinic acid moiety.

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The skilled person will appreciate that the additives used in the invention typically comprise mixtures of compounds and will be prepared from a mixture of monomaleated and bismaleated PIBSAs. The PIBSAs may be defined in terms of their level of bismaleation.

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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 molecule.

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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.

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

One way in which the P value can be determined empirically is described in relation to the examples.

10 The present invention relates in particular to the use of quaternary ammonium salts 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.  
15 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.

20 The present inventors have surprisingly found that when the quaternary ammonium salt additive is prepared from a hydrocarbyl substituted succinic acid derived acylating agent comprising on average at least 1.2 succinic acid moieties per molecule improved clean up of deposits in an indirect injection diesel engine is achieved.

25 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  
30 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.

35 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.

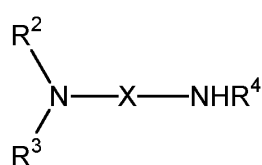
The hydrocarbyl substituted succinic acid derived acylating agent is reacted with a compound able to react with said acylating agent and which includes a tertiary amine group. The tertiary amine group is quaternised to provide the quaternary ammonium salt additive.

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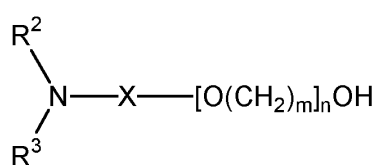
Examples of suitable compounds able to react with the hydrocarbyl substituted succinic acid derived acylating agent and which include a tertiary amine group can include but are not limited to: N,N-dimethylaminopropylamine, N,N-diethylaminopropylamine, N,N-dimethylamino ethylamine. The nitrogen or oxygen 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.

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Preferably the compound able to react with hydrocarbyl substituted succinic acid derived acylating agent and which includes a tertiary amine group is an amine of formula (I) or (II):



(I)



(II)

wherein  $\text{R}^2$  and  $\text{R}^3$  are the same or different alkyl, alkenyl, aryl, alkaryl or aralkyl groups having from 1 to 22 carbon atoms; X is a bond or an optionally substituted alkylene group having from 1 to 20 carbon atoms; n is from 0 to 20; m is from 1 to 5; and  $\text{R}^4$  is hydrogen or a  $\text{C}_1$  to  $\text{C}_{22}$  alkyl group.

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When a compound of formula (I) is used, R<sup>4</sup> is preferably hydrogen or a C<sub>1</sub> to C<sub>16</sub> alkyl group, preferably a C<sub>1</sub> to C<sub>10</sub> alkyl group, more preferably a C<sub>1</sub> to C<sub>6</sub> alkyl group. When R<sup>4</sup> is alkyl it may be straight chained or branched. It may be substituted for example with a hydroxy or alkoxy substituent. Preferably R<sup>4</sup> is not a substituted alkyl group. More preferably R<sup>4</sup> is selected from hydrogen, methyl, ethyl, propyl, butyl and isomers thereof. Most preferably R<sup>4</sup> is hydrogen.

When a compound of formula (II) 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 (II) is an alcohol.

Preferably the hydrocarbyl substituted acylating agent is reacted with a diamine compound of formula (I).

R<sup>2</sup> and R<sup>3</sup> are the same or different alkyl, alkenyl, aryl, alkaryl or aralkyl groups having from 1 to 22 carbon atoms. In some embodiments R<sup>2</sup> and R<sup>3</sup> may be joined together to form a ring structure, for example a piperidine, imidazole or morpholine moiety. Thus R<sup>2</sup> and R<sup>3</sup> may together form an aromatic and/or heterocyclic moiety. R<sup>2</sup> and R<sup>3</sup> may be branched alkyl or alkenyl groups. Each may be substituted, for example with a hydroxy or alkoxy substituent.

Preferably each of R<sup>2</sup> and R<sup>3</sup> is independently a C<sub>1</sub> to C<sub>16</sub> alkyl group, preferably a C<sub>1</sub> to C<sub>10</sub> alkyl group. R<sup>2</sup> and R<sup>3</sup> may independently be methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, or an isomer of any of these. Preferably R<sup>2</sup> and R<sup>3</sup> is each independently C<sub>1</sub> to C<sub>4</sub> alkyl. Preferably R<sup>2</sup> is methyl. Preferably R<sup>3</sup> is methyl.

X is a bond or an optionally substituted 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 X may include a heteroatom within the alkylene chain, for example X may include an ether functionality.

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. In some preferred embodiments X is an unsubstituted alkylene group. Most preferably X is an ethylene, propylene or butylene group, especially a propylene group.

Examples of compounds of formula (I) 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, 5 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), 3-(2-(dimethylamino)ethoxy) propylamine, or combinations thereof.

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In some preferred embodiments the compound of formula (I) is selected from N,N-dimethyl-1,3-diaminopropane, N,N-diethyl-1,3-diaminopropane, N,N-dimethylethylenediamine, N,N-diethylethylenediamine, N,N-dibutylethylenediamine, 3-(2-(dimethylamino)ethoxy) propylamine, or combinations thereof.

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Examples of compounds of formula (II) 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-(dimethylamino)ethoxy]-ethanol, N-ethyldiethanolamine, N-methyldiethanolamine, N-butyl-20 diethanolamine, N,N-diethylaminoethanol, N,N-dimethyl amino-ethanol, 2-dimethylamino-2-methyl-1-propanol, 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, and N,N,N'-trimethylaminoethylethanolamine.

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In some preferred embodiments the compound of formula (B2) is selected from Triisopropanolamine, 1-[2-hydroxyethyl]piperidine, 2-[2-(dimethylamino)ethoxy]-ethanol, N-ethyldiethanolamine, N-methyldiethanolamine, N-butyl-25 diethanolamine, N,N-diethylaminoethanol, N,N-dimethylaminoethanol, 2-dimethylamino-2-methyl-1-propanol, or combinations thereof.

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An especially preferred compound of formula (I) is N,N-dimethyl-1,3-diaminopropane (dimethylaminopropylamine).

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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 R<sup>4</sup> 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 R<sup>4</sup> is not hydrogen the resulting product is an amide.

To form the quaternary ammonium salt additive the hydrocarbyl substituted succinic acid derived acylating agent is reacted with a compound able to react with said acylating agent and which includes a tertiary amine group. This reaction product is then quaternised by reaction with a quaternising agent.

The reaction product of the acylating agent and compound which includes a tertiary amine group is preferably reacted with at least one molar equivalent of quaternising agent per mole of tertiary amine group present in the reaction product.

Preferably the reaction product of the acylating agent and compound which includes a tertiary amine group is reacted with more than one molar equivalent of quaternising agent per mole of tertiary amine group present in the reaction product, preferably at least 1.2 molar equivalents of quaternising agent per mole of tertiary amine group, more preferably at least 1.5 molar equivalents of quaternising agent, suitably at least 1.7 molar equivalents of quaternising agent, for example at least 1.9 molar equivalents of quaternising agent.

Preferably the reaction product of the acylating agent and compound which includes a tertiary amine group is reacted with two or more molar equivalents of quaternising agent per mole of tertiary amine group present in the reaction product, preferably at least 2.1 molar equivalents of quaternising agent.

In some embodiments the reaction product of the acylating agent and compound which includes a tertiary amine group is reacted with more than 2.2 molar equivalents of quaternising agent per mole of tertiary amine group present in the reaction product, for example from 2.3 to 4 molar equivalents, from 2.3 to 3 molar equivalents, or from 2.3 to 2.7 or from 2.5 to 3 molar equivalents.

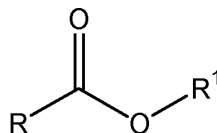
Any suitable quaternising agent may be used. The quaternising agent may suitably be selected from esters and non-esters.

Suitable quaternising agents include 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 some preferred embodiments, quaternising agents used to form the quaternary ammonium salt additives of the present invention are esters.

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



(III)

in which R is an optionally substituted alkyl, alkenyl, aryl or alkylaryl group and R<sup>1</sup> is a C1 to C22 alkyl, aryl or alkylaryl group. The compound of formula (III) is suitably an ester of a carboxylic acid capable of reacting with a tertiary amine to form a quaternary ammonium salt.

Suitable quaternising agents include esters of carboxylic acids having a pK<sub>a</sub> of 3.5 or less.

The compound of formula (III) 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 (III) is an ester of a substituted aromatic carboxylic acid and thus R is a substituted aryl group.

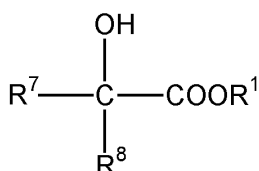
Preferably R is a substituted aryl group having 6 to 10 carbon atoms, preferably a phenyl or naphthyl group, most preferably a phenyl group. R is suitably substituted with one or more groups selected from carboalkoxy, nitro, cyano, hydroxy, SR<sub>5</sub> or NR<sub>5</sub>R<sub>6</sub>. Each of R<sub>5</sub> and R<sub>6</sub> may be hydrogen or optionally substituted alkyl, alkenyl, aryl or carboalkoxy groups. Preferably each of R<sub>5</sub> and R<sub>6</sub> is hydrogen or an optionally substituted C1 to C22 alkyl group, preferably hydrogen or a C1 to C16 alkyl group, preferably hydrogen or a C1 to C10 alkyl group, more preferably hydrogen or a C1 to C4 alkyl group. Most preferably R<sub>5</sub> and R<sub>6</sub> are both hydrogen. Preferably R is an aryl group substituted with one or more groups selected from hydroxyl, carboalkoxy, nitro, cyano and NH<sub>2</sub>. R may be a poly-substituted aryl group, for example trihydroxyphenyl. In some embodiments R may be a hydrocarbyl substituted aryl group, for example an alkyl substituted aryl group. In some embodiments R may be an aryl group substituted with a hydroxy group and a hydrocarbyl group, such as an alkyl group, for example as described in EP2631283.

Preferably R is a mono-substituted aryl group. Preferably R is an ortho substituted aryl group. Suitably R is substituted with a group selected from OH, NH<sub>2</sub>, NO<sub>2</sub> or COOMe. Preferably R is substituted with an OH or NH<sub>2</sub> group. Suitably R is a hydroxy substituted aryl group. Most preferably R is a 2-hydroxyphenyl group.

Preferably R<sup>1</sup> is an alkyl, aralkyl or alkaryl group. R<sup>1</sup> may be a C1 to C16 alkyl group, preferably a C1 to C10 alkyl group, suitably a C1 to C8 alkyl group. R<sup>1</sup> may be C7 to C16 aralkyl or alkaryl group, preferably a C7 to C10 aralkyl or alkaryl group. R<sup>1</sup> may be methyl, ethyl, propyl, butyl, pentyl, benzyl or an isomer thereof. Preferably R<sup>1</sup> is benzyl or methyl. Most preferably R<sup>1</sup> is methyl.

Especially preferred compounds of formula (III) are lower alkyl esters of salicylic acid such as methyl salicylate, ethyl salicylate, n and i propyl salicylate, and butyl salicylate, preferably methyl salicylate.

In some embodiments the compound of formula (III) is an ester of an α-hydroxycarboxylic acid. In such embodiments the compound has the structure:



wherein R<sup>7</sup> and R<sup>8</sup> 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 EP 1254889.

Examples of compounds of formula (III) in which RCOO 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 (III) 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 RCOO is preferably present in the form of an ester, that is the one or more further acid groups present in the group R are in esterified form. However embodiments in which not all acid groups are esterified are within the invention. Mixed esters of polycarboxylic acids may also be used. Preferred esters are C1 to C4 alkyl esters.

The ester quaternising agent 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 (III) is dimethyl oxalate.

- 5 In preferred embodiments the compound of formula (III) is an ester of a carboxylic acid having a pKa 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.

10 The ester quaternising agent may be selected from an ester of a carboxylic acid selected from one or more of oxalic acid, phthalic acid, salicylic acid, maleic acid, malonic acid, citric acid, nitrobenzoic acid, aminobenzoic acid and 2, 4, 6-trihydroxybenzoic acid.

Preferred ester quaternising agents include dimethyl oxalate, methyl 2-nitrobenzoate and methyl salicylate.

15 In some preferred embodiments, quaternising agents used to form the quaternary ammonium salt additives of the present invention are esters selected from dimethyl oxalate, methyl 2-nitrobenzoate and methyl salicylate, preferably dimethyl oxalate and methyl salicylate.

20 Suitable non-ester quaternising agents include 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.

25 In some embodiments the quaternary ammonium salt may be prepared from, for example, an alkyl or benzyl halide (especially a chloride) and then subjected to an ion exchange reaction to provide a different anion as part of the quaternary ammonium salt. Such a method may be suitable to prepare quaternary ammonium hydroxides, alkoxides, nitrites or nitrates.

30 Preferred non-ester quaternising agents include dialkyl sulfates, benzyl halides, hydrocarbyl substituted carbonates, hydrocarbyl substituted epoxides in combination with an acid, alkyl halides, alkyl sulfonates, sultones, hydrocarbyl substituted phosphates, hydrocarbyl substituted borates, N-oxides, chloroacetic acid or salts thereof, or mixtures thereof.

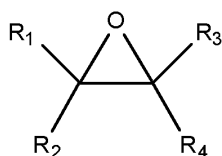
35 Suitable dialkyl sulfates for use herein as quaternising agents include those including alkyl groups having 1 to 10, preferably 1 to 4 carbon atoms in the alkyl chain. A preferred compound is dimethyl sulfate.

Suitable benzyl halides include chlorides, bromides and iodides. The phenyl group may be optionally substituted, for example with one or more alkyl or alkenyl groups, especially when the chlorides are used. A preferred compound is benzyl bromide.

- 5 Suitable hydrocarbyl substituted carbonates may include two hydrocarbyl groups, which may be the same or different. Each hydrocarbyl group may contain from 1 to 50 carbon atoms, preferably from 1 to 20 carbon atoms, more preferably from 1 to 10 carbon atoms, suitably from 1 to 5 carbon atoms. Preferably the or each hydrocarbyl group is an alkyl group. Preferred compounds of this type include diethyl carbonate and dimethyl carbonate.

10

Suitable hydrocarbyl substituted epoxides have the formula:



- wherein each of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> is independently hydrogen or a hydrocarbyl group having 1 to 50 carbon atoms. Examples of suitable epoxides include ethylene oxide, propylene oxide, butylene oxide, styrene oxide and stilbene oxide. The hydrocarbyl epoxides are used as quaternising agents in combination with an acid.
- 15

- The hydrocarbyl substituted succinic acylating agent includes two acyl groups. In some embodiments only one of these groups reacts with the compound of formula (I) or formula (II) to form a compound having an ester or an amide functional group and a free carboxylic acid. In these embodiments if an epoxide is used as the quaternising agent, no separate acid needs to be added. However in other embodiments an acid for example acetic acid may be used.
- 20

- Especially preferred epoxide quaternising agents are propylene oxide and styrene oxide, optionally in combination with an additional acid.
- 25

Suitable alkyl halides for use herein include chlorides, bromides and iodides.

- Suitable alkyl sulfonates include those having 1 to 20, preferably 1 to 10, more preferably 1 to 4 carbon atoms.
- 30

Suitable sultones include propane sultone and butane sultone.

- Suitable hydrocarbyl substituted phosphates include monoalkyl phosphates, dialkyl phosphates, trialkyl phosphates and O,O-dialkyl di thiophosphates. Preferred alkyl groups have 1 to 12 carbon atoms.
- 35

Suitable hydrocarbyl substituted borate groups include alkyl borates having 1 to 12 carbon atoms.

5 Preferred alkyl nitrites and alkyl nitrates have 1 to 12 carbon atoms.

Preferably the non-ester quaternising agent is selected from dialkyl sulfates, benzyl halides, hydrocarbyl substituted carbonates, hydrocarbyl substituted epoxides optionally in combination with an additional acid, chloroacetic acid or a salt thereof, and mixtures thereof.

10

Especially preferred non-ester quaternising agents for use herein are hydrocarbyl substituted epoxides in combination with an acid. These may include embodiments in which a separate acid is provided or embodiments in which the acid is provided by the tertiary amine compound that is being quaternised. Preferably the acid is provided by the tertiary amine molecule that is being

15

Preferred quaternising agents for use herein include dimethyl oxalate, methyl 2-nitrobenzoate, methyl salicylate, chloroacetic acid or a salt thereof, and styrene oxide or propylene oxide optionally in combination with an additional acid.

20

In some embodiments mixtures of two or more quaternising agents may be used.

To form some preferred quaternary ammonium salt additives of the present invention the compound of formula (III) is reacted with a compound formed by the reaction of a hydrocarbyl substituted succinic acid acylating agent and an amine of formula (I) or (II).

25

The compounds of formula (I) or formula (II) are as described above.

The amine of formula (I) or (II) is reacted with a hydrocarbyl substituted succinic acid derived acylating agent such as a succinic acid or succinic anhydride.

30

Suitably approximately one equivalent of amine is added per succinic acid moiety present in the acylating agent. The ratio of amine used will thus typically depend on the average number of succinic acid moieties present in each molecule of the acylating agent.

35

An especially preferred quaternary ammonium salt for use herein is formed by reacting methyl salicylate or dimethyl oxalate with the reaction product of a polyisobutylene-substituted succinic anhydride having a PIB molecular weight of 700 to 1300 and dimethylaminopropylamine;

wherein the polyisobutylene-substituted succinic anhydride includes on average at least 1.2 succinic acid moieties per molecule.

5 US2012/0010112 describes an acid-free process for preparing quaternized nitrogen compounds, wherein a) a compound comprising at least one oxygen- or nitrogen-containing group reactive with the anhydride and additionally comprising at least one quaternizable amino group is added onto a polycarboxylic anhydride compound, and b) the product from stage a) is quaternized using an epoxide quaternizing agent without an additional acid. Such methods could be used to prepare the quaternary ammonium salt additives of the present invention.

10

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

15

In some embodiments the first aspect of the present invention provides a method of cleaning up deposits in an indirect injection diesel engine, the method comprising combusting in the engine a diesel fuel composition comprising a quaternary ammonium salt additive; and one or more further nitrogen-containing detergents; wherein the quaternary ammonium salt additive comprises the quaternised reaction product of a hydrocarbyl substituted succinic acid derived acylating agent and a compound able to react with said acylating agent and which includes a tertiary amine group; wherein each molecule of the hydrocarbyl substituted succinic acid derived acylating agent includes on average at least 1.2 succinic acid moieties.

20

In some embodiments the second aspect of the present invention provides the use of a combination of a quaternary ammonium salt additive and one or more further nitrogen-containing detergents in a diesel fuel composition to clean up deposits in an indirect injection diesel engine; wherein the quaternary ammonium salt additive comprises the quaternised reaction product of a hydrocarbyl substituted succinic acid derived acylating agent and a compound able to react with said acylating agent and which includes a tertiary amine group; wherein each molecule of the hydrocarbyl substituted succinic acid derived acylating agent includes on average at least 1.2 succinic acid moieties.

25

30

The present invention may involve the use of a further nitrogen containing detergent. Any suitable nitrogen containing detergent which is not a quaternary ammonium salt additive as previously defined herein may be used.

35

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

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

- 5
- (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.
- 10

Preferably the further nitrogen containing detergent is selected from:

- 15
- (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;
- 20
- 25 and mixtures thereof.

In some preferred embodiments the further nitrogen containing detergent comprises:

- 30
- (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:

- 35
- (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.

5 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
- 10 (ii) the reaction product of a carboxylic acid-derived acylating agent and an amine.

The further nitrogen containing detergent may comprise the product of a Mannich reaction between an aldehyde, an amine and an optionally substituted phenol.

15 Preferably the further nitrogen containing detergent comprises the product of a Mannich reaction between:

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

20

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.

25 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  
30 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  
35 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.

5 Sutable 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.

10 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.

15 The further nitrogen containing detergent may comprise 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.

20 Sutable 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.

25 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.

30 Especially preferred PIBSAs are those having a PIB molecular weight (Mn) 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.

35 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 (Mn) 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

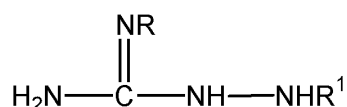
about 8 ethylene groups. These acylated nitrogen compounds are suitably formed by the reaction of a molar ratio of acylating agent:amino compound of from 10:1 to 1:10, preferably from 5:1 to 1:5, more preferably from 2:1 to 1:2 and most preferably from 2:1 to 1:1. In especially preferred embodiments, 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 comprises the reaction product of a polyisobutene-substituted succinic acid or succinic anhydride and a polyethylene polyamine selected from ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenhexamine, hexaethyleneheptamine 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 further nitrogen containing detergent may comprise 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.

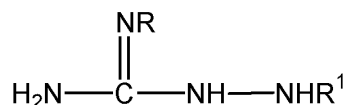
In such embodiments the further nitrogen containing detergent is suitably reaction product of a hydrocarbyl substituted dicarboxylic acid or anhydride and an amine compound having the formula:



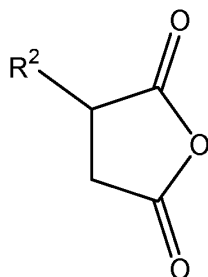
wherein R is selected from the group consisting of a hydrogen and a hydrocarbyl group containing from about 1 to about 15 carbon atoms, and R<sup>1</sup> is selected from the group consisting of hydrogen and a hydrocarbyl group containing from about 1 to about 20 carbon atoms.

The further nitrogen containing detergent may comprise the reaction product of an amine compound having the formula:

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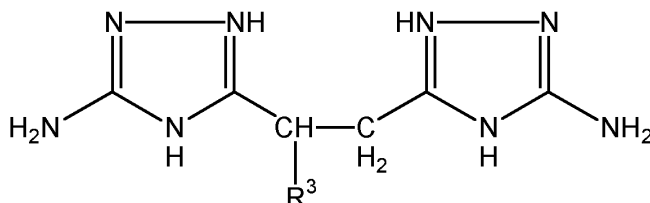
and a hydrocarbyl carbonyl compound of the formula:



5

wherein  $\text{R}^2$  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:

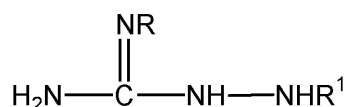


including tautomers having a number average molecular weight ranging from about 200 to about 3000 containing from about 40 to about 80 carbon atoms. The five-membered ring of the triazole is considered to be aromatic.

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 above.

25

Suitable amine compounds of the formula:



may be chosen from guanidines and aminoguanidines or salts thereof wherein R and R<sup>1</sup> 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 further nitrogen containing detergent comprises 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 are as defined in US2009/0282731.

Suitable treat rates of the quaternary ammonium salt additive and, when present, the one or more further nitrogen-containing detergents may depend on the type of fuel used and different levels of additive may be needed to achieve different levels of performance.

Suitably the quaternary ammonium salt additive is present in the diesel fuel composition in an amount of from 0.1 to 10000 ppm, preferably from 1 to 1000ppm, preferably from 5 to 500 ppm, for example 5 to 250 ppm or 5 to 100 ppm.

Suitably the one or more further nitrogen containing detergents, when present, are present in the diesel fuel composition in an amount of from 0.1 to 10000 ppm, preferably from 1 to 1000 ppm, preferably from 5 to 500 ppm. Preferably from 5 to 250 ppm, for example 5 to 100 ppm.

Each of the quaternary ammonium salt additive and the one or more further nitrogen containing detergents, when present, may be provided as a mixture of compounds. The above amounts refer to the total of all such compounds present in the composition.

For the avoidance of doubt the above amounts refer to the amount of active additive compound present in the composition and ignore any impurities, solvents or diluents which may be present.

The weight ratio of the quaternary ammonium salt additive and the one or more further nitrogen containing detergents is preferably from 1:10 to 10:1, preferably from 1:4 to 4:1, more preferably from 1:2 to 2:1.

5 In some embodiments the diesel fuel composition comprises from 0.1 to 10000 ppm, preferably from 1 to 1000 ppm, preferably from 5 to 250 ppm, for example 5 to 100 ppm of a quaternary ammonium salt additive and from 0.1 to 10000 ppm, preferably from 1 to 1000 ppm, preferably from 5 to 250 ppm, for example 5 to 100 ppm, of the product of a Mannich reaction between an aldehyde, an amine and an optionally substituted phenol.

10

In some embodiments the diesel fuel composition comprises from 0.1 to 10000 ppm, preferably from 1 to 1000 ppm, preferably from 5 to 250 ppm, for example 5 to 100 ppm of a quaternary ammonium salt additive and from 0.1 to 10000 ppm, preferably from 1 to 1000 ppm, preferably from 5 to 250 ppm, for example 5 to 100 ppm of the reaction product of a carboxylic acid-derived acylating agent and an amine.

15

In some embodiments the diesel fuel composition comprises from 0.1 to 10000 ppm, preferably from 1 to 1000 ppm, preferably from 5 to 250 ppm, for example 5 to 100 ppm of a quaternary ammonium salt additive and from 0.1 to 10000 ppm, preferably from 1 to 1000 ppm, preferably from 5 to 250 ppm, for example 5 to 100 ppm of 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.

20

In some embodiments the diesel fuel composition comprises from 0.1 to 10000 ppm, preferably from 1 to 1000 ppm, preferably from 5 to 500 ppm, for example 5 to 100 ppm of a quaternary ammonium salt additive; from 0.1 to 10000 ppm, preferably from 1 to 1000 ppm, preferably from 5 to 500 ppm, for example 5 to 100 ppm of the product of a Mannich reaction between an aldehyde, an amine and an optionally substituted phenol; and from 0.1 to 10000 ppm, preferably from 1 to 1000 ppm, preferably from 5 to 500 ppm, for example 5 to 100 ppm of reaction product of a carboxylic acid-derived acylating agent and an amine.

25

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When the one or more further nitrogen containing detergents includes the product of a Mannich reaction between an aldehyde, an amine and an optionally substituted phenol and the reaction product of a carboxylic acid-derived acylating agent and an amine, the weight ratio of the quaternary ammonium salt additive to the Mannich reaction product additive to the reaction product of a carboxylic acid-derived acylating agent and an amine is preferably 1 part quaternary ammonium salt to 0.1 to 10 parts Mannich reaction product to 0.1 to 10 parts of the reaction product of a carboxylic acid-derived acylating agent and an amine.

35

In some embodiments the diesel fuel composition comprises from 0.1 to 10000 ppm, preferably from 1 to 1000 ppm, preferably from 5 to 500 ppm, for example 5 to 100 ppm of a quaternary ammonium salt additive; from 0.1 to 10000 ppm, preferably from 1 to 1000 ppm, preferably from 5 to 500 ppm, for example 5 to 100 ppm of the product of a Mannich reaction between an aldehyde, an amine and an optionally substituted phenol; and from 0.1 to 10000 ppm, preferably from 1 to 1000 ppm, preferably from 5 to 500 ppm, for example 5 to 100 ppm of 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.

When the one or more further nitrogen containing detergents includes the product of a Mannich reaction between an aldehyde, an amine and an optionally substituted phenol and 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, the weight ratio of the quaternary ammonium salt additive to the Mannich additive to the amino triazole additive is preferably 1 part quaternary ammonium salt to 0.1 to 10 parts Mannich additive to 0.1 to 10 parts amino triazole additive.

In some embodiments the diesel fuel composition comprises from 0.1 to 10000 ppm, preferably from 1 to 1000 ppm, preferably from 5 to 500 ppm, for example 5 to 100 ppm of a quaternary ammonium salt additive; from 0.1 to 10000 ppm, preferably from 1 to 1000 ppm, preferably from 5 to 500 ppm, for example 5 to 100 ppm of 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 from 0.1 to 10000 ppm, preferably from 1 to 1000 ppm, preferably from 5 to 500 ppm, for example 5 to 100 ppm of the reaction product of a carboxylic acid-derived acylating agent and an amine.

When the one or more further nitrogen containing detergents includes the reaction product of a carboxylic acid-derived acylating agent and an amine and 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, the weight ratio of the quaternary ammonium salt additive to the reaction product of a carboxylic acid-derived acylating agent and an amine to the amino triazole additive is preferably 1 part quaternary ammonium salt to 0.1 to 10 parts of the reaction product of a carboxylic acid-derived acylating agent and an amine to 0.1 to 10 parts amino triazole additive.

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.

- 5 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.

10 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.

- 15 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).

20 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, 25 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.

30 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.

35 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.

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

10 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%.

15 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%.

20 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.

25 As mentioned above, various metal species may be present in fuel compositions. This may be due to contamination of the fuel during manufacture, storage, transport or use or due to contamination of fuel additives. Metal species may also be added to fuels deliberately. For example transition metals are sometimes added as fuel borne catalysts, for example to improve the performance of diesel particulate filters.

30 In preferred embodiments the diesel fuel compositions used in the present invention comprise sodium and/or calcium. Preferably they comprise sodium. The sodium and/or calcium is typically present in a total amount of from 0.01 to 50 ppm, preferably from 0.05 to 5 ppm preferably 0.1 to 2ppm such as 0.1 to 1 ppm.

35 Other metal-containing species may also be present as a contaminant, for example through the corrosion of metal and metal oxide surfaces by acidic species present in the fuel or from lubricating oil. In use, fuels such as diesel fuels routinely come into contact with metal surfaces for example, in vehicle fuelling systems, fuel tanks, fuel transportation means etc. Typically,

metal-containing contamination may comprise transition metals such as zinc, iron and copper; other group I or group II metals and other metals such as lead.

5 In addition to metal-containing contamination which may be present in diesel fuels there are circumstances where metal-containing species may deliberately be added to the fuel. For example, as is known in the art, metal-containing fuel-borne catalyst species may be added to aid with the regeneration of particulate traps.

10 Metal-containing contamination, depending on its source, may be in the form of insoluble particulates or soluble compounds or complexes. Metal-containing fuel-borne catalysts are often soluble compounds or complexes or colloidal species.

15 In some embodiments, the diesel fuel may comprise metal-containing species comprising a fuel-borne catalyst. Preferably, the fuel borne catalyst comprises one or more metals selected from iron, cerium, platinum, manganese, Group I and Group II metals e.g., calcium and strontium. Most preferably the fuel borne catalyst comprises a metal selected from iron and cerium.

20 In some embodiments, the diesel fuel may comprise metal-containing species comprising zinc. Zinc may be present in an amount of from 0.01 to 50 ppm, preferably from 0.05 to 5 ppm, more preferably 0.1 to 1.5 ppm.

25 Typically, the total amount of all metal-containing species in the diesel fuel, expressed in terms of the total weight of metal in the species, is between 0.1 and 50 ppm by weight, for example between 0.1 and 20 ppm, preferably between 0.1 and 10 ppm by weight, based on the weight of the diesel fuel.

The present invention provides a method and use for removing deposits in an indirect injection diesel engine. The removal of deposits may be regarded as providing "clean-up" of the engine.

30 "Clean-up" of a fouled engine may provide significant advantages. For example, superior clean up may lead to an increase in power and/or an increase in fuel economy and/or reduced emissions. In addition removal of deposits from an engine, in particular from injectors may lead to an increase in interval time before injector maintenance or replacement is necessary thus reducing maintenance costs.

35 In some preferred embodiments, clean up may also provide a power increase. Thus a fouled engine may be treated to remove the existing deposits and provide an additional power gain.

The removal of deposits according to the present invention will lead to an improvement in performance of the engine.

5 The improvement in performance of the diesel engine system may be measured by a number of ways.

“Clean up” performance can be observed by an improvement in performance of an already fouled engine.

10 The effectiveness of fuel additives is often assessed using a controlled engine test.

For indirect engines an improvement in performance may be measured using the a standard industry test – CEC test method No. CEC F-23-A-01. This test measures injector nozzle coking using a Peugeot XUD9 A/L Engine and is commonly referred to in the art as the XUD9 test.

15 In the XUD9 engine test the flow of air through an injector is measured. The airflow at the end of the test is recorded as a percentage of the initial flow at the start of the test.

20 In the XUD9 engine test, injector fouling is determined by measurement of injector nozzle air flow before and after completion of the engine test cycle. Where injector fouling has occurred, nozzle air flow at the end of test is reduced, relative to the value measured at the start of the test. Flow loss may be recorded as a percentage of the initial injector nozzle air flow at the start of the test.

25 To measure clean up of injectors, a first XUD9 test is carried out starting with clean injectors using unadditised fuel. The test is then repeated starting from the resultant dirty injectors using additised fuel. The flow rate through the injectors at the end of each test is compared. Preferably the method and use of the present invention increase the airflow through the injectors as measured by an XUD9 test after 10 hours by at least 10%, preferably by at least 20%, more preferably at least 30%, for example at least 40% or at least 50%, compared with the airflow through the dirty injectors.

30 As mentioned above to measure clean up of injectors, a first XUD9 test is carried out starting from clean injectors using unadditised fuel. This is referred to as the dirty up cycle and injector nozzle air flow is measured before and after completion of this cycle. The test is then repeated starting from the resultant dirty injectors using additised fuel. This is referred to as the clean up cycle, and injector nozzle air flow is measured after completion of this cycle. For both cycles, flow loss may be recorded as a percentage of the initial injector nozzle air flow prior to the dirty

up cycle (ie with clean injectors). The skilled person will understand that the flow loss may decrease during the clean up cycle when an additised fuel is used.

5 The present invention is effective even for highly fouled engines. Preferably the method and use of the present invention can decrease the flow loss through an engine having an initial flow loss following the dirty up cycle of more than 60%, for example more than 65% or more than 70%. Preferably the method and use of the present invention decrease the flow loss of a highly fouled engine having an initial flow loss of more than 60% to provide a flow loss after the clean up cycle of less than 50%, for example less than 40%, less than 30%, less than 20% or less  
10 than 10%.

In some preferred embodiments the present invention involves the combination of 5 to 100 ppm of a quaternary ammonium salt additive and 5 to 100 ppm of one or more nitrogen containing detergents selected from:

- 15
- the product of a Mannich reaction between an aldehyde, an amine and an optionally substituted phenol;
  - the reaction product of a carboxylic acid-derived acylating agent and an amine; and
  - 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.

20 In some preferred embodiments the present invention involves the combination of 5 to 100 ppm of a quaternary ammonium salt additive; 5 to 100 ppm of the product of a Mannich reaction between an aldehyde, an amine and an optionally substituted phenol.

25 The invention will now be further defined with reference to the following non-limiting examples.

#### **Raw materials**

30 The polyisobutylene used in the synthesis examples was purchased under the trade mark HRPB1000 (Daelim, South Korea) and had a number average molecular weight ( $M_n$ ) of approximately 1,000 and a terminal vinylidene content  $\geq 80\%$  ( $^{13}\text{C}$  NMR).

#### **Analytical Methods**

35 The acid value of PIBSA was determined by non-aqueous titration against lithium methoxide solution (ca 0.1 M in toluene/methanol) using thymol blue (0.4 % w/v in 1,4-dioxane) as the indicator. The titre of lithium methoxide solutions was regularly confirmed by titration against analytical grade benzoic acid.

The residual maleic anhydride content of polyisobutylenesuccinic anhydride (PIBSA) was measured by quantitative FTIR against a calibration curve. The characteristic absorbance at 696  $\text{cm}^{-1}$  was used for the analysis.

- 5 The residual (unreacted) polyisobutylene content of polyisobutylenesuccinic anhydride (PIBSA) was measured by quantitative HPLC against a polyisobutylene standard, under normal phase column conditions (eluent : isohexane).

10 The 'P value' (average number of succinyl residues per polyisobutylene side chain, in the sample) may be calculated using the following formula:

$$P = \frac{\text{Acid value} \times \text{PIB MW}}{(20(100 - \text{PIB content}) - (\text{Acid Value} \times 98.06))}$$

15 wherein 'PIB MW' is the number average molecular weight ( $M_n$ ) of the polyisobutenyl substituent and PIB content is the residual (unreacted) polyisobutylene content as described above.

The derivation of this equation is described below.

20 PIB content is measured as a percentage by weight (g/100g).

Acid value (AV) is recorded as the number of acid groups (mmol) per gram of sample.

$x$  = mmol monomaleated PIBSA/g

$y$  = mmol bismaleated PIBSA/g

25

$$x + 2y = \frac{1}{2} AV$$

$$2x + 4y = AV$$

30

$$x = \frac{(AV - 4y)}{2}$$

$$(MW + 98)x + (MW + 196)y = 10(100 - PIB) \text{ [units each side mg/g]}$$

$$(MW + 98)(AV - 4y) + 2(MW + 196)y = 20(100 - PIB)$$

35

$$(MW + 98)AV - 4y(MW + 196) + 2(MW + 196)y = 20(100 - PIB)$$

31

$$(MW + 98)AV - 20(100 - PIB) = 4y(MW + 98) - 2(MW + 196)y$$

$$= 4yMW + 392y - 2yMW - 392y$$

$$y = \frac{(MW + 98)AV - 20(100 - PIB)}{2MW}$$

5

$$P = \frac{x + 2y}{x + y} = \frac{x + 2y}{(x + 2y) - y} = \frac{\frac{1}{2} AV}{\frac{1}{2} AV - \frac{(MW + 98)AV - 20(100 - PIB)}{2MW}}$$

$$P = \frac{AV}{AV - \left( \frac{AV(mw + 98) - 20(100 - PIB)}{mw} \right)}$$

$$10 \quad P = \frac{AV \cdot mw}{AV \cdot mw - AV \cdot mw - AV \cdot 98 + 20(100 - PIB)}$$

$$P = \frac{AV \cdot mw}{20(100 - PIB) - (AV \cdot 98)}$$

### Example 1 – Preparation of polyisobutylenesuccinic anhydride (PIBSA) - inventive

15

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  $\leq 0.05$  wt%. The reaction mass was cooled to  $\leq 80^\circ\text{C}$  then discharged from the reactor.

20

### 25 Example 2 – Preparation of PIBSA - comparative

The synthesis procedure was substantially identical to Example 1 and used the same grade of polyisobutylene ( $M_n$  1000). The charge of maleic anhydride was reduced (1 eq relative to polyisobutylene) and the reaction was held between 190 – 210 °C during the 8 hour heating period. Residual maleic anhydride was also measured as  $\leq 0.05$  wt%.

30

The properties of the reaction products of Examples 1 and 2 are summarised in Table 1.

**Table 1**

| Example | Acid value<br>(mmolH+/g) | Unreacted PIB<br>(wt%) | Molecular weight of PIB<br>starting material (Mn) | P value |
|---------|--------------------------|------------------------|---------------------------------------------------|---------|
| 1       | 1.89                     | 18.5                   | 1000                                              | 1.31    |
| 2       | 1.68                     | 20.2                   | 1000                                              | 1.17    |

**Example 3 – Additive Q1 - inventive**

5

PIBSA prepared according to Example 1 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 Q2 – comparative**

15

PIBSA prepared according to Example 2 was charged to a nitrogen flushed, jacketed reactor fitted with an overhead stirrer and heated to 90 °C. 3-(dimethylamino)propylamine (DMAPA) (1eq relative to anhydride groups) was charged slowly, maintaining the reaction temperature between 90 - 100 °C. After stirring at 90 – 100 °C for a further 1 hr, the reaction temperature was increased to 140 °C and held for 4 hrs with concurrent distillation of water. 2-ethylhexanol was added to adjust the solids content to 60 wt% then methyl salicylate (1 eq relative to anhydride groups) was added in a single portion and heating was continued at 140 °C for 15 hours. The reaction mass was cooled to 60 °C prior to discharging from the reactor.

25

**Example 5 – Preparation of DMAPA polyisobutylene succinimide propylene oxide / acetic acid quaternary ammonium salt – inventive additive Q3**

PIBSA according to Example 1 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. The reaction mass was cooled to room

30

temperature, then acetic acid (0.71 eq relative to anhydride groups), 2-ethylhexanol (1.34 eq relative to anhydride groups) and water (0.81 eq relative to anhydride groups) were added. The reaction mass was heated to 75 °C and propylene oxide (2.39 eq relative to anhydride groups) was added over 3 hrs via a dropping funnel. Heating was continued for 4 hrs. 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 6 – Preparation of DMAPA polyisobutylene succinimide propylene oxide / acetic acid quaternary ammonium salt - comparative**

PIBSA according to Example 2 was used. Formation of the DMAPA succinimide and subsequent quaternization using propylene oxide / AcOH was carried out in identical manner to Example 5. Reactant charges were calculated relative to anhydride groups in the PIBSA starting material.

**Example 7 – Preparation of DMAPA polyisobutylene succinamide propylene oxide quaternary ammonium salt - inventive**

PIBSA according to Example 1 (1 part) and Caromax 20 (1 part) were charged to a nitrogen flushed, jacketed reactor fitted with an overhead stirrer and heated to 80 °C to ensure proper mixing, then cooled to room temperature. 3-(dimethylamino)propylamine (DMAPA) (1eq relative to anhydride groups in the PIBSA starting material) was added over 3 hrs, maintaining the reaction temperature below 40 °C. The reaction mass was stirred for a further 4 hrs, then propylene oxide (2 eq relative to anhydride groups) was added over 3 hrs, then the reaction mass stirred at room temperature for 4 hrs. After nitrogen sparging to remove residual propylene oxide, the reaction mass was discharged from the reactor.

**Example 8 – Preparation of DMAPA polyisobutylene succinamide propylene oxide quaternary ammonium salt - comparative**

PIBSA according to Example 2 was used. Formation of the DMAPA succinamide and subsequent quaternization using propylene oxide was carried out in identical manner to Example 7. Reactant charges were calculated relative to anhydride groups.

**Example 9 – Additive A1**

Additive A1, a Mannich reaction product additive of the prior art was prepared as follows:

A 1 L reactor was charged with dodecylphenol (170.6g, 0.65 mol), ethylenediamine (30.1 g, 0.5 and Caromax 20 (123.9g). The mixture was heated to 95 °C and formaldehyde solution, 37 wt%

(73.8g, 0.9 mol) charged over 1 hour. The temperature was increased to 125 °C for 3 hours and water removed. In this example the molar ratio of aldehyde (a) : amine (b) : phenol (c) was approximately 1.8:1 :1.3.

#### 5 Example 10 – Additive A2

Additive A2 is a 60 wt% active ingredient solution (in aromatic solvent) of a polyisobutenyl succinimide obtained from the condensation reaction of a polyisobutenyl succinic anhydride (PIBSA) derived from polyisobutene of Mn approximately 750 with a polyethylene polyamine  
 10 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 11

15

Fuel compositions were prepared by adding additives Q1, Q2 and A1 to diesel fuel.

The diesel fuel complied with the RF06 base fuel, the details of which are given in table 1 below.

20

**Table 1**

| Property                                      | Units                | Limits |      | Method       |
|-----------------------------------------------|----------------------|--------|------|--------------|
|                                               |                      | Min    | Max  |              |
| Cetane Number                                 |                      | 52.0   | 54.0 | EN ISO 5165  |
| Density at 15°C                               | kg/m <sup>3</sup>    | 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 <sup>2</sup> /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  |

35

|                                     |          |   |            |               |
|-------------------------------------|----------|---|------------|---------------|
| 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 |               |

Example 12

5 The ability of additives of the invention to remove deposits in an indirect injection diesel engine may be measured according to a standard industry test – CEC test method No. CEC F-23-A-01. This may be referred to as the XUD9 test.

10 This test measures injector nozzle coking using a Peugeot XUD9 A/L Engine and provides a means of discriminating between fuels of different injector nozzle coking propensity. Nozzle coking is the result of carbon deposits forming between the injector needle and the needle seat. Deposition of the carbon deposit is due to exposure of the injector needle and seat to combustion gases, potentially causing undesirable variations in engine performance.

15 The Peugeot XUD9 A/L engine is a 4 cylinder indirect injection Diesel engine of 1.9 litre swept volume, obtained from Peugeot Citroen Motors specifically for the CEC PF023 method.

20 The test engine is fitted with cleaned injectors utilising unflatted injector needles. The airflow at various needle lift positions have been measured on a flow rig prior to test. The engine is operated for a period of 10 hours under cyclic conditions.

| Stage | Time (secs) | Speed (rpm) | Torque (Nm) |
|-------|-------------|-------------|-------------|
| 1     | 30          | 1200 ± 30   | 10 ± 2      |
| 2     | 60          | 3000 ± 30   | 50 ± 2      |
| 3     | 60          | 1300 ± 30   | 35 ± 2      |
| 4     | 120         | 1850 ± 30   | 50 ± 2      |

25 The propensity of the fuel to promote deposit formation on the fuel injectors is determined by measuring the injector nozzle airflow again at the end of test, and comparing these values to those before test. The results are expressed in terms of percentage airflow reduction at various needle lift positions for all nozzles. The average value of the airflow reduction at 0.1mm needle lift of all four nozzles is deemed the level of injector coking for a given fuel.

In a clean up test a first test cycle (dirty-up phase) is carried out using an unadditised fuel. A further test is then carried out starting with the dirty injectors but using additised fuel. The percentage clean up is recorded as the relative improvement in flow loss compared with the flow loss at the end of the dirty up phase.

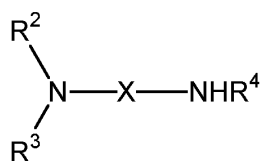
Example 13

Diesel fuel compositions were prepared comprising the additives indicated in the table below and tested according to the clean up procedure detailed in example 12.

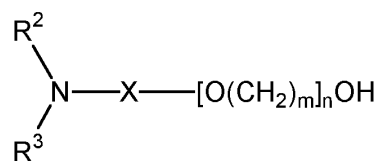
| Additive<br>Q1<br>(ppm<br>active) | Additive<br>Q2<br>(ppm<br>active) | Additive<br>Q3<br>(ppm<br>active) | Additive<br>A1<br>(ppm<br>active) | Flow loss<br>after dirty<br>up (%) | Flow loss<br>after<br>clean up<br>(%) | % clean<br>up |
|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|------------------------------------|---------------------------------------|---------------|
| 39                                |                                   |                                   | 42                                | 70                                 | 0                                     | 100           |
|                                   | 24                                |                                   | 16                                | 72.3                               | 31.5                                  | 56            |
| 21                                |                                   |                                   | 16                                | 69                                 | 8                                     | 88            |
| 36                                |                                   |                                   |                                   | 74.1                               | 8.1                                   | 89            |
|                                   |                                   | 36                                |                                   | 71.6                               | 22.8                                  | 68            |

## Claims

1. A method of cleaning up deposits in an indirect injection diesel engine, the method comprising combusting in the engine a diesel fuel composition comprising a quaternary ammonium salt additive wherein the quaternary ammonium salt additive comprises the quaternised reaction product of a hydrocarbyl substituted succinic acid derived acylating agent and a compound able to react with said acylating agent and which includes a tertiary amine group; wherein each molecule of the hydrocarbyl substituted succinic acid derived acylating agent includes on average at least 1.2 succinic acid moieties.
2. The use of a combination of a quaternary ammonium salt additive in a diesel fuel composition to clean up deposits in an indirect injection diesel engine; wherein the quaternary ammonium salt additive comprises the quaternised reaction product of a hydrocarbyl substituted succinic acid derived acylating agent and a compound able to react with said acylating agent and which includes a tertiary amine group; wherein each molecule of the hydrocarbyl substituted succinic acid derived acylating agent includes on average at least 1.2 succinic acid moieties.
3. A method or use according to claim 1 or claim 2 wherein the hydrocarbyl substituted succinic acid derived acylating agent is a polyisobutene-substituted succinic acid or succinic anhydride wherein the polyisobutene substituent has a number average molecular weight of between 450 and 2300, preferably between 500 and 1300.
4. A method or use according to any preceding claim wherein the compound able to react with the hydrocarbyl substituted succinic acid derived acylating agent and which includes a tertiary amine group comprises one or more compounds formed by the reaction of a hydrocarbyl-substituted acylating agent and an amine of formula (I) or (II):



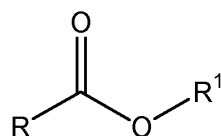
(I)



(II)

- wherein  $\text{R}^2$  and  $\text{R}^3$  are the same or different alkyl, alkenyl, aryl, alkaryl or aralkyl groups having from 1 to 22 carbon atoms; X is an optionally substituted alkylene group having from 1 to 20 carbon atoms; n is from 0 to 20; m is from 1 to 5; and  $\text{R}^4$  is hydrogen or a  $\text{C}_1$  to  $\text{C}_{22}$  alkyl group.

5. A method or use according to claim 4 wherein X is a propylene group.
6. A method or use according to any preceding claim wherein the quaternising agent used to prepare the quaternary ammonium salt additive is selected from the group consisting of an ester 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.
7. A method or use according to any preceding claim wherein the quaternising agent used to prepare the quaternary ammonium salt additive is selected from the group consisting of dialkyl sulfates, benzyl halides, hydrocarbyl substituted carbonates, hydrocarbyl substituted epoxides in combination with an acid, alkyl halides, alkyl sulfonates, sultones, hydrocarbyl substituted phosphates, hydrocarbyl substituted borates, N-oxides, chloroacetic acid or salts thereof, or mixtures thereof.
8. A method or use according to any of claims 1 to 6 wherein the quaternising agent used to prepare the quaternary ammonium salt additive is a compound of formula (III):



(III)

- wherein R is an optionally substituted alkyl, alkenyl, aryl or alkylaryl group and R<sup>1</sup> is a C<sub>1</sub> to C<sub>22</sub> alkyl, aryl or alkylaryl group.
9. A method or use according to claim 8 wherein the quaternizing agent is selected from dimethyl oxalate, methyl 2-nitrobenzoate and methyl salicylate.
10. A method or use according to claim 8 wherein the quaternizing agent is an ester of a polycarboxylic acid.
11. A method or use according to any preceding claim wherein the diesel fuel composition comprises one or more further nitrogen containing detergents.

12. A method or use according to claim 11 wherein the one or more further nitrogen containing detergents comprises the product of a Mannich reaction between an aldehyde, an amine and an optionally substituted phenol.
- 5 13. A method or use according to claim 12 wherein the one or more further nitrogen containing detergents comprises the product of a Mannich reaction between:  
(x) formaldehyde;  
(y) a polyethylene polyamine; and  
(z) para-substituted monoalkyl phenol.
- 10 14. A method or use according to any of claims 11 to 13 wherein the one or more further nitrogen containing detergents comprises the reaction product of a carboxylic acid-derived acylating agent and an amine.
- 15 15. A method or use according to claim 14 wherein the reaction product of a carboxylic acid-derived acylating agent and an amine comprises the reaction product of a polyisobutene-substituted succinic acid or succinic anhydride and a polyethylene polyamine selected from ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, hexaethylene-heptamine and mixtures and isomers thereof;  
20 wherein polyisobutene substituent has a number average molecular weight of between 500 and 2000, preferably between 600 and 1000.
- 25 16. A method or use according to any of claims 11 to 15 wherein the one or more further nitrogen containing detergents comprises 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.
- 30 17. A method or use according to any preceding claim which increases the airflow through the injectors as measured by an XUD9 test after 10 hours by at least 50% compared with the airflow through dirty injectors.