

Use and Method

The present invention relates to methods and uses for improving the performance of diesel engines. In particular the invention relates to reducing particular types of deposits that occur in the exhaust
5 gas recirculation system of diesel engines.

Exhaust gas recirculation (EGR) systems are fitted to diesel vehicles to reduce NO_x emissions. This is achieved by recirculating exhaust gases to the combustion chamber in a controlled manner and thereby increasing the heat capacity of and reducing the oxygen concentration in gases within the
10 combustion chamber. Several types of EGR systems have been developed. High pressure EGR systems are arranged to divert exhaust gases from the combustion chamber, before the exhaust gases reach any turbocharger and/or diesel particulate filter present in the engine, and supply said exhaust gases to the intake manifold downstream of the compressor. The high pressure EGR system therefore operates on the high pressure sides of the intake and exhaust manifolds and
15 supplies the combustion chamber with unfiltered recirculated exhaust gases. Low pressure EGR systems are arranged to divert exhaust gases from the combustion chamber downstream of any turbocharger and/or diesel particulate filter present in the engine, and to supply said exhaust gases to the intake tract upstream of the compressor. The low pressure EGR system therefore operates on the low pressure sides of the intake and exhaust manifolds and supplies the combustion chamber
20 with filtered recirculated exhaust gases. Hybrid (or combined) EGR systems integrate both high pressure EGR and low pressure EGR on the same engine, to combine the benefits of each system. Dedicated EGR (D-EGR) systems are arranged to route the entire exhaust of a sub-group of power cylinders (dedicated cylinders) directly into the intake manifold.

25 Over time deposits can form within an EGR system. This is a particular issue in diesel engines with high pressure EGR systems, due to the recirculated exhaust gas stream being taken upstream of any turbocharger and diesel particulate filter, meaning that problematic particulate combustion products are re-introduced into the intake manifold and the combustion chamber. One area where such deposits cause a particular problem is within the cooler component of the EGR system. If the
30 level of deposits becomes significant then the engine management systems in sophisticated diesel engines may cause the engine to operate with reduced performance and/or enter into a safe running mode. This scenario would have significant impact on the vehicle's operability and would require inspection by a suitably qualified workshop.

35 A typical EGR system comprises an intake pipe, a valve, a housing, a cooler and an outlet pipe. Deposits build up on the interior surfaces of all portions of the EGR system, but particularly in the cooler.

It would be beneficial to combat such deposits, particularly in the cooler of an EGR system,
40 particularly in the cooler of a high pressure EGR system.

The present inventors have surprisingly found that the inclusion of certain compounds as fuel additives is able to reduce the formation of deposits in EGR systems.

5 According to a first aspect of the present invention there is provided the use of one or more nitrogen-containing compounds as an additive in a diesel fuel composition to reduce the impact of deposits in the exhaust gas recirculation system of a diesel engine when combusting said diesel fuel composition, wherein the one or more nitrogen-containing compounds comprise at least 4% by mass of nitrogen atoms.

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According to a second aspect of the present invention there is provided a method of reducing the impact of deposits in the exhaust gas recirculation system of a diesel engine, the method comprising combusting in the engine a diesel fuel composition comprising as an additive one or more nitrogen-containing compounds, wherein the nitrogen-containing compounds comprise at least 4% by mass of nitrogen atoms.

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The present invention relates to a method and use which reduces the impact of deposits in the EGR system of a diesel engine. The presence of such deposits typically has a negative effect on the performance of the engine.

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Reducing the impact of deposits may involve reducing or preventing the formation of deposits and/or removing existing deposits and/or changing the nature of the deposits.

In some embodiments reducing the impact of deposits may involve changing the nature of deposits.

25 This means that the structure or composition of deposits which are formed is different in a way that is less detrimental to the performance of the engine, for example by increasing the combustibility and/or thermal conductivity of the deposits.

In some preferred embodiments, reducing the impact of deposits involves reducing and/or preventing the formation of deposits and/or the removal of existing deposits.

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Preferably the use of the first aspect reduces the formation of deposits in the EGR system.

Preferably the method of the second aspect reduces the formation of deposits in the EGR system.

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

The present invention relates to the use of an additive in a diesel fuel composition to reduce the formation of deposits in an exhaust gas recirculation (or EGR) system. The additive is a nitrogen-

containing compound comprising at least 4% by mass of nitrogen atoms, and mixtures thereof. This additive may be referred to herein as an EGR deposit control additive.

5 For the avoidance of doubt the nitrogen-containing compound used in the present invention may comprise a mixture of compounds and references to an additive or the additive include mixtures, unless otherwise stated. In particular mixtures of isomers and mixtures of homologues are within the scope of the invention. The skilled person will appreciate that commercial sources of some of the additive compounds described herein may comprise mixtures of isomers and/or mixtures of homologues.

10 The nitrogen-containing compounds used in the present invention comprise at least 4% by mass of nitrogen atoms. By this we mean that at least 4% of the molecular weight of the nitrogen-containing compounds is provided by nitrogen atoms, preferably by number average molecular weight. The amount by mass of nitrogen in such compounds can be calculated using standard methods or
15 determined by elemental analysis. As the nitrogen-containing compounds may be a mixture of compounds, for example isomers, homologues and/or structurally similar compounds produced by the reactions used to form the nitrogen-containing compounds, the percent by mass of nitrogen referred to above is suitably an average value of such a mixture of nitrogen-containing compounds.

20 Preferably the nitrogen-containing compounds comprise at least 5% by mass of nitrogen atoms, preferably at least 7% or at least 10%.

Suitably the nitrogen-containing compounds comprise up to 50% by mass of nitrogen atoms or up to 40%. Suitably the nitrogen-containing compounds comprise up to 35% by mass of nitrogen atoms,
25 suitably up to 30%.

Suitably the nitrogen-containing compounds comprise from 4 to 50% by mass of nitrogen atoms, suitably from 4 to 40%. In preferred embodiments, the nitrogen-containing compounds comprise from 4 to 35% by mass of nitrogen atoms, suitably from 5 to 30% or from 10 to 30%.

30 The inventors have found that this relatively high proportion of nitrogen atoms present in the additive is required to provide the beneficial effects in the EGR system of a diesel engine as described herein.

The nitrogen-containing compounds used in the present invention preferably comprise no more than
35 12 N-H bonds. The N-H bonds may be referred to as "free" N-H bonds. Preferably the nitrogen-containing compounds contain fewer than five N-H bonds, fewer than four N-H bonds or fewer than three N-H bonds. Preferably the limits to the number of N-H bonds described above apply only to N-H bonds on amino groups in the nitrogen-containing molecule. For example, N-H bonds of amide groups and/or N-H bonds of nitrogen atoms in aromatic heterocyclic rings are not included in the N-H
40 bond limits described herein.

The inventors have found that this relatively low number of such free N-H bonds in the additive, which contains a relatively high proportion of nitrogen, may be required for the nitrogen-containing compounds to provide the beneficial effects in the EGR system of a diesel engine as described
5 herein.

A suitable nitrogen-containing compound is the reaction product of a) a hydrocarbyl substituted reagent and b) a nitrogen-containing reagent.

10 In some embodiments, the nitrogen-containing compound is the reaction product of:

a) hydrocarbyl substituted carboxylic acid acylating agent; and

b) a nitrogen-containing reagent;

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as further described below.

In some embodiments, the nitrogen-containing compound is the reaction product of:

20 a) an amine or polyamine comprising a hydrocarbyl group;

b) a nitrogen-containing reagent; and

c) an aldehyde;

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as further described below.

The nitrogen-containing compound may be a mixture of reaction products of a) a hydrocarbyl substituted reagent and b) a nitrogen-containing reagent. For example, the nitrogen-containing
30 compound may comprise a reaction product of:

a) hydrocarbyl substituted carboxylic acid acylating agent; and

b) a nitrogen-containing reagent;

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and a reaction product of:

a) an amine or polyamine comprising a hydrocarbyl group;

40 b) a nitrogen-containing reagent; and

c) an aldehyde;

as further described below.

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When the nitrogen-containing compound is the reaction product of a) a hydrocarbyl substituted reagent and b) a nitrogen-containing reagent, the nitrogen-containing reagent b) suitably comprises a nitrogen-containing group A. The hydrocarbyl substituted reagent a) suitably comprises a hydrocarbyl group R¹.

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The A group suitably provides a significant amount of the required nitrogen content of the additive and the R¹ group may be a solubilising group which provides the additive with sufficient solubility in the diesel fuel for the additive to be effective in use. The A and R¹ groups are suitably selected to provide the required nitrogen content of at least 4% by mass in the nitrogen-containing compound.

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In some embodiments the nitrogen-containing reagent b) suitably comprises a nitrogen-containing heterocyclic group. The heterocyclic group suitably provides a significant amount of the required nitrogen content of the additive. In such embodiments, the A group of the nitrogen-containing reagent b) is a nitrogen-containing heterocyclic group.

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The nitrogen-containing heterocyclic group may be any heterocyclic group, either aromatic or aliphatic, which contains at least one nitrogen atom. The nitrogen-containing heterocyclic group may contain other heteroatoms, for example at least one oxygen atom or at least one sulphur atom, preferably at least one oxygen atom. In some embodiments, the nitrogen-containing heterocyclic group contains no other heteroatoms other than nitrogen. The nitrogen-containing heterocyclic group of the A group may be selected from optionally substituted piperazine, pyridine, pyrazine, pyridazine, pyrimidine, triazine, quinoline, isoquinoline, quinazoline, a five-membered heterocyclic ring such as pyrazole or imidazole or a benzo-fused five-membered heterocyclic ring such as benzimidazole, and derivatives thereof. The nitrogen-containing heterocyclic group is suitably selected to provide the required nitrogen content of at least 4% by mass, along with any other nitrogen atoms present in the R¹ groups.

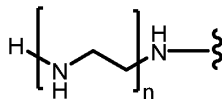
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Preferably the A group is selected from an optionally substituted five-membered nitrogen-containing heterocyclic ring or a benzo-fused five-membered nitrogen-containing heterocyclic ring and derivatives thereof. Preferably the A group is an optionally substituted benzotriazole, an indazole, a triazole, a tetrazole, an imidazole, a benzimidazole or an imidazoline, or a derivative thereof. Suitably the A group is an optionally substituted benzotriazole, benzimidazole, an indazole, a triazole or a tetrazole.

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In some embodiments, the A group is a non-cyclic nitrogen-containing group. In such embodiments the A group may be an amine or a polyamine. Suitable polyamines may have the formula (II):



(II)

wherein n is from 1 to 10. The nitrogen-containing compound may be a mixture compounds having different n numbers in the "A" group. Therefore n is suitably an average value of the different n numbers present in the mixture. Therefore n may be a non-integer value, of from 1 to 10, i.e from 1.0 to 10.0. Preferably n is from 1 to 6, from 1 to 4 or from 1 to 3.

Therefore the A group may be provided by ethylenediamine, diethylene triamine (DETA) or triethylene tetramine (TETA) or tetraethylene pentaamine (TEPA). Preferably the A group is provided by TETA or TEPA.

The R¹ group of the hydrocarbyl substituted reagent a) preferably has a molecular weight (Mn) of up to 1,000, up to 600 or up to 400. The R¹ group preferably has a molecular weight (Mn) of at least 50, at least 100 or at least 150. The R¹ preferably has a molecular weight (Mn) in the range of from 50 to 500, preferably from 100 to 400 or from 150 to 350.

In some embodiments, the R¹ group is a hydrocarbyl group. The term "hydrocarbyl" as used herein denotes a group having a carbon atom directly attached to the remainder of the molecule and having a predominantly aliphatic hydrocarbon character. Suitable hydrocarbyl based groups may contain non-hydrocarbon moieties. For example, they may contain up to one non-hydrocarbyl group for every ten carbon atoms provided this non-hydrocarbyl group does not significantly alter the predominantly hydrocarbon character of the group. Those skilled in the art will be aware of such groups, which include for example hydroxyl, oxygen, halo (especially chloro and fluoro), alkoxyl, alkyl mercapto, alkyl sulphony, etc. Preferred hydrocarbyl based substituents are purely aliphatic hydrocarbon in character and do not contain such groups.

The hydrocarbyl-based substituents are preferably predominantly saturated, that is, they contain no more than one carbon-to-carbon unsaturated bond for every ten carbon-to-carbon single bonds present.

The hydrocarbyl group preferably comprises at least 10 carbon atoms, more preferably at least 14 carbon atoms or at least 18 carbon atoms. Preferably the hydrocarbyl group comprises up to 30 carbon atoms, preferably up to 28 carbon atoms or up to 26 carbon atoms. The hydrocarbyl group may comprise from 10 to 30 carbon atoms, from 14 to 26 carbon atoms, from 18 to 26 carbon atoms or more preferably from 20 to 24 carbon atoms.

The hydrocarbyl substituent may be a mixture of hydrocarbyl groups having the above range of carbon atoms, on average. Therefore the molecular weight of the hydrocarbyl group is suitably defined as a number average molecular weight (Mn). The hydrocarbyl group preferably has an Mn
5 of from 50 to 500, preferably from 100 to 400 or from 150 to 350.

The skilled person would be familiar with standard techniques to measure number average molecular weight, such as by vapor pressure osmometry, end-group titration, proton NMR, boiling point elevation, freezing depression (cryoscopy), and GPC (gel permeation chromatography).
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The hydrocarbyl substituent may be an olefin having the number of carbons and/or Mn described above.

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-monoolefins. The hydrocarbyl substituent may also be derived from the halogenated (e.g. chlorinated or brominated) analogs of such homo- or interpolymers. Alternatively the substituent may be made from other sources, for example monomeric high molecular weight alkenes (e.g. 1-tetra-contene) and chlorinated analogs and hydrochlorinated analogs thereof, aliphatic petroleum fractions, for example paraffin waxes and cracked and chlorinated analogues and hydrochlorinated analogues 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
20 known in the art.
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The hydrocarbyl substituent may be a polyisobutene, preferably having the number of carbons and/or the Mn described above. Conventional polyisobutenes and so-called "highly-reactive" polyisobutenes are suitable for use in the invention. Highly reactive polyisobutenes in this context
30 are defined as polyisobutenes wherein at least 50%, preferably 70% or more, of the terminal olefinic double bonds are of the vinylidene type as described in EP0565285. Particularly preferred polyisobutenes are those having more than 80 mol% and up to 100% of terminal vinylidene groups such as those described in EP1344785.

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

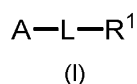
An internal olefin as used herein means any olefin containing predominantly a non-alpha double bond, that is a beta or higher olefin. Preferably such materials are substantially completely beta or
40 higher olefins, for example containing less than 10% by weight alpha olefin, more preferably less

than 5% by weight or less than 2% by weight. Typical internal olefins include Neodene 1518 IO available from Shell.

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

The reaction of the hydrocarbyl substituted reagent a) and the nitrogen-containing reagent b) preferably forms a linking group L between the nitrogen-containing group A and the hydrocarbyl group R¹. The L group may be a bond, an amine, an amide, a succinimide, a succinic acid or an amide of a succinic acid.

The nitrogen-containing compound which is the reaction product of a) a hydrocarbyl substituted reagent and b) a nitrogen-containing reagent, suitably has the formula (I):



wherein:

A is a nitrogen-containing group;
L is either a bond or a linker group; and
R¹ is an optionally substituted alkyl, alkenyl or aminoalkyl group having a molecular weight (Mn) of up to 1,000. The groups A, L and R¹ are preferably as defined above.

Therefore the nitrogen-containing compound used in the first and second aspects of the present invention is preferably of formula (I).

In some embodiments, the nitrogen-containing compound is the reaction product of a) a hydrocarbyl substituted reagent and b) a nitrogen-containing reagent, wherein a) is a hydrocarbyl substituted carboxylic acid acylating agent.

Therefore in such embodiments, the nitrogen-containing compound is preferably a reaction product of:

a) a hydrocarbyl substituted carboxylic acid acylating agent; and
b) a nitrogen-containing reagent.

In such embodiments, the linking group L between the hydrocarbyl group R¹ and the nitrogen-containing group A is provided by an amide of a succinic acid or succinic acid derivative, as further described below.

- 5 Suitably component a) comprises the group R¹ as defined above. Suitably the component a) comprises a hydrocarbyl group as defined above, preferably a polyisobutylene or an alkene group as defined above.

Component a) suitably has the formula (al):



wherein R¹ is an optionally substituted alkyl, alkenyl or aminoalkyl group having a molecular weight (Mn) of up to 1,000.

- 15 R¹ is preferably a hydrocarbyl group as discussed above, preferably having from 18 to 26 carbon atoms and/or an Mn of from 100 to 400.

R¹ may be a polyisobutylene group or an internal olefin group having from 18 to 26 carbon atoms and/or an Mn of from 100 to 400.

- 20 In some embodiments, component a) is a polyisobutenyl succinic anhydride. These compounds are commonly referred to as "PIBSAs" and are known to the person skilled in the art. Suitably the polyisobutylene group of the PIBSA is as defined above.

- 25 The PIBSA may be prepared by reacting a suitable polyisobutene with maleic anhydride.

- The preparation of polyisobutenyl substituted succinic anhydrides (PIBSA) is documented in the art. Suitable processes include thermally reacting polyisobutenes with maleic anhydride (see for example US-A-3,361,673 and US-A-3,018,250), and reacting a halogenated, in particular, a chlorinated, polyisobutene (PIB) with maleic anhydride (see for example US-A-3,172,892). Alternatively, the polyisobutenyl succinic anhydride can be prepared by mixing the polyolefin with maleic anhydride and passing chlorine through the mixture (see for example GB-A-949,981).
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In some embodiments, component a) is PIB having an Mn from 250-270.

- 35 In some embodiments, component a) is an alkenyl succinic anhydride. These compounds are commonly referred to as "ASAs" and are known to the person skilled in the art. Suitably the alkene

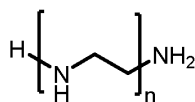
group of the ASA is as defined above. Preferably the ASA is a C16 to C18 alkenyl succinic anhydride (ASA), for example Pentasize 68.

The reaction of component a) with component b) suitably forms an amide bond, an imide bond or a mixture thereof.

Component b) preferably contains a reactive amino group or a reactive nitrogen which is part of a nitrogen-containing heterocyclic compound.

- 10 In some embodiments, component b) comprises a nitrogen-containing heterocycle, preferably selected from an optionally substituted piperazine, pyridine, pyrazine, pyridazine, pyrimidine, triazine, quinoline, isoquinoline, quinazoline, 2-aminoimidazoline, 5-phenyl-2-aminoimidazoline, 5-methyl-2-aminoimidazole, 5-amino-indazole, 6-aminoindazole, 2-aminobenzimidazole, a five-membered heterocyclic ring or a benzo-fused five-membered heterocyclic ring. Preferably component b)
- 15 comprises a five-membered heterocyclic ring such as pyrazole or imidazole, a benzo-fused five membered heterocyclic ring such as benzimidazole, an amino substituted five-membered heterocyclic ring or an amino substituted benzo-fused five membered heterocyclic ring. Preferably component b) comprises a benzotriazole, an indazole, a triazole or a tetrazole. Component b) may be selected from an optionally substituted benzotriazole, amino-benzotriazole, indazole, amino-
- 20 indazole, triazole, amino-triazole, tetrazole or amino-tetrazole.

In some embodiments, component b) comprises an amine or polyamine compound. Suitably component b) is a polyamine. Suitably component b) has the formula (bl):



(bl)

- wherein n is from 1 to 10. The nitrogen-containing compound may be a mixture compounds having different n numbers in the "A" group. Therefore n is suitably an average value of the different n numbers present in the mixture. Therefore n may be a non-integer value, of from 1 to 10, i.e from
- 30 1.0 to 10.0. Preferably n is from 1 to 6, from 1 to 4 or from 1 to 3.

Component b) may be selected from ethylenediamine, diethylene triamine (DETA), triethylene tetramine (TETA) and tetraethylene pentamine (TEPA). Component b) may be selected from ethylenediamine, diethylene triamine (DETA) and triethylene tetramine (TETA).

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Preferably, the nitrogen-containing compound is a reaction product of:

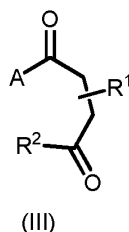
a) a polyisobutenyl succinic anhydride or an alkenyl succinic anhydride; and

- b) a polyamine selected from ethylenediamine, diethylene triamine (DETA), triethylene tetramine (TETA) and tetraethylene pentamine (TEPA); or a nitrogen-containing heterocycle selected from an optionally substituted benzotriazole, amino-benzotriazole, indazole, amino-indazole, triazole, amino-triazole, tetrazole or amino-tetrazole.

In such embodiments, the nitrogen-containing compound formed by the reaction of a) and b) may have the structures described below, for example as the major component in a mixture of compounds produced by the reaction.

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The L group of the nitrogen-containing compound of formula (I) may be provided by an amide of a succinic acid or succinic acid derivative. In such embodiments, the nitrogen-containing compound formed from the reaction of a) and b) may have the formula (III):



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wherein:

A is the nitrogen-containing group;

R¹ is an optionally substituted alkyl, alkenyl or aminoalkyl group having a molecular weight (Mn) of up to 1,000; and

- 20 R² is OH, NH₂, OR⁴, OM, NHR⁴ or NR⁴R⁵, or is a bond to A, wherein M is a cation, preferably an alkali metal cation or an ammonium cation, and wherein R⁴ and R⁵ are independently selected from optionally substituted C1-6 alkyl or alkenyl groups. The R⁴ and R⁵ may independently comprise a quaternary ammonium group.

- 25 Therefore in some embodiments the nitrogen-containing compound used in the first and second aspects of the present invention is preferably of formula (III).

In some preferred embodiments, R² is OH and therefore the L group is an amide of succinic acid.

- 30 The R¹ solubilising group may be bonded to either of the carbon atoms between the acid and amide groups. The nitrogen-containing compound may be a mixture of isomers which differ in the position of the R¹ group.

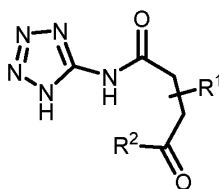
- In such embodiments, R¹ is preferably a hydrocarbyl group as discussed above, preferably having from 18 to 26 carbon atoms and/or an Mn of from 100 to 400.

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In such embodiments, R¹ may be a polyisobutylene group or an internal olefin group having from 18 to 26 carbon atoms and/or an Mn of from 100 to 400.

In some embodiments of the nitrogen-containing compounds of formula (III), the nitrogen-containing group A may be selected from optionally substituted piperazine, pyridine, pyrazine, pyridazine, pyrimidine, triazine, quinoline, isoquinoline, quinazoline, a five-membered heterocyclic ring such as pyrazole or imidazole or a benzo-fused five-membered heterocyclic ring such as benzimidazole, and derivatives thereof. Preferably the A group is selected from an optionally substituted five-membered heterocyclic ring or a benzo-fused five membered heterocyclic ring, or derivatives thereof. Preferably the A group is an optionally substituted benzotriazole, an indazole, a triazole or a tetrazole.

In such embodiments, the A group is suitably a tetrazole. Therefore the nitrogen-containing compound preferably may have the formula (IV):



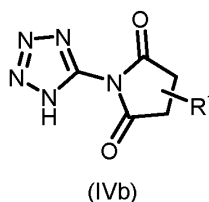
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(IV)

wherein R¹ and R² are as defined above.

In such embodiments, the compound of formula (IV) may also be present in an imide form having the formula (IVb):

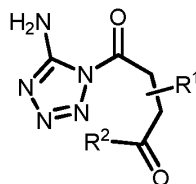
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(IVb)

In such embodiments, the nitrogen-containing compound may have the formula (IVc), which is an isomer of formula (IV):

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(IVc)

wherein R¹ and R² are as defined above.

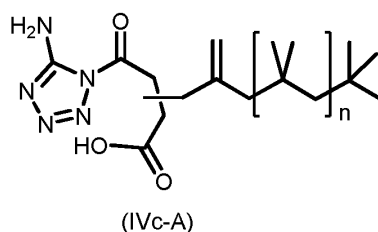
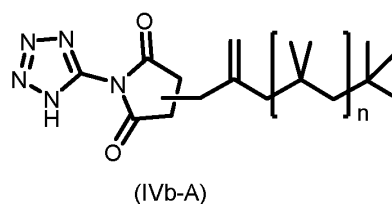
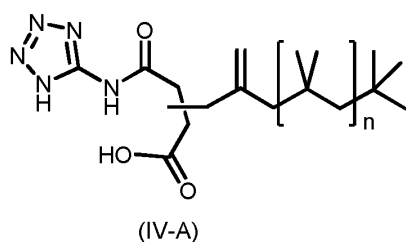
In such embodiments the nitrogen-containing compound may be a mixture of compounds of formulas (IV), (IVb) and (IVc).

In such embodiments, R^2 is preferably OH or O^-X^+ wherein X is a cation, for example a metal cation of an ammonium ion.

In such embodiments, R^1 is preferably a hydrocarbyl group having an Mn of from 100 to 500, preferably from 150 to 350 or from 200 to 300.

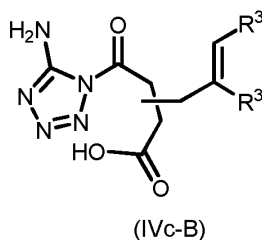
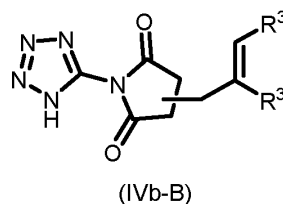
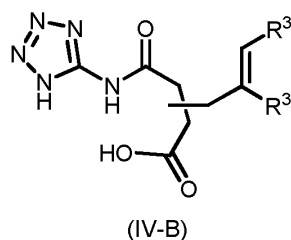
For example, R^1 may be a polyisobutylene or an alkene, having an Mn of from 100 to 500, preferably from 150 to 350 or from 200 to 300.

In some embodiments, R^1 is a polyisobutylene group and therefore the nitrogen-containing compound has the formula (IV-A), (IVb-A) or (IVc-A), or a mixture thereof:



wherein n is from 1 to 3. The nitrogen-containing compound may be a mixture compounds having different n numbers in the polyisobutylene group. Therefore n is suitably an average value of the different n numbers present in the mixture. Therefore n may be a non-integer value, of from 1 to 3, i.e. from 1.0 to 3.0.

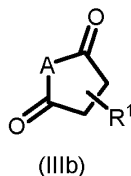
In some embodiments, R^1 is a C10-24 alkene group, preferably a C12-22 alkene group or a C16-18 alkene group. In such embodiments, the nitrogen-containing compound may have the formula (IV-B), (IVb-B) or (IVc-B), or a mixture thereof:



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wherein each R^3 is an alkyl group and are independently selected to provide the R^1 group having from 12 to 22 carbon atoms.

10 In some embodiments of the nitrogen-containing compounds of formula (III), the A group is a non-cyclic nitrogen-containing group as described above, for example an amine or a polyamine group. In such embodiments, the major component of the nitrogen-containing compound may be a cyclic imide wherein R^2 is a bond with the A group, suitably with an amine group of the A group. Therefore the nitrogen-containing compound may have the formula (IIIb)

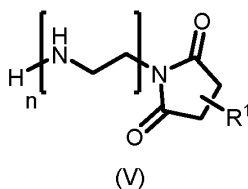


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wherein R^1 is as defined above.

In such embodiments, the A group may be a polyethyleneimine. Therefore the nitrogen-containing compound may have the formula (V):

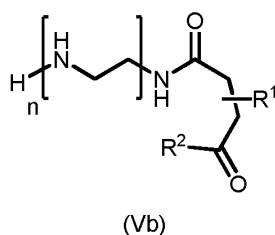
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25 wherein n is from 1 to 10. The nitrogen-containing compound may be a mixture compounds having different n numbers in the "A" group. Therefore n is suitably an average value of the different n

numbers present in the mixture. Therefore n may be a non-integer value, of from 1 to 10, i.e from 1.0 to 10.0. Preferably n is from 1 to 6, from 1 to 4 or from 1 to 3.

In such embodiments, the nitrogen-containing compound may comprise some of the ring-opened analogue having the formula (Vb):



- 10 wherein R^2 is preferably OH or O^-X^+ wherein X is a cation, for example a metal cation or an ammonium ion.

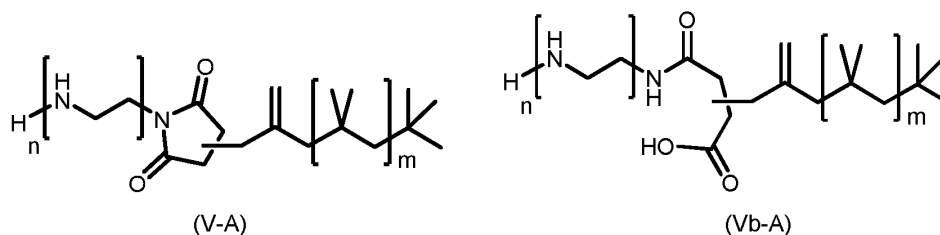
In such embodiments of the compounds of formula (V) and/or (Vb), R^1 is preferably a hydrocarbyl group having an M_n of from 100 to 500, preferably from 150 to 350 or from 200 to 300.

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For example, R^1 may be a polyisobutylene or an alkene, having an M_n of from 100 to 500, preferably from 150 to 350 or from 200 to 300.

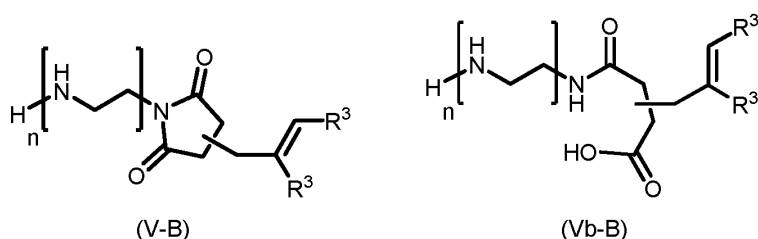
In some embodiments, R^1 is a polyisobutylene group and therefore the nitrogen-containing compound has the formula (V-A) and/or (Vb-A):

20



- 25 wherein n is from 1 to 10; and wherein m is from 1 to 3. Preferably n is from 1 to 4 or from 1 to 3. As noted above, n and m can be average values wherein a mixture of compounds comprising different n and m numbers are present. Therefore n and m may be non-integer values representing averages, such that n is from 1.0 to 10.0 and m is from 1.0 to 3.0.

- 30 In some embodiments, R^1 is a C10-24 alkene group, preferably a C12-22 alkene group or a C16-18 alkene group. Therefore the nitrogen-containing compound has the formula (V-B) and/or formula (Vb-B) or a mixture thereof:



- 5 wherein n is from 1 to 10 and may be a non-integer average value; and wherein each R³ is an alkyl group and are independently selected to provide the R¹ group having from 12 to 22 carbon atoms. Preferably n is from 1 to 4 or from 1 to 3.

In some embodiments of the invention, the nitrogen-containing compound is the reaction product of
 10 a) a hydrocarbyl substituted reagent and b) a nitrogen-containing reagent, wherein a) is an amine or polyamine comprising the hydrocarbyl group. In such embodiments, the nitrogen-containing compound may be the product of a Mannich reaction involving an aldehyde. Therefore the nitrogen-containing compound may be a reaction product of:

- 15 a) an amine or polyamine comprising a hydrocarbyl group;
 b) a nitrogen-containing reagent; and
 c) an aldehyde.

20

In such embodiments, the linking group L between the hydrocarbyl group R¹ and the nitrogen-containing group A is provided by a bond, as further described below.

- Suitably component a) comprises the group R¹ as defined above. Suitably the component a) is an
 25 alkylamine as defined above, preferably having the formula NHR⁷R⁸ wherein R⁷ and R⁸ are each independently selected from H, optionally substituted C1-20 alkyl groups or optionally substituted C1-20 alkenyl groups. Therefore component a) is preferably dialkylamine. Preferably R⁷ and R⁸ are each independently selected from C1-20 alkyl groups, preferably C2-20 alkyl groups. The alkyl groups may be branched, linear or cyclic alkyl groups. Preferably branched or linear alkyl groups.
 30 Preferably R⁷ and R⁸ are the same and are selected from C1-20 alkyl groups, preferably C2-20 alkyl groups.

Component a) may be selected from diethylamine, dipropylamine, dibutylamine, dipentylamine, dihexylamine, bis(2-ethylhexyl)amine or dicocoalkylamine.

35

Component b) is preferably a nitrogen-containing reagent comprising a nitrogen containing heterocycle. Preferably component b) is selected from an optionally substituted five-membered nitrogen-containing heterocyclic compound or a benzo-fused five-membered nitrogen-containing heterocyclic compound. Preferably component b) is selected from an optionally substituted triazole, tetrazole, indole, indazole or benzotriazole. Preferably component b) is selected from triazole, tetrazole, indole, indazole or benzotriazole, preferably triazole, tetrazole or benzotriazole.

Component c) is suitably an aliphatic aldehyde. Preferably the aldehyde has 1 to 10 carbon atoms. Most preferably the aldehyde is formaldehyde or a source of formaldehyde.

10

In preferred embodiments, the nitrogen-containing compound is the reaction product of:

a) an alkylamine having the formula NHR^7R^8 wherein R^7 and R^8 are each independently selected from H, optionally substituted C1-20 alkyl groups or optionally substituted C1-20 alkenyl groups;

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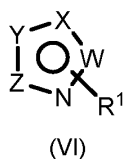
b) a nitrogen-containing reagent selected from an optionally substituted triazole, tetrazole, indole, indazole or benzotriazole, and.

c) formaldehyde or a source of formaldehyde.

20

In such embodiments, the nitrogen-containing compound formed by the reaction of a), b) and c) may have the structures described below, for example as the major component in a mixture of compounds produced by the reaction.

In some embodiments of the invention, the nitrogen-containing compound of formula (I), L may be a bond. In such embodiments, the nitrogen-containing compound may have the formula (VI):



wherein:

R^1 is an optionally substituted alkyl, alkenyl or aminoalkyl group having a molecular weight (Mn) of up to 1,000;

W, X, Y and Z are each independently selected from CH, C, N, NH, S and SH, which are optionally substituted where appropriate; and

wherein the compound optionally comprises a cycloalkyl or aryl ring linking Y and Z.

35

Therefore in some embodiments the nitrogen-containing compound used in the first and second aspects of the present invention are preferably of formula (VI).

The R¹ solubilising group may be bonded to any suitable atoms of the nitrogen-containing heterocyclic group. The nitrogen-containing compound may be a mixture of isomers which differ in the position of the R¹ group. Preferably the R¹ is bonded to a nitrogen of the nitrogen-containing heterocyclic group.

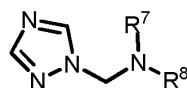
5

In such embodiments, R¹ is preferably an aminoalkyl group having a molecular weight (Mn) of up to 1,000. The aminoalkyl group preferably has a molecular weight (Mn) of from 50 to 500, preferably from 50 to 350 or from 50 to 300.

- 10 R¹ may have the formula -CH₂NR⁷R⁸ wherein R⁷ and R⁸ are each independently selected from H, optionally substituted C1-20 alkyl groups or optionally substituted C1-20 alkenyl groups. Preferably R⁷ and R⁸ are each independently selected from C1-20 alkyl groups, preferably C2-20 alkyl groups. The alkyl groups may be branched or linear alkyl groups. Preferably R⁷ and R⁸ are the same and are selected from C1-20 alkyl groups, preferably C2-20 alkyl groups. In some embodiments, R⁷ and R⁸
- 15 are each independently selected from C1-12 alkyl groups, preferably from C2-10 alkyl groups.

In some embodiments of the nitrogen-containing compound of formula (VI), the heterocyclic group is an optionally substituted five-membered nitrogen-containing heterocycle. In such embodiments, W, X, Y and Z are each independently selected from CH, C, N and NH. In such embodiments, the

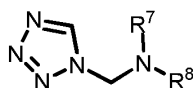
20 heterocyclic group is preferably selected from an optionally substituted triazole or tetrazole. For example, the nitrogen-containing compound may have the formula (VII):



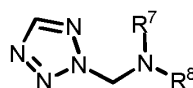
(VII)

- 25 wherein R⁷ and R⁸ are each independently selected from optionally substituted C1-20 alkyl groups, preferably optionally substituted C2-20 alkyl groups. In some embodiments, R⁷ and R⁸ are each independently selected from optionally substituted C1-12 alkyl groups, preferably from optionally substituted C2-10 alkyl groups.

- 30 The nitrogen-containing compound may have the formula (VIII) and/or (VIIIb) or a mixture thereof:



(VIIIa)

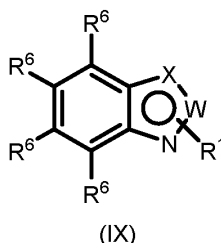


(VIIIb)

wherein R⁷ and R⁸ are each independently selected from C1-20 alkyl groups, preferably C2-20 alkyl

35 groups. The nitrogen-containing compound may be a mixture of such compounds. For example, the nitrogen-containing compound may be a mixture of compounds of formula (VIII) and (VIIIb) in a ratio of from 1:10 to 10:1, suitably from 1:5 to 5:1,

In some embodiments of the nitrogen-containing compound of formula (VI), the heterocyclic group is an optionally substituted benzo-fused five-membered nitrogen-containing heterocycle. In such embodiments, the nitrogen-containing compound has the formula (IX):



wherein:

R¹ is an optionally substituted alkyl, alkenyl or aminoalkyl group having a molecular weight (Mn) of up to 1,000;

- 10 W and X are each independently selected from C and N; and
each R⁶ is independently selected from H, C1-6 alkyl or C1-6 alkenyl.

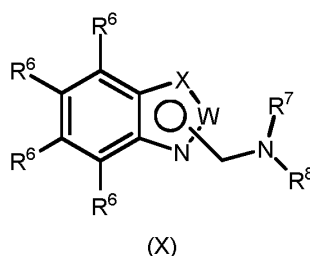
Preferably each R⁶ is H.

- 15 In such embodiments, R¹ is preferably an aminoalkyl group having a molecular weight (Mn) of up to 1,000. The aminoalkyl group preferably has a molecular weight (Mn) of from 50 to 500, preferably from 50 to 350 or from 50 to 300.

- As described above, R¹ preferably has the formula -CH₂NR⁷R⁸ wherein R⁷ and R⁸ are each
20 independently selected from H, optionally substituted C1-20 alkyl groups or optionally substituted C1-20 alkenyl groups. Preferably R⁷ and R⁸ are each independently selected from C1-20 alkyl groups, preferably C2-20 alkyl groups. The alkyl groups may be branched, linear or cyclic alkyl groups. Preferably branched or linear alkyl groups. Preferably R⁷ and R⁸ are the same and are selected from C1-20 alkyl groups, preferably C2-20 alkyl groups.

25

Therefore the nitrogen-containing compound may have the formula (X):

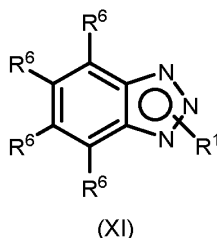


- 30 wherein:

W and X are each independently selected from C and N;

each R^6 is independently selected from H, C1-6 alkyl or C1-6 alkenyl; and
 R^7 and R^8 are each independently selected from C1-20 alkyl groups, preferably C2-20 alkyl groups.

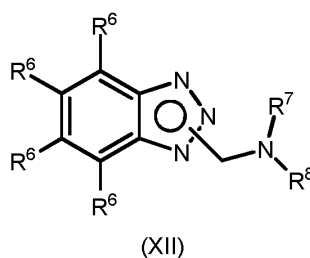
In some embodiments, the nitrogen-containing heterocycle is an optionally substituted benzo-triazole and the nitrogen compound has the formula (XI):



wherein:

R^1 is an optionally substituted alkyl, alkenyl or aminoalkyl group having a molecular weight (M_n) of up to 1,000; and
 each R^6 is independently selected from H, C1-6 alkyl or C1-6 alkenyl.

In a preferred embodiment, the nitrogen compound has the formula (XII):



wherein:

each R^6 is independently selected from H, C1-6 alkyl or C1-6 alkenyl; and
 R^7 and R^8 are each independently selected from C1-20 alkyl groups, preferably C2-20 alkyl groups.

The nitrogen-containing compound used in the first and second aspects of the present invention may be present in an additive composition. The additive composition may contain other components in addition to the nitrogen-containing compound or compounds. For example, the additive composition may comprise solvents and/or other fuel additives, as further described below.

Therefore the present invention may provide the use of an additive composition comprising a nitrogen-containing compound as an additive in a diesel fuel composition to reduce the impact of deposits in the EGR system of a diesel engine when combusting said diesel fuel composition, wherein the nitrogen-containing compound comprises at least 4% by mass of nitrogen atoms.

Similarly, the present invention may provide a method of reducing the impact of deposits in the EGR system of a diesel engine, the method comprising combusting in the engine a diesel fuel composition comprising an additive composition, wherein the additive composition comprises a nitrogen-containing compound comprising at least 4% by mass of nitrogen atoms.

5

Preferably the additive composition comprises at least 20 wt% of the nitrogen-containing compound, preferably at least 30 wt% or at least 45 wt% of the nitrogen-containing compound.

10 In such embodiments, it may be convenient to refer to the % by mass of nitrogen atoms of the whole additive composition. The majority of the nitrogen content of the additive composition is suitably provided by the nitrogen-containing compound. Preferably the additive composition comprises at least 5% by mass of nitrogen atoms, preferably at least 6% or at least 7%.

15 Suitably the additive composition comprises up to 35% by mass of nitrogen atoms, suitably up to 30% or up to 25%.

In preferred embodiments, the additive composition comprises from 4 to 35% by mass of nitrogen atoms, suitably from 5 to 30% or from 6 to 25%.

20 In such embodiments, the additive composition may be a direct product of the reaction used to form the nitrogen-containing compound. Such a direct product may comprise other components as a result of the reaction used to form the nitrogen-containing compound. The additive composition may therefore comprise solvent, for example relatively low volatility solvents, by-products of the reaction, unreacted starting materials and isomers or analogues of the nitrogen-containing compound formed
25 in the reaction. The reaction may be as described above, i.e. the reaction of components a) and b) or the reaction of components a), b) and c).

In some embodiments, the additive composition may contain additional components which are added subsequently to the reaction which forms the nitrogen-containing compound. For example, the
30 additive composition may comprise additional solvents or additional fuel additives, as described in more detail below.

In summary, the nitrogen-containing compound, or compounds used in the first and second aspects of the present invention is preferably the reaction product of:

35

a) hydrocarbyl substituted carboxylic acid acylating agent; and

b) a nitrogen-containing reagent;

40 or is the reaction product of:

a) an amine or polyamine comprising a hydrocarbyl group;

b) a nitrogen-containing reagent; and

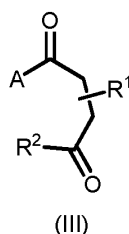
c) an aldehyde.

The nitrogen-containing compound used in the first and second aspects of the present invention is preferably the reaction product of:

a) hydrocarbyl substituted carboxylic acid acylating agent; and

b) a nitrogen-containing reagent;

having the formula (III):



wherein:

R^1 is an optionally substituted alkyl, alkenyl or aminoalkyl group having a molecular weight (Mn) of up to 1,000; and

R^2 is OH, NH_2 , OR^4 , OM, NHR^4 or NR^4R^5 , or is a bond to A, wherein M is a cation, preferably an alkali metal cation or an ammonium cation, and wherein R^4 and R^5 are independently selected from optionally substituted C1-6 alkyl or alkenyl groups and may independently comprise a quaternary ammonium group;

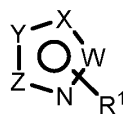
or is the reaction product of:

a) an amine or polyamine comprising a hydrocarbyl group;

b) a nitrogen-containing reagent; and

c) an aldehyde;

having the formula (VI):



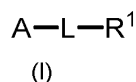
(VI)

wherein:

5 R^1 is an optionally substituted alkyl, alkenyl or aminoalkyl group having a molecular weight (Mn) of up to 1,000;

W, X, Y and Z are each independently selected from CH, C, N, NH, S and SH; and
wherein the compound optionally comprises a cycloalkyl or aryl ring linking Y and Z.

10 The nitrogen-containing compound used in the first and second aspects of the present invention suitably has the formula (I):



wherein:

A is a nitrogen-containing group;

15 L is either a bond or a linker group; and

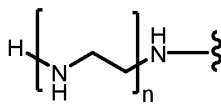
R^1 is an optionally substituted alkyl, alkenyl or aminoalkyl group having a molecular weight (Mn) of up to 1,000;

wherein A is selected from:

20

1) an optionally substituted piperazine, pyridine, pyrazine, pyridazine, pyrimidine, triazine, quinoline, isoquinoline, quinazoline, a five-membered heterocyclic ring such as pyrazole or imidazole or a benzo-fused five-membered heterocyclic ring such as benzimidazole; or

25 2) a non-cyclic nitrogen-containing group having the formula (II):

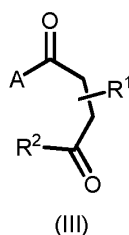


(II)

wherein n is from 1 to 10.

30

The nitrogen-containing compound used in the first and second aspects of the present invention preferably has the formula (III):

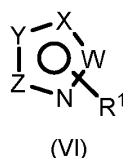


wherein:

5 R^1 is an optionally substituted alkyl, alkenyl or aminoalkyl group having a molecular weight (Mn) of up to 1,000; and

R^2 is OH, NH₂, OR⁴, OM, NHR⁴ or NR⁴R⁵, or is a bond to A, wherein M is a cation, preferably an alkali metal cation or an ammonium cation, and wherein R⁴ and R⁵ are independently selected from optionally substituted C1-6 alkyl or alkenyl groups and R⁴ and R⁵ may
10 independently comprise a quaternary ammonium group;

or has the formula (VI):



15 wherein:

R^1 is an optionally substituted alkyl, alkenyl or aminoalkyl group having a molecular weight (Mn) of up to 1,000;

W, X, Y and Z are each independently selected from CH, C, N, NH, S and SH; and
20 wherein the compound optionally comprises a cycloalkyl or aryl ring linking Y and Z.

Suitably the nitrogen-containing compound is present in the diesel fuel composition in an amount of at least 1ppm, preferably at least 10 ppm, more preferably at least 20 ppm, suitably at least 30 ppm, preferably at least 40 ppm, for example at least 50ppm or at least 60 ppm.

25 Suitably the nitrogen-containing compound is present in the diesel fuel composition in an amount of up to 10000 ppm, preferably up to 9000 ppm, suitably up to 8000 ppm, for example up to 7000 ppm.

In some preferred embodiments the nitrogen-containing compound is present in the diesel fuel composition in an amount of less than 1000 ppm, preferably less than 700 ppm, more preferably less
30 than 500 ppm, suitably less than 400 ppm, for example less than 350 ppm or less than 300ppm.

In some embodiments the nitrogen-containing compound is present in the diesel fuel composition in an amount of from 50 to 6000 ppm.

In some embodiments the nitrogen-containing compound is present in the diesel fuel composition in an amount of from 50 to 3000 ppm, more preferably from 50 to 2000 ppm.

5 In some embodiments the nitrogen-containing compound is present in the diesel fuel composition in an amount of from 50 to 750 ppm.

Preferably the nitrogen-containing compound is present in the diesel fuel composition in an amount of from 50 to 350 ppm.

10 In some especially preferred embodiments the nitrogen-containing compound is present in the diesel fuel composition in an amount of from 50 to 300 ppm.

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

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

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

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,
30 industrial fuel oil, etc.

The diesel fuel composition used in 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
35 distillate, cracked gas oil, or a blend in any proportion of straight run and refinery streams such as thermally and/or catalytically cracked and hydro-cracked distillates.

The diesel fuel composition 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).

40

The diesel fuel composition may comprise a renewable fuel such as a biofuel composition or biodiesel composition.

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

10 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, using, for example, hydroprocessing such as the H-Bio process developed by Petrobras. Second generation biodiesel may be similar in properties and quality to petroleum based
15 fuel oil streams, for example renewable diesel produced from vegetable oils, animal fats etc. and marketed by ConocoPhillips as Renewable Diesel and by Neste as NExBTL.

The diesel fuel composition may comprise third generation biodiesel. Third generation biodiesel utilises gasification and Fischer-Tropsch technology including those described as BTL (biomass-to-
20 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.

In some embodiments the diesel fuel composition may comprise a pyrolysis oil, for example a plastic
25 pyrolysis oil or a biomass (wood, vegetable oil, algae) pyrolysis oil.

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

In some embodiments the diesel fuel composition 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
30 to 2%, up to 3%, up to 4%, up to 5%, up to 10%, up to 20%, up to 30%, up to 40%, up to 50%, up to 60%, up to 70%, up to 80%, up to 90%, up to 95% or up to 99%.

In some embodiments the fuel composition may comprise neat biodiesel.

35 In some preferred embodiments the fuel composition comprises at least 5 wt% biodiesel.

In some embodiments the fuel composition may comprise GTL fuel or be a neat GTL fuel.

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

The diesel fuel composition used in 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%.

- 5 However, in preferred embodiments the diesel fuel composition 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.
- 10 The diesel fuel composition used in the present invention preferably comprises at least 5 wt% biodiesel and less than 50 ppm sulphur.

- Various metal species may be present in the diesel fuel composition. This may be due to contamination of the fuel during manufacture, storage, transport or use or due to contamination of
- 15 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.

- Other metal-containing species may also be present as a contaminant, for example through the
- 20 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; Group I or Group II metals and other metals such as lead.

- 25 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. The presence of such catalysts may also give rise to injector
- 30 deposits when the fuels are used in diesel engines having high pressure EGR systems.

- 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
- 35 compounds or complexes or colloidal species.

- 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.

- 40

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.

5

The diesel fuel compositions 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, 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.

10

Suitable cetane number improvers may be selected from C2-24 alkyl nitrates and dialkyl peroxides, preferably decyl nitrate, 2-ethylhexyl nitrate and di-tert-butyl peroxides. Such cetane number improvers are suitably used at a concentration of 50-6,000 ppm, preferably at 50-750 ppm based on the diesel fuel composition.

15

In some preferred embodiments the diesel fuel composition of the present invention comprises one or more detergents. Nitrogen-containing detergents are preferred.

20

The one or more detergents may be selected from:

25

- (i) a quaternary ammonium salt additive;
- (ii) the product of a Mannich reaction between an aldehyde, an amine and an optionally substituted phenol;
- (iii) the reaction product of a carboxylic acid-derived acylating agent and an amine;
- (iv) the reaction product of a carboxylic acid-derived acylating agent and hydrazine;
- (v) a salt formed by the reaction of a carboxylic acid with di-n-butylamine or tri-n-butylamine;
- (vi) 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
- (vii) a substituted polyaromatic detergent additive.

30

35

40 Preferably one or more detergents are selected from one or more of:

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

The ratio of the nitrogen-containing compound to the detergent is suitably from 5:1 to 1:5, preferably from 2:1 to 1:2.

In some embodiments the diesel fuel composition further comprises (i) a quaternary ammonium salt additive.

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

The nitrogen containing species may be selected from:

- (x) the reaction product of a hydrocarbyl-substituted acylating agent and a compound comprising at least one tertiary amine group and a primary amine, secondary amine or alcohol group;
- (y) a Mannich reaction product comprising a tertiary amine group; and
- (z) a polyalkylene substituted amine having at least one tertiary amine group.

Examples of quaternary ammonium salt and methods for preparing the same are described in the following patents, which are hereby incorporated by reference, US2008/0307698, US2008/0052985, US2008/0113890 and US2013/031827.

The preparation of some suitable quaternary ammonium salt additives in which the nitrogen-containing species includes component (x) is described in WO 2006/135881 and WO2011/095819.

Component (y) is a Mannich reaction product having a tertiary amine. The preparation of quaternary ammonium salts formed from nitrogen-containing species including component (y) is described in US 2008/0052985.

The preparation of quaternary ammonium salt additives in which the nitrogen-containing species includes component (z) is described for example in US 2008/0113890.

To form the quaternary ammonium salt additive (i) the nitrogen-containing species having a tertiary amine group is reacted with a quaternising agent.

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

5

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

10 An especially preferred additional 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 number average molecular weight of 700 to 1300 and dimethylaminopropylamine.

15 Other suitable quaternary ammonium salts include quaternised terpolymers, for example as described in US2011/0258917; quaternised copolymers, for example as described in US2011/0315107; and the acid-free quaternised nitrogen compounds disclosed in US2012/0010112.

Further suitable quaternary ammonium compounds for use in the present invention include the
20 quaternary ammonium compounds described in the applicants copending applications WO2011/095819, WO2013/017889, WO2015/011506, WO2015/011507, WO2016/016641 and PCT/GB2016/052312.

In some embodiments the diesel fuel composition used in the present invention comprises from 1 to
25 500 ppm, preferably 50 to 250 ppm of the quaternary ammonium salt additive (i).

In some embodiments the diesel fuel composition further comprises (ii) the product of a Mannich reaction between an aldehyde, an amine and an optionally substituted phenol. This Mannich reaction product is suitably not a quaternary ammonium salt.

30

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

Suitable amines for use in preparing the Mannich additive include monoamines and polyamines.

35 One suitable monoamine is butylamine.

The amine used to prepare the Mannich additive is preferably a polyamine. This may be selected from any compound including two or more amine groups. Preferably the polyamine is a polyalkylene polyamine, preferably a polyethylene polyamine. Most preferably the polyamine comprises
40 tetraethylenepentamine or ethylenediamine.

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

10

In some embodiments the diesel fuel composition of the present invention comprises from 1 to 500 ppm, preferably 50 to 250 ppm of a Mannich additive (ii).

In some embodiments the diesel fuel composition further comprises (iii) the reaction product of a carboxylic acid-derived acylating agent and an amine.

15

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

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

20

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.

25

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

30

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

A preferred acylated nitrogen-containing compound for use herein is prepared by reacting a poly(isobutene)-substituted succinic acid-derived acylating agent (e.g., anhydride, acid, ester, etc.) wherein the poly(isobutene) substituent has a number average molecular weight (M_n) of between 170 to 2800 with a mixture of ethylene polyamines having 2 to about 9 amino nitrogen atoms, preferably about 2 to about 8 nitrogen atoms, per ethylene polyamine and about 1 to about 8 ethylene groups. These acylated nitrogen compounds are suitably formed by the reaction of a molar ratio of acylating agent:amino compound of from 10:1 to 1:10, preferably from 5:1 to 1:5, more preferably

35

40

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 some embodiments the diesel fuel composition of the present invention comprises from 1 to 500 ppm, preferably 50 to 250ppm of an additive which is the reaction product of an acylating agents and an amine (iii).

In some embodiments the diesel fuel composition comprises (iv) the reaction product of a carboxylic acid-derived acylating agent and hydrazine.

Suitably the additive comprises the reaction product between a hydrocarbyl-substituted succinic acid or anhydride and hydrazine.

Preferably, the hydrocarbyl group of the hydrocarbyl-substituted succinic acid or anhydride comprises a C₈-C₃₆ group, preferably a C₈-C₁₈ group. Alternatively, the hydrocarbyl group may be a polyisobutylene group with a number average molecular weight of between 200 and 2500, preferably between 800 and 1200.

Hydrazine has the formula NH₂-NH₂. Hydrazine may be hydrated or non-hydrated. Hydrazine monohydrate is preferred.

The reaction between the hydrocarbyl-substituted succinic acid or anhydride and hydrazine produces a variety of products, such as is disclosed in US 2008/0060259.

In some embodiments the diesel fuel composition further comprises (v) a salt formed by the reaction of a carboxylic acid with di-n-butylamine or tri-n-butylamine. Exemplary compounds of this type are described in US 2008/0060608.

Such additives may suitably be the di-n-butylamine or tri-n-butylamine salt of a fatty acid of the formula [R'(COOH)_x]_y, where each R' is a independently a hydrocarbyl group of between 2 and 45 carbon atoms, and x is an integer between 1 and 4.

In a preferred embodiment, the carboxylic acid comprises tall oil fatty acid (TOFA).

Further preferred features of additives of this type are described in EP1900795.

- 5 In some embodiments the diesel fuel composition further comprises (vi) 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.

Further preferred features of additive compounds of this type are as defined in US2009/0282731.

- 10 In some embodiments the diesel fuel composition further comprises (vii) a substituted polyaromatic detergent additive.

One preferred compound of this type is the reaction product of an ethoxylated naphthol and paraformaldehyde which is then reacted with a hydrocarbyl substituted acylating agent.

15

Further preferred features of these detergents are described in EP1884556.

The present invention suitably reduces the formation of deposits in the EGR system of a diesel engine.

20

Most preferably the engine is a direct injection diesel engine.

The nitrogen-containing compounds used in the present invention have been found to be particularly effective in modern diesel engines having a high pressure fuel system.

25

Suitably the present invention may be used to reduce the formation or deposits in the EGR system of a diesel engine having a high pressure fuel system. Suitably the diesel engine has a fuel pressure in excess of 1350 bar (1.35×10^8 Pa). It may have a pressure of up to 2000 bar (2×10^8 Pa) or more.

- 30 Such diesel engines may be characterised in a number of ways.

Such engines are typically equipped with fuel injection equipment meeting or exceeding "Euro 5" emissions legislation or equivalent legislation in the US or other countries.

- 35 Such engines are typically equipped with fuel injectors having a plurality of apertures, each aperture having an inlet and an outlet.

Such engines may be characterised by apertures which are tapered such that the inlet diameter of the spray-holes is greater than the outlet diameter.

40

Such modern engines may be characterised by apertures having an outlet diameter of less than 500µm, preferably less than 200µm, more preferably less than 150µm, preferably less than 100µm, most preferably less than 80µm or less.

- 5 Such modern diesel engines may be characterised by apertures where an inner edge of the inlet is rounded.

Such modern diesel engines may be characterised by the injector having more than one aperture, suitably more than 2 apertures, preferably more than 4 apertures, for example 6 or more apertures.

10

Such modern diesel engines may be characterised by an operating tip temperature in excess of 250°C.

- 15 Such modern diesel engines may be characterised by a fuel injection system which provides a fuel pressure of more than 1350 bar, preferably more than 1500 bar, more preferably more than 2000 bar.

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

- 25 Preferably, the diesel engine has a fuel injection system which comprises a common rail injection system.

- 30 In common rail systems, the fuel is stored at high pressure in the central accumulator rail or separate accumulators prior to being delivered to the injectors. Often, some of the heated fuel is returned to the low pressure side of the fuel system or returned to the fuel tank. In unit injection systems the fuel is compressed within the injector in order to generate the high injection pressures. This in turn increases the temperature of the fuel.

- 35 In both systems, fuel is present in the injector body prior to injection where it is heated further due to heat from the combustion chamber. The temperature of the fuel at the tip of the injector can be as high as 250 - 350 °C.

- 40 Thus the fuel is stressed at pressures from 1350 bar (1.35×10^8 Pa) to over 2000 bar (2×10^8 Pa) and temperatures from around 100°C to 350°C prior to injection, sometimes being recirculated back within the fuel system thus increasing the time for which the fuel experiences these conditions.

The EGR system recirculates the exhaust gases to lower the oxygen concentration in the combustion chamber. This reduces the generation of NO_x gases.

- 5 The EGR system includes a cooler. This component lowers the temperature of the recirculated exhaust gases.

Exhaust gases enter the EGR system after they pass through or are generated within the combustion chamber. The exhaust gases may contain materials resulting from incomplete combustion. These materials may deposit within the EGR system. One component where deposit build up frequently occurs is in the cooler of the EGR system.

Previously these deposits have not been studied in the same level of detail as other fuel system or combustion deposits. Indeed the finding of such deposits appears to be a relatively recent phenomenon. Particularly strong reviews of the work done to elucidate how they may form and why they are a problem can be found in Lance *et al* International Journal of Heat and Mass Transfer 126, (2018), 509-520 and SAE 2014-01-0629.

The present inventors have studied the nature of the deposits found in the EGR system and in particular within the cooler. It has been surprisingly found that the formation of these deposits in particular can be reduced by the addition of the one or more nitrogen-containing compounds into the diesel fuel combusted in the engine.

The use of the first aspect and/or the method of the second aspect may involve reducing the impact of deposits in the exhaust gas recirculation system of a diesel engine which is a high pressure, low pressure, hybrid or dedicated EGR system. Suitably the exhaust gas recirculation system is a high pressure, hybrid or dedicated EGR system. Preferably the exhaust gas recirculation system is a high pressure system. The high pressure EGR may be either a stand-alone high pressure EGR system or part of a hybrid or a dedicated EGR system.

Preferably the use or method of the present invention reduces the formation of deposits in a high pressure EGR system of a diesel engine.

By reducing the formation of deposits in an EGR system we mean that when a fuel comprising the EGR deposit reducing additive is combusted in an engine, a reduced level of deposits is obtained compared to when an otherwise identical fuel is combusted under identical conditions except for the inclusion of the EGR deposit reducing additive.

Suitably addition of the one or more nitrogen-containing compounds into the diesel fuel combusted in an engine reduces the formation of deposits in an EGR system by at least 5%, preferably by at least 10%, for example at least 15% or at least 20%.

- 5 In some embodiments the addition of the one or more nitrogen-containing compounds into the diesel fuel combusted in an engine may reduce the formation of deposits in an EGR system by at least 30%, for example at least 40% or at least 50%.

- 10 Suitably addition of the one or more nitrogen-containing compounds into the diesel fuel combusted in an engine reduces the formation of deposits in the cooler an EGR system by at least 5%, preferably by at least 10%, for example at least 15% or at least 20%.

- 15 In some embodiments the addition of the one or more nitrogen-containing compounds into the diesel fuel combusted in an engine may reduce the formation of deposits in the cooler of an EGR system by at least 30%, for example at least 40% or at least 50%.

The reduction in deposits in an EGR system may be measured by any suitable means.

- 20 One simple means by which the level of deposits in an EGR system may be determined is by weighing the system before and after use. One or more parts of the system may be weighed.

- 25 Preferably the present invention reduces the total amount of deposits formed in an EGR system by at least 5%, preferably at least 10%, more preferably at least 15%, for example at least 20% or at least 30%.

Suitably the present invention reduces the total amount of deposits formed within the cooler of an EGR system.

- 30 Preferably the present invention reduces the total amount of deposits formed within the cooler of an EGR system by at least 5%, preferably at least 10%, more preferably at least 15%, for example at least 20% or at least 30%.

- 35 The deposits that form in the EGR system may be analysed. This may be achieved, for example by extracting the deposits or a portion thereof into a solvent. The sample may be separated into soluble and non soluble fractions; these may then be separately analysed by methods known to those skilled in the art, for example elemental analysis, thermogravimetric analysis and/or gas chromatography mass spectrometry.

- 40 The deposits that form in the EGR system may be analysed for example by thermogravimetric analysis (TGA). A significant proportion of the deposits that occur on the cooler of an EGR system

were found to be carbonaceous deposits that degrade at temperatures of between 400 to 540°C when subjected to thermogravimetric analysis (TGA).

Thermogravimetric analysis (or TGA) involves measuring the mass of a sample over time as it is heated. This technique is well known to the person skilled in the art and the selection of an appropriate method and suitable equipment will be within the competence of one skilled in the art.

Any feature of the invention may be combined with any other feature as appropriate.

According to a third aspect of the present invention, there is provided a fuel additive composition comprising one or more nitrogen-containing compounds and a detergent additive, wherein the nitrogen-containing compounds comprise at least 4% by mass of nitrogen atoms.

The nitrogen-containing compound of the fuel additive composition of this third aspect may have any of the suitable features and advantages described above in relation to the nitrogen-containing compound used in the first and second aspects.

The detergent additive is suitably as described above in relation to the first and second aspects.

According to a fourth aspect of the present invention, there is provided a diesel fuel composition comprising one or more nitrogen-containing compounds and a detergent additive, wherein the nitrogen-containing compounds comprise at least 4% by mass of nitrogen atoms.

The nitrogen-containing compound and detergent additive of this fourth aspect are as described above in relation to the first, second and third aspects of the present invention.

The diesel fuel composition of this fourth aspect may have any of the suitable features described above in relation to the first and second aspects.

The diesel fuel composition of this fourth aspect may comprise one or more further additives selected from antioxidants, 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.

In some embodiments of the fuel additive composition of the third aspect or the diesel fuel composition of the fourth aspect, the detergent additive is:

a reaction product of a carboxylic acid-derived acylating agent and an amine is the reaction product of tetraethylene pentamine (TEPA) and a PIBSA having a PIB number average molecular weight (M_n) of from 300 to 2800; or

- 5 a quaternary ammonium salt formed by reacting methyl salicylate or dimethyl oxalate with the reaction product of dimethylaminopropylamine and a polyisobutylene-substituted succinic anhydride having a PIB number average molecular weight (M_n) of 700 to 1300; or a mixture thereof.

The invention will now be further described with reference to the following non-limiting examples. In
10 the examples which follow the values given in parts per million (ppm) for treat rates denote active agent amount, not the amount of a formulation as added, and containing an active agent. All parts per million are by weight.

Examples

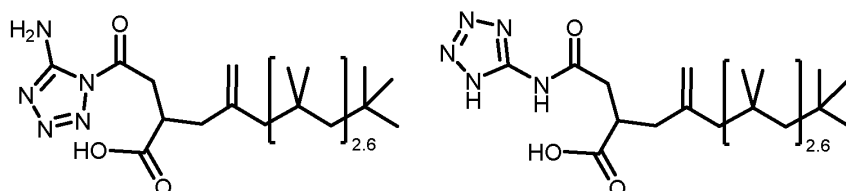
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Example nitrogen-containing compounds for use as additives in a diesel fuel composition according to the invention were prepared as follows.

Example 1 - PIB₂₆₀SA 5-amino-[1H]-tetrazole reaction product

20

Major components:



- 25 The nitrogen-containing compound of Example 1 was prepared as follows. Thermal reaction of a high-reactive grade of 260 number average highly reactive (HR) poly(isobutene) (PIB₂₆₀) with maleic anhydride (MA) provided a sample of poly(isobutene)succinic anhydride (PIB₂₆₀SA). The PIB₂₆₀SA was characterised in part by titration against lithium methoxide and found to have an activity of 2.38 mmol.g⁻¹.

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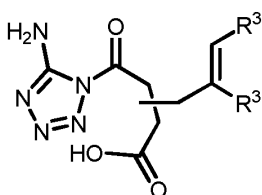
A reactor was charged with a sample (135.01 g, 321.3 mmol) of the PIB₂₆₀SA and Caromax20 solvent (162.3 g) and heated to 90°C. 5-amino-[1H]-tetrazole monohydrate (33.10 g, 321.1 mmol) was added and the flask contents were heated to above 100°C for an hour. Following this the temperature was increased to achieve an internal temperature of 170°C, facilitating the formation of the amide.

- 35 progress of the reaction was monitored using ATR-FTIR.

Nitrogen contents for three essentially identically prepared samples were determined by analysis using a Leco Flash 1112 series analyser and found to range from 6.45 to 6.53 wt%. The theoretical nitrogen content of the target compound is from 15.1 to 17.2 wt%.

5 Example 2 - C₁₆/C₁₈ ASA 5-amino-[1H]-tetrazole reaction product

Major components:



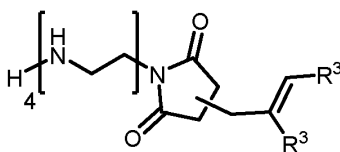
10 wherein the R³ groups sum to C₁₃H₂₈ or C₁₅H₃₂ or a mixture thereof.

The nitrogen-containing compound of Example 2 was prepared as follows. The activity of a sample of Pentasize 68 (a commercially available C16 to C18 alkenyl succinic anhydride (ASA)) was determined by lithium methoxide titration to be 2.97 mmol.g⁻¹. A reaction flask was charged with
 15 16.86 g (50 mmol activity) in a high aromatic solvent Innosol PP (20.256 g). 5-amino-[1H]-tetrazole monohydrate (5.164 g 50 mmol) was added and stirred to form a dispersion.

The dispersion was heated using a thermostat-controlled oil bath to an eventual internal temperature of 170°C. Progress of the reaction was monitored at intervals using ATR-FTIR spectroscopy. The
 20 product contained approximately 50 wt% of the C16/C18 ASA 5-amino-[1H]-tetrazole reaction product. The theoretical nitrogen content of the target compound is from 16.1 to 17.8 wt%.

Example 3 - Imide from reaction of C16/C18 ASA with tetraethylenepentamine (TEPA)

25 Major components:



wherein the R³ groups sum to C₁₃H₂₈ or C₁₅H₃₂ or a mixture thereof.

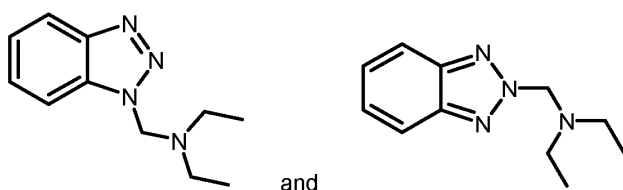
The nitrogen-containing compound of Example 3 was prepared as follows. The activity of a sample of Pentasize 68 (a commercially available C16 to C18 alkenyl succinic anhydride (ASA)) was determined by lithium methoxide titration to be 2.97 mmol.g⁻¹. A reaction flask was charged with
 30 150.02 g (446 mmol activity) of Pentasize 68 and 2-ethylhexan-1-ol solvent (234.09 g). A pressure-equalised dropping funnel was charged with TEPA (84.40 gg, 446 mmol, 1.0 moles per anhydride

group). The flask contents were warmed in an oil bath controlled by a thermostat set at 70°C. The oil bath set point was increased to 175°C and the reactor contents allowed to warm.

Reaction progress was monitored at intervals using ATR-FTIR spectroscopy. The product comprised
5 49.88 wt% of the imide products. The theoretical nitrogen content of the target compound is from 13.0 to 13.7 wt%.

Example 4 - Mannich reaction product of diethylamine, formaldehyde and benzotriazole

10 Major components:



The nitrogen-containing compound of Example 4 was prepared as follows. Following the method of Katritzky et al J Chem Soc Perkin Trans 1987, 2673, diethylamine (21.945 g, 301 mmol) was added
15 to methanol (100 cm³). This mixture was cooled back to 3°C and 1H benzotriazole (35.739 g, 301 mmol) was added. Aqueous formaldehyde (nominally 37 wt%, 24.324 g, 300 mmol, 1.0 equivalents) was added to the reactor over 10 minutes and the reaction mixture was stirred for 50 minutes before being allowed to warm to ambient temperature whilst stirring overnight. Methanol was removed at the rotary evaporator and 58.441 g (expected 61.33 g) of a slightly viscous yellow oil were recovered.

20

The product obtained was confirmed by comparison of the ATR-FTIR spectra with the literature. ¹H NMR was consistent with the Katritzky reference but indicated a ratio of 1-isomer to 2-isomer of 3.71. The product was found by a Thermoflash elemental analyser to contain 62.24 wt% C, 7.55 wt% H and 27.09 wt% N. The theoretical nitrogen content of the target compound is 27.4 wt%.

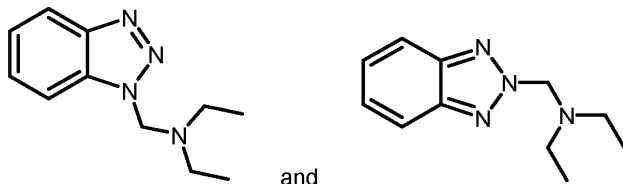
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A solution at 63.5 wt% of the target compound in 2-ethylhexanol gave clean and bright diesel fuel solutions at up to 5 wt% active material.

Example 5 - Two phase Mannich reaction product of diethylamine, formaldehyde and benzotriazole

Major components:

5



A reaction flask was charged with benzotriazole powder (60.0 g, 0.504 mol) and solvent 150 (102.8g). The slurry was warmed to 30°C before diethylamine (15.1g) was added. Aqueous formaldehyde (36.8g of a 37wt% formaldehyde solution) was then added over a period of 25 minutes, keeping the temperature at 40-47°C. After two hours stirring at 40°C the reactor contained two liquid phases which were heated to 70°C before transfer to a separating funnel. The recovered aqueous phase comprised 27.4 g of material. Additional water, accompanied by some organics, was removed by vacuum distillation at 70°C, 25 mBar leaving a clear solution of organic material.

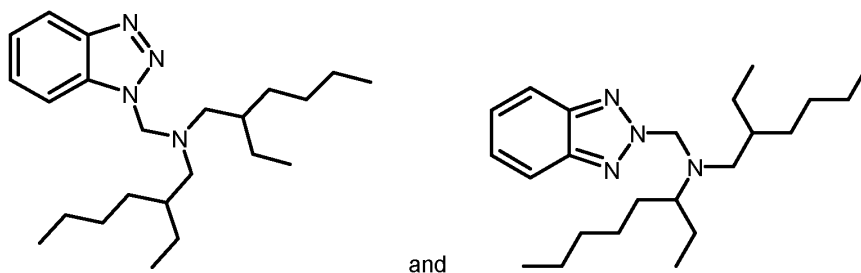
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The product structure was confirmed by FTIR. Theoretical N content of this product is 13.7 wt%.

Example 6 - Two phase Mannich reaction product of benzotriazole, formaldehyde and bis(2-ethylhexyl)amine

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Major components:



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The nitrogen-containing compound of Example 6 was prepared as follows. A reaction flask was charged with benzotriazole powder (50.1 g, 0.421 mole) and 157 g of solvent 150. The slurry was warmed to approximately 30°C before adding bis(2-ethylhexyl)amine (101.7g) over 20 minutes, followed by 34.1 g of 37 wt% active formaldehyde solution.

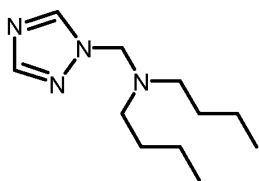
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The reaction mixture was heated to 80°C and transferred to a separating funnel and the organic layer was separated. Distillation of water from the separated organic layer resulted in a clear organic phase giving an FTIR spectrum similar to that of the product of Example 5.

- 5 The theoretical nitrogen content of the target compound is 15.0 wt%.

Example 7 - Two phase Mannich reaction product of 1,2,4-triazole, formaldehyde and di-n-butylamine

- 10 Major component:



- The nitrogen-containing compound of Example 7 was prepared as follows. 1,2,4-triazole (40.4 g, 0.585 mole) and 133.6 g of solvent 150 were charged to a reaction flask, followed by the di-n-butylamine (75.6 g). After further warming (39°C), addition of the aqueous formaldehyde (47.4 g of 37 wt% solution) commenced.

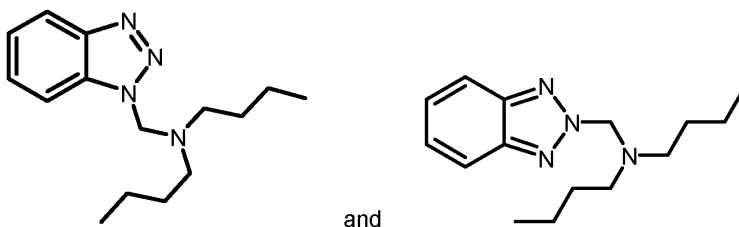
- The organic layer was separated from the reaction mixture and dried by vacuum distillation to yield the 249.6 g of the product solution. Theoretical N content of the product mixture (including solvent) is 13.3 wt%, by analysis the concentrate contained 13.0 wt% N, 60.8 wt% C and 8.7 wt% H.

The theoretical nitrogen content of the target compound is 26.6 wt%.

Example 8: benzotriazole – formaldehyde – dibutylamine

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Major components:



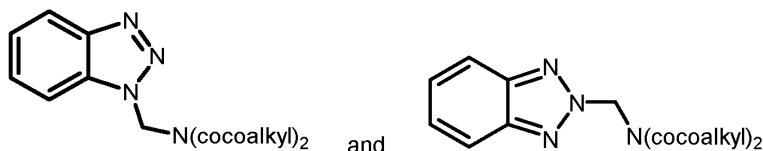
- 30 In a 500ml round bottomed flask, charged benzotriazole (60.1 g, 0.505 moles, 1.0 eq) and A150 solvent (131.5 g) and heated to 30°C, forming a white slurry. Added dibutylamine (65.3 g, 1 eq, 0.505 moles) via dropping funnel over 25 mins. With the mixture in the flask at 31°C, formalin addition

(37% w/w, 41.0 g, 0.505 moles, 1.0 eq) started and carried out of a period of 15-20 mins. A milky white liquid forms immediately after addition, with the contents two phases. The temperature of the reactor contents were then adjusted to 45-50°C and held at this temperature for 5 hrs. The reaction mixture was allowed to cool overnight. To separate the reaction mixture, it was heated to 70°C. The separation is clear, and the lower now hazy aqueous layer was ran off. Collected 30.9 g, theoretical water in the reaction is 34.9 g. Heated the organic phase to 75°C and applied vacuum to ~20 mbar. Isolated 254.9 g of clear bright yellow liquid (as ~50% actives solution).

The theoretical nitrogen content of the target compound is 21.5 wt%.

Example 9: Benzotriazole – formaldehyde – Armeen 2C (dicocoalkylamine)

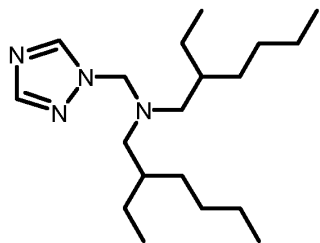
Major components:



In a 500ml round bottomed flask, charged benzotriazole (26.0 g, 0.218 moles, 1.0 eq) and A150 solvent (116.0 g) and heated to 90°C. The flask was charged the Armeen 2C (87.4 g, 0.218 moles, 1 eq [equivalent weight is 401 g/mol]) (dicocoalkylamine wherein cocoalkyl = mixture of C6-18 alkyl). Formalin (37% w/w, 0.218 moles, 1.0 eq) was then added over 5 mins and then the reaction mixture was stirred at 90°C for 2.5 hrs. The temperature in the reaction flask was increased over a period of 3 hrs to 119°C and water removed via Dean and Stark trap. When no further aqueous phase was being collected and the product was clear and bright the temperature was cooled to ambient. Collected 222.5 g of clear bright amber liquid (as 50% actives solution).

Example 10: 1,2,4 – triazole – formaldehyde – bis (2-ethylhexyl)amine

Major component:



Formalin (159.6 g of 26.6% active formaldehyde, 1.9447 mol, 0.995 eqs) and 1,2,4-triazole (156.0 g, 1.9545 mols, 1.0 equiv) are charged and heated to 60°C. Bis-(2-ethylhexyl) amine (462.5 g,

1.9154 mols, 0.98 equivalents) is added to the water mixture over 2.5 hrs at 60°C and the batch is stirred for 1hr to complete reaction. Water from the formalin solution and water of reaction is removed by vacuum distillation and 60-100°C (100-200 mbar). Following water removal, residual volatiles and trace water are removed by stripping under increased vacuum and the product (615.4 g) is
5 discharged via a filter as pale-yellow liquid.

The theoretical nitrogen content of the target compound is 17.4 wt%.

Engine Testing

10

Engine testing was carried out as described below to assess the performance of the nitrogen-containing additives of the present invention in the reduction of deposits in the exhaust gas recirculation system of a diesel engine.

15 *Engine Details*

A Euro 6 compliant 2.0 litre, HSDI engine was connected to a test automation system and test bed fitted with an engine dynamometer. The engine was controlled by an ECU supplied by the engine manufacturer. The engine had had over 1100h of use prior to the first test. The engine oil was
20 changed prior to performing the first test.

Modifications / Test Setup

1. No SCR Catalyst or associated components were present in the exhaust system.
- 25 2. High pressure EGR cooler is artificially controlled to 40°C for the duration of the test.

The base fuel was an RF-06-03 diesel fuel (Haltermann Carless, UK) having the following specification:

Feature	Units	Results	Minimum	Maximum	Method
Density 15 °C	kg/m ³	836.0	833.0	837.0	ASTM D4052
Marker (Red)	-	Pass	-	-	VISUAL
Cetane Number	-	53.9	52.0	54.0	ASTM D613
I.B.Pl.	°C	214.3	-	-	ASTM D88
10% v/v Recovered at	°C	232.0	-	-	ASTM D88
50% v/v Recovered at	°C	275.5	245.0	-	ASTM D88
90% v/v Recovered at	°C	330.2	-	-	ASTM D88
95% v/v Recovered at	°C	348.0	345.0	350.0	ASTM D88
F.B.Pl.	°C	356.2	-	370.0	ASTM D88
Aromatics by FIA	%(V/V)	19.8	Corrected for	-	ASTM D1319
Olefins by FIA	%(V/V)	5.5	-	-	-
Flash Point, Pensky Closed	°C	92.5	55.0	-	ASTM D93
Sulphur Content	mg/kg	< 3.0	-	10.0	ASTM D5453
Viscosity at 40 °C	mm ² /s	3.062	2.300	3.300	ASTM D445
Cloud Point	°C	-18	-	-	ASTM D2500
CFPP	°C	-20	-	-15	EN 116
Lubricity (WSD 1.4) at 60 °C	µm	180	-	400	ISO 12156-1
Carbon Residue (on 10% Dist. Res)	%(m/m)	< 0.10	-	0.20	ASTM D4530
Ash	%(m/m)	< 0.001	-	0.010	ASTM D482
FAME Content: None Detected	-	Pass	-	-	EN 14078
Polycyclic Aromatic Hydrocarbons	%(m/m)	5.8	3.0	8.0	EN 12916
Total Aromatic Hydrocarbons	%(m/m)	22.2	-	-	EN 12916
Water Content	mg/kg	50	-	200	IP 438
Water & Sediment	%(V/V)	< 0.010	-	-	ASTM D2709
Strong Acid Number	mg	0 KOH/g	-	0.02	ASTM D974
Oxidation Stability	mg	< 0.1 per 100ml	-	2.5	ASTM D2274
Copper Corrosion, 3hrs at 100 °C	-	1B	-	-	ASTM D130
Oxygen Content	%(m/m)	< 0.04	ELEMENTAL	-	Elemental Analysis
Carbon Content	%(m/m)	86.89	ASTM D5291	-	ASTM D5291
Hydrogen Content	%(m/m)	13.11	ASTM D5291	-	ASTM D5291
Carbon Weight Fraction	-	0.8689	CALCULATION	-	Calculation
C/H Mass Ratio	-	8.63	CALCULATION	-	Calculation
Atomic H/C Ratio	-	1.7979	CALCULATION	-	Calculation
Atomic O/C Ratio	-	< 0.0003	CALCULATION	-	Calculation
Gross Heat of Combustion	MJ/kg	45.72	IP 12	-	IP 12
Net Heat of Combustion	MJ/kg	42.94	IP 12	-	IP 12
Net Heat of Combustion	btu/lb	18480	CALCULATION	-	Calculation

5

Test Additives, Treat Rate:

The example nitrogen-containing compounds were dosed at 100 mg/kg into the base diesel fuel described above. The nitrogen-containing compound of Example 1 was dosed into the base fuel to provide test fuel A

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The quantity of soot deposited in the EGR cooler was established by weighing the component before and after each test.

The EGR cooler is thoroughly cleaned using tap water sprayed at high pressure through the cooler matrix. This cleaning process is performed until no more deposit can be seen in the cooler matrix with the naked eye.

- 5 The EGR cooler was then placed into an oven, pre-heated to 185°C, affixed to a set of scales. The weight measurement was taken as an average is taken over 15 minutes, once the scales had stabilised. This weighing process is repeated at the end of the test. The variance between the weight measured before and after the test represents the change in mass due to soot deposition.

10 *Test Procedure*

- [D] EGR Cleaned and weighed
 - [D] DPF + *Slave* EGR Installation
 - Engine Start + Warm-Up
 - 15 - Passive DPF Regeneration by varying the engine speed and load until the regeneration is complete. The differential pressure across the is used to monitor the regeneration progress.
 - Engine Stop
 - Change to test fuel
 - [C] DPF + *Slave* EGR Removal
 - 20 - [C] DPF Start-of-Test (SOT) Weighing
 - [C] DPF + [C] EGR Installation
 - Engine Start + Warm-Up
 - 8-Hour Steady-State Test Cycle
 - 1200RPM
 - 25 - 60Nm
 - Engine Stop
 - [D] DPF Removal and End-of-Test (EOT) Weighing
 - [D] EGR Removal and EGR End of Test Weighing
- 30 [C] indicates a clean component
[D] indicates a fouled component

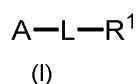
Results

Test fuel	Additive	Treat rate (mg/kg)	EGR Soot Weight [g]
Base fuel	-	-	1.59
A	Example 1	100	1.25

These results demonstrate that the use of the nitrogen-containing compounds described herein as additives in a diesel fuel composition may provide a significant reduction in deposits in an exhaust gas recirculation system of a diesel engine combusting said fuel.

Claims

1. Use of one or more nitrogen-containing compounds as an additive in a diesel fuel composition to reduce the impact of deposits in the exhaust gas recirculation system of a diesel engine when combusting said diesel fuel composition, wherein the nitrogen-containing compounds comprise at least 4% by mass of nitrogen atoms.
2. A method of reducing the impact of deposits in the exhaust gas recirculation system of a diesel engine, the method comprising combusting in the engine a diesel fuel composition comprising as an additive one or more nitrogen-containing compounds, wherein the nitrogen-containing compounds comprise at least 4% by mass of nitrogen atoms.
3. The use or method according to claim 1 or claim 2 which reduces the formation of deposits in the exhaust gas recirculation system of said diesel engine.
4. The use or method of according to any preceding claim, wherein the exhaust gas recirculation system is a high pressure exhaust gas recirculation system, wherein the high pressure EGR system is either a stand-alone high pressure EGR system or is part of a hybrid or a dedicated EGR system.
5. The use or method according to any preceding claim wherein the nitrogen-containing compound is the reaction product of a) a hydrocarbyl substituted reagent and b) a nitrogen-containing reagent.
6. The use or method according to any preceding claim wherein the nitrogen-containing compound has the formula (I):



wherein:

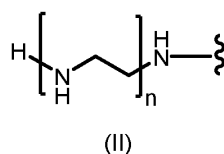
A is a nitrogen-containing group;

L is either a bond or a linker group; and

R¹ is an optionally substituted alkyl, alkenyl or aminoalkyl group having a molecular weight (Mn) of up to 1,000.

7. The use or method according to claim 6, wherein the nitrogen-containing group A is a nitrogen-containing heterocycle and is selected from an optionally substituted piperazine, pyridine, pyrazine, pyridazine, pyrimidine, triazine, quinoline, isoquinoline, quinazoline, a five-membered heterocyclic ring such as pyrazole or imidazole or a benzo-fused five-membered heterocyclic ring such as benzimidazole.

8. The use or method according to claim 6, wherein the A group is a non-cyclic nitrogen-containing group having the formula (II):



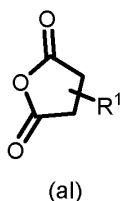
wherein n is from 1 to 10.

9. The use or method according to any one of claims 6 to 8, wherein L is a bond, an amide, a succinimide, a succinic acid or an amide of a succinic acid.
10. The use or method according to any preceding claim, wherein the nitrogen-containing compound is the reaction product of:

a) a hydrocarbyl substituted carboxylic acid acylating agent; and

b) a nitrogen-containing reagent.

11. The use or method according to claim 10, wherein component a) has the formula (a1):

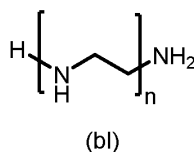


wherein R¹ is an optionally substituted alkyl, alkenyl or aminoalkyl group having a molecular weight (Mn) of up to 1,000.

12. The use or method according to claim 10 or claim 11, wherein component b) is either:

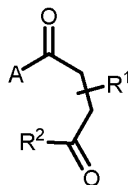
selected from an optionally substituted benzotriazole, amino-benzotriazole, indazole, amino-indazole, triazole, amino-triazole, tetrazole or amino-tetrazole; or

has the formula (b1):



wherein n is from 1 to 10.

13. The use or method according to any preceding claim, wherein the nitrogen-containing compound has the formula (III):



(III)

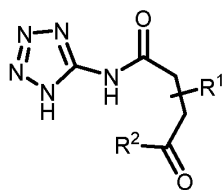
wherein:

A is a nitrogen-containing group;

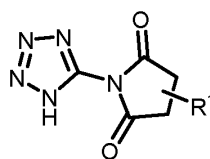
R¹ is an optionally substituted alkyl, alkenyl or aminoalkyl group having a molecular weight of up to 1,000; and

R² is OH, NH₂, OR⁴, NHR⁴ or NR⁴R⁵, wherein R⁴ and R⁵ are independently selected from optionally substituted C1-6 alkyl or alkenyl groups, or is a bond to A.

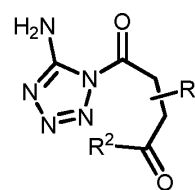
14. The use or method according to claim 13, wherein the nitrogen-containing compound has the formula (IV), (IVb) or (IVc), or a mixture thereof:



(IV)



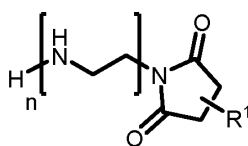
(IVb)



(IVc)

wherein R¹ and R² are as defined in claim 12.

15. The use or method according to claim 13, wherein the nitrogen-containing compound has the formula (V):



(V)

wherein n is from 1 to 3, or a mixture thereof; and

wherein R¹ is as defined in claim 12.

16. The use or method according to any of claims 1 to 7, wherein the nitrogen-containing compound is the reaction product of:

a) an amine or polyamine comprising a hydrocarbyl group;

b) a nitrogen-containing reagent; and

c) an aldehyde.

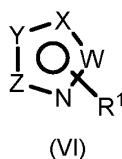
17. The use or method according to claim 16, wherein:

a) is an alkylamine having the formula NHR^7R^8 wherein R^7 and R^8 are each independently selected from H, optionally substituted C1-20 alkyl groups or optionally substituted C1-20 alkenyl groups;

b) is a nitrogen-containing reagent selected from an optionally substituted triazole, tetrazole, indole, indazole or benzotriazole, and.

c) is formaldehyde or a source of formaldehyde.

18. The use or method according to any one of claims 1 to 7, 16 or 17, wherein the nitrogen-containing compound has the formula (VI):

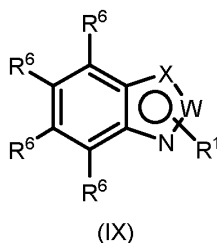


wherein:

R^1 is an optionally substituted alkyl, alkenyl or aminoalkyl group having a molecular weight of up to 1,000;

W, X, Y and Z are each independently selected from CH, C, N, NH, S and SH; and wherein the compound optionally comprises a cycloalkyl or aryl ring linking Y and Z.

19. The use or method according to claim 18, wherein the nitrogen-containing compound has the formula (IX):



wherein:

R¹ is an optionally substituted alkyl, alkenyl or aminoalkyl group having a molecular weight of up to 1,000;

W and X are each independently selected from C and N; and

each R⁶ is independently selected from H, C1-6 alkyl or C1-6 alkenyl.

20. The use or method according to claim 19, wherein R¹ is CH₂NR⁷R⁸ and R⁷ and R⁸ are each independently selected from H, optionally substituted C1-20 alkyl groups or optionally substituted C1-20 alkenyl groups.
21. The use or method according to any preceding claim wherein the nitrogen-containing compound comprises fewer than five N-H bonds
22. The use or method according to any preceding claim wherein the diesel fuel composition comprises from 50 to 2000 ppm of the one or more nitrogen-containing compounds.
23. The use or method according to any preceding claim wherein the diesel fuel composition comprises from 50 to 350 ppm of the one or more nitrogen-containing compounds.
24. The use or method according to any preceding claim which reduces deposits in the exhaust gas recirculation system of a diesel engine having a pressure in excess of 1350 bar.
25. The use or method according to any preceding claim which reduces the formation of deposits on the cooler of the EGR system.
26. The use or method according to any preceding claim which reduces the formation of deposits in an EGR system by at least 5%.
27. The use or method according to any preceding claim wherein the diesel fuel composition comprises one or more nitrogen containing detergents.
28. The use or method according to claim 27 wherein the one or more nitrogen containing detergents are selected from:
 - (i) a quaternary ammonium salt additive;
 - (ii) the product of a Mannich reaction between an aldehyde, an amine and an optionally substituted phenol; and
 - (iii) the reaction product of a carboxylic acid-derived acylating agent and an amine.

29. A fuel additive composition comprising one or more nitrogen-containing compound and a detergent additive, wherein the nitrogen-containing compounds comprise at least 4% by mass of nitrogen atoms.
30. A diesel fuel composition comprising one or more nitrogen-containing compound and a detergent additive, wherein the nitrogen-containing compounds comprise at least 4% by mass of nitrogen atoms.
31. The diesel fuel composition according to claim 30, comprising one or more further additives selected from antioxidants, 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.
32. The fuel additive composition according to claim 29 or the diesel fuel composition according to claim 30 or claim 31, wherein the detergent additive is:

a reaction product of tetraethylene pentamine (TEPA) and a PIBSA having a PIB number average molecular weight (Mn) of from 300 to 2800; or

a quaternary ammonium salt formed by reacting methyl salicylate or dimethyl oxalate with the reaction product of dimethylaminopropylamine and a polyisobutylene-substituted succinic anhydride having a PIB number average molecular weight (Mn) of 700 to 1300; or a mixture thereof.