Fuel Compositions

The present invention relates to fuel compositions and additives thereto. In particular the invention relates to additives for diesel fuel compositions, especially those suitable for use in modern diesel engines with high pressure fuel systems.

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

These improvements in performance and emissions have been brought about by improvements in the combustion process. To achieve the fuel atomisation necessary for this improved combustion, fuel injection equipment has been developed which uses higher injection pressures and reduced fuel injector nozzle hole diameters. The fuel pressure at the injection nozzle is now commonly in excess of 1500 bar (1.5×10^8 Pa). To achieve these pressures the work that must be done on the fuel also increases the temperature of the fuel. These high pressures and temperatures can cause degradation of the fuel.

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

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

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

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.

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 ºC.

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 100ºC to 350ºC prior to injection, sometimes being recirculated back within the fuel system thus increasing the time for which the fuel experiences these conditions.

A common problem with diesel engines is fouling of the injector, particularly the injector body, and the injector nozzle. Fouling may also occur in the fuel filter. Injector nozzle fouling occurs when the nozzle becomes blocked with deposits from the diesel fuel. Fouling of fuel filters may be related to the recirculation of fuel back to the fuel tank. Deposits increase with degradation of the fuel. Deposits may take the form of carbonaceous coke-like residues or sticky or gum-like residues. Diesel fuels become more and more unstable the more they are heated, particularly if heated under pressure. Thus diesel engines having high pressure fuel systems may cause increased fuel degradation.

The problem of injector fouling may occur when using any type of diesel fuels. However, some fuels may be particularly prone to cause fouling or fouling may occur more quickly when these fuels are used. For example, fuels containing biodiesel have been found to produce injector fouling more readily. Diesel fuels containing metallic species may also lead to increased deposits. Metallic species may be deliberately added to a fuel in additive compositions or may be present as contaminant species. Contamination occurs if metallic species from fuel distribution systems, vehicle distribution systems, vehicle fuel systems, other metallic components and lubricating oils become dissolved or dispersed in fuel.

Transition metals in particular cause increased deposits, especially copper and zinc species. These may be typically present at levels from a few ppb (parts per billion) up to 50 ppm, but it is believed that levels likely to cause problems are from 0.1 to 50 ppm, for example 0.1 to 10 ppm.

When injectors become blocked or partially blocked, the delivery of fuel is less efficient and there is poor mixing of the fuel with the air. Over time this leads to a loss in power of the engine, increased exhaust emissions and poor fuel economy.

As the size of the injector nozzle hole is reduced, the relative impact of deposit build up becomes more significant. By simple arithmetic a 5 µm layer of deposit within a 500 µm hole reduces the flow area by 4% whereas the same 5 µm layer of deposit in a 200 µm hole reduces the flow area by 9.8%.

At present, nitrogen-containing detergents may be added to diesel fuel to reduce coking. Typical nitrogen-containing detergents are those formed by the reaction of a polyisobutylene-substituted succinic acid derivative with a polyalkylene polyamine. However, newer engines including finer injector nozzles are more sensitive and current diesel fuels may not be suitable for use with the new engines incorporating these smaller nozzle holes.

The present inventor has developed diesel fuel compositions which when used in diesel engines having high pressure fuel systems provide improved performance compared with diesel fuel compositions of the prior art.

It is advantageous to provide a diesel fuel composition which prevents or reduces the occurrence of deposits in a diesel engine. Such fuel compositions may be considered to perform a "keep clean" function i.e. they prevent or inhibit fouling.

However it would also be desirable to provide a diesel fuel composition which would help clean up deposits that have already formed in an engine, in particular deposits which have formed on the injectors. Such a fuel composition which when combusted in a diesel engine removes deposits therefrom thus effecting the "clean-up" of an already fouled engine.

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

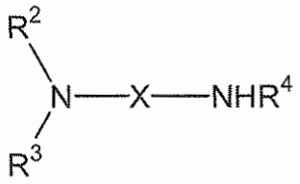
Although for the reasons mentioned above deposits on injectors is a particular problem found in modern diesel engines with high pressure fuels systems, it is desirable to provide a diesel fuel composition which also provides effective detergency in older traditional diesel engines such that a single fuel supplied at the pumps can be used in engines of all types.

It is also desirable that fuel compositions reduce the fouling of vehicle fuel filters. It would be useful to provide compositions that prevent or inhibit the occurrence of fuel filter deposits i.e, provide a "keep clean" function. It would be useful to provide compositions that remove

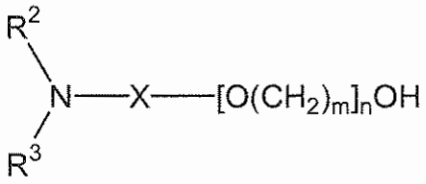
existing deposits from fuel filter deposits i.e. provide a "clean up" function. Compositions able to provide both of these functions would be especially useful.

When formulating a fuel additive package it is necessary to consider the effect that an additive will have on the fuel composition as a whole. When compounds including polar and non-polar groups are used as additives these can sometimes cause problems as they may assist mixing of water into the fuel and the formation of emulsions. Fuels containing water and particularly fuel/water emulsions are undesirable. They can lead to problems such as microbial contamination, corrosion etc. It is therefore desirable to use additives where possible which have a reduced tendency to form emulsions

According to a first aspect of the present disclosure there is provided a diesel fuel composition comprising a first additive (i) comprising a quaternary ammonium salt and a second additive (ii) comprising a Mannich reaction product; wherein the quaternary ammonium salt additive (i) is formed by the reaction of a quaternising agent which is not an ester and a compound formed by the reaction of a hydrocarbyl-substituted acylating agent and an amine of formula (B1) or (B2):



(B1)



(B2)

wherein R^2 and R^3 are the same or different alkyl, alkenyl or aryl groups having from 1 to 22 carbon atoms; X is a bond or alkylene group having from 1 to 20 carbon atoms; n is from 0 to 20; m is from 1 to 5; and R^4 is hydrogen or a C_1 to C_{22} alkyl group; and wherein the Mannich reaction product additive (ii) is the product of a Mannich reaction between:

(a) an aldehyde;
(b) an amine; and
(c) a substituted phenol;

wherein the phenol is substituted with at least one branched hydrocarbyl group having a molecular weight of between 200 and 3000.

Additive compounds (i) may be referred to herein as "the quaternary ammonium salt additives" or additive (i).

Additive compounds (ii) may be referred to herein as "the Mannich additives" or additive (ii).

The quaternising agents used to form the quaternary ammonium salt additives of the present invention are not esters. By this definition we mean to exclude in particular compounds of formula $RCOOR^1$ in which R is an optionally substituted alkyl, alkenyl, aryl or alkylaryl group and R^1 is a C_1 to C_{22} alkyl, aryl or alkylaryl group.

The quaternising agent may suitably be selected from dialkyl sulfates, benzyl halides, hydrocarbyl substituted carbonates, hydrocarbyl susbsituted epoxides in combination with an acid, alkyl halides, alkyl sulfonates, sultones, hydrocarbyl substituted phosphates, hydrocarbyl substituted borates, alkyl nitrites, alkyl nitrates, hydroxides, N-oxides or mixtures thereof.

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

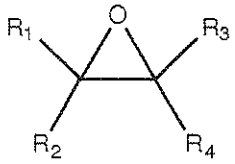
Preferred quaternising agents include dialkyl sulfates, benzyl halides, hydrocarbyl substituted carbonates, hydrocarbyl susbsituted epoxides in combination with an acid, alkyl halides, alkyl sulfonates, sultones, hydrocarbyl substituted phosphates, hydrocarbyl substituted borates, N-oxides or mixtures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

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

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

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

Suitable hydrocarbyl susbsituted epoxides have the formula:



wherein each of R^1, R^2, R^3 and R^4 is independently hydrogen or a hydrocarbyl group having 1 to 50 carbon atoms. Examples of suitable epoxides include ethylene oxide, propylene oxide, butylene oxide, styrene oxide and stillbene oxide. The hydrocarbyl epoxides are used as quaternising agents in combination with an acid. In embodiments in which the hydrocarbyl substituted acylating agent is a dicarboxylic acylating agent no separate acid needs to be added. However in other embodiments an acid such as acetic acid may be used.

Particularly preferred epoxides are propylene oxide and styrene oxide.

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

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

Suitable sultones include propane sultone and butane sultone.

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

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

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

Preferably the quaternising agent is selected from dialkyl sulfates, benzyl halides, hydrocarbyl substituted carbonates, hydrocarbyl susbsituted epoxides in combination with an acid, and mixtures thereof.

Especially preferred quaternising agents for use herein are hydrocarbyl substituted epoxides in combination with an acid. This includes embodiments where the acid is an additional reactant or where the acid group is present as a part of the structure of the compound which is being quaternised. Preferably the acid group is present as a part of the structure of the compound which is being quaternised.

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

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

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

Preferably the hydrocarbyl substituted acylating agent is reacted with a diamine compound of formula (B1).

R^2 and R^3 are the same or different alkyl, alkenyl or aryl groups having from 1 to 22 carbon atoms. In some embodiments R^2 and R^3 may be joined together to form a ring structure, for example a piperidine or imidazole moiety. R^2 and R^3 may be branched alkyl or alkenyl groups. Each may be substituted, for example with a hydroxy or alkoxy substituent.

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

X is a bond or alkylene group having from 1 to 20 carbon atoms. In preferred embodiments when X alkylene group this group may be straight chained or branched. The alkylene group may include a cyclic structure therein. It may be optionally substituted, for example with a hydroxy or alkoxy substituent.

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

Examples of compounds of formula (B1) suitable for use herein include 1-aminopiperidine, 1-(2-aminoethyl)piperidine, 1- (3-aminopropyl)-2-pipecoline, 1-methyl-(4-methylamino)piperidine, 4-(1-pyrrolidinyl)piperidine, 1-(2-aminoethyl)pyrrolidine, 2-(2-aminoethyl)-1- methylpyrrolidine, N,N-diethylethylenediamine, N,N-dimethylethylenediamine, N,N-dibutylethylenediamine, N,N-diethyl-l,3-diaminopropane, N,N-dimethyl-1,3-diaminopropane, N,N,N'-trimethylethylenediamine, N,N-dimethyl-N'-ethylethylenediamine, N,N-diethyl-N'-methylethylenediamine, N,N,N'- triethylethylenediamine, 3-dimethylaminopropylamine, 3-diethylaminopropylamine, 3-dibutylaminopropylamine, N,N,N'-trimethyl- 1,3- propanediamine, N,N,2,2-tetramethyl-l,3-propanediamine, 2-amino-5-diethylaminopentane, N,N,N',N'-tetraethyldiethylenetriamine, 3,3'-diamino-N-methyldipropylamine, 3,3'-iminobis(N,N-dimethylpropylamine), 1-(3-aminopropyl)imidazole and 4-(3-aminopropyl)morpholine, 1-(2-aminoethyl)piperidine, 3,3-diamino-N-methyldipropylamine, 3,3-aminobis(N,N- dimethy lpropy lamine), or combinations thereof.

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

Examples of compounds of formula (B2) suitable for use herein include alkanolamines including but not limited to triethanolamine, N,N-dimethylaminopropanol, N,N-diethylaminopropanol, N,N-diethylaminobutanol, triisopropanolamine, 1-[2-hydroxyethyl]piperidine, 2-[2-(dimethylamine)ethoxy]-ethanol, N-ethyldiethanolamine, N-methyldiethanolamine, N-butyldiethanolamine, N,N-diethylaminoethanol, N,N-dimethyl amino-ethanol, 2-dimethylamino-2-methyl-1-propanol.

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

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

The amine of formula (B1) or (B2) is reacted with a hydrocarbyl substituted acylating agent. The hydrocarbyl substituted acylating agent may be based on a hydrocarbyl substituted mono- di- or polycarboxylic acid or a reactive equivalent thereof. Preferably the hydrocarbyl substituted acylating agent is a hydrocarbyl substituted succinic acid compound such as a succinic acid or succinic anhydride.

The hydrocarbyl substituent preferably comprises at least 10, more preferably at least 12, for example 30 or 50 carbon atoms. It may comprise up to about 200 carbon atoms. Preferably the hydrocarbyl substituent has a number average molecular weight (Mn) of between 170 to 2800, for example from 250 to 1500, preferably from 500 to 1500 and more preferably 500 to 1100. An Mn of 700 to 1300 is especially preferred.

The hydrocarbyl 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 analogs and hydrochlorinated analogs thereof, white oils, synthetic alkenes for example produced by the Ziegler-Natta process (e.g. poly(ethylene) greases) and other sources known to those skilled in the art. Any unsaturation in the substituent may if desired be reduced or eliminated by hydrogenation according to procedures known in the art.

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 sulphoxy, 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. Most preferably they contain no more than one carbon-to-carbon unsaturated bond for every 50 carbon-to-carbon bonds present.

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

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

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

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

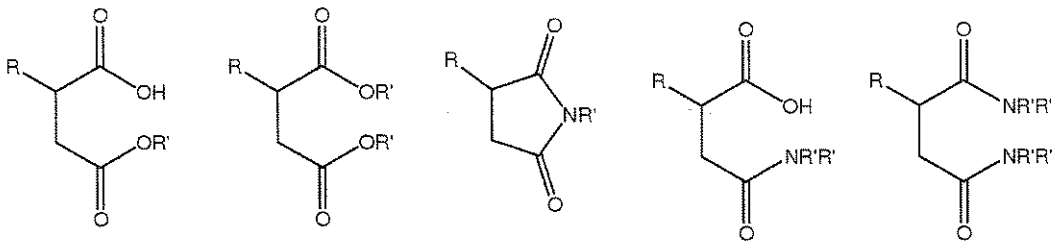
Internal olefins are sometimes known as isomerised olefins and can be prepared from alpha olefins by a process of isomerisation known in the art, or are available from other sources. The fact that they are also known as internal olefins reflects that they do not necessarily have to be prepared by isomerisation.

Some preferred acylating agents for use in the preparation of the quaternary ammonium salt additives of the present invention are polyisobutene-substituted succinic acids or succinic anhydrides. When a compound of formula (B2) is reacted with a succinic acylating agent the resulting product is a succinic ester. When a succinic acylating agent is reacted with a compound of formula (B1) in which R^4 is hydrogen the resulting product may be a succinimide or a succinamide. When a succinic acylating agent is reacted with a compound of formula (B1) in which R^4 is not hydrogen the resulting product is an amide.

In preferred embodiments, the reaction product of the hydrocarbyl substituted acylating agent and the amine of formula (B1) or (B2) is an amide or an ester.

In preferred embodiments, the reaction product of the hydrocarbyl substituted acylating agent and the amine of formula (B1) or (B2) also has at least one remaining carboxylic acid group. This may be achieved by choosing hydrocarbyl substituted acylating agents having di or polycarboxylic acids or reactive equivalents thereof and by choosing suitable molar ratios of amines of formula (B1) or (B2). In the case of amides prepared from amines of formula (B2) where R^4 is hydrogen, it may also be necessary to control the reaction conditions to avoid forming imides. Such techniques are within the capability of someone of ordinary skill in the art.

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



C1 C2 C3 C4 C5

In especially preferred embodiments the quaternary ammonium salt additives of the present invention are salts of tertiary amines prepared from dimethylamino propylamine and a polyisobutylene-substituted succinic anhydride. The average molecular weight of the polyisobutylene substituent is preferably from 700 to 1300, more preferably from 900 to 1100.

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

fuel composition comprising the reaction product of a quaternising agent and the reaction product of a hydrocarbyl substituted acylating agent and an amine formula (B1) or (B2).

Particularly preferred quaternary ammonium salts of the present invention are the reaction product of a polyisobutenyl succinic acylating agent with dimethylaminopropylamine (N,N dimethyl 1,3 propane diamine) to form the half amide, half acid and then quaternised using propylene oxide.

The composition of the present invention further comprises a second additive (ii) which is the product of a Mannich reaction between:

(a) an aldehyde;

(b) an amine; and

(c) a substituted phenol; wherein the phenol is substituted with at least one branched hydrocarbyl group having a molecular weight of between 200 and 3000.

Any aldehyde may be used as aldehyde component (a) of the Mannich additive. Preferably the aldehyde component (a) is an aliphatic aldehyde. Preferably the aldehyde has 1 to 10 carbon atoms, preferably 1 to 6 carbon atoms, more preferably 1 to 3 carbon atoms. Most preferably the aldehyde is formaldehyde.

Amine component (b) of the Mannich additive may be at least one amino or polyamino compound having at least one NH group. Suitable amino compounds include primary or secondary monoamines having hydrocarbon substituents of 1 to 30 carbon atoms or hydroxyl-substituted hydrocarbon substituents of 1 to about 30 carbon atoms.

In preferred embodiments the amine component (b) is a polyamine.

Polyamines may be selected from any compound including two or more amine groups. Preferably the polyamine is a (poly)alkylene polyamine (by which is meant an alkylene polyamine or a polyalkylene polyamine; including in each case a diamine, within the meaning of "polyamine"). Preferably the polyamine is a (poly)alkylene polyamine in which the alkylene component has 1 to 6, preferably 1 to 4, most preferably 2 to 3 carbon atoms. Most preferably the polyamine is a (poly) ethylene polyamine (that is, an ethylene polyamine or a polyethylene polyamine).

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

Preferably the polyamine component (b) includes the moiety $R^1R^2NCHR^3CHR^4NR^5R^6$ wherein each of R^1, R^2 R^3, R^4, R^5 and R^6 is independently selected from hydrogen, and an optionally substituted alkyl, alkenyl, alkynyl, aryl, alkylaryl or arylalkyl substituent.

Thus the polyamine reactants used to make the Mannich reaction products of the present invention preferably include an optionally substituted ethylene diamine residue.

Preferably at least one of R^1 and R^2 is hydrogen. Preferably both of R^1 and R^2 are hydrogen.

Preferably at least two of R^1, R^2, R^5 and R^6 are hydrogen.

Preferably at least one of R^3 and R^4 is hydrogen. In some preferred embodiments each of R^3 and R^4 is hydrogen. In some embodiments R^3 is hydrogen and R^4 is alkyl, for example C_1 to C_4 alkyl, especially methyl.

Preferably at least one of R^5 and R^6 is an optionally substituted alkyl, alkenyl, alkynyl, aryl, alkylaryl or arylalkyl substituent.

In embodiments in which at least one of R^1, R^2, R^3, R^4, R^5 and R^6 is not hydrogen, each is independently selected from an optionally substituted alkyl, alkenyl, alkynyl, aryl, alkylaryl or arylalkyl moiety. Preferably each is independently selected from hydrogen and an optionally substituted C(1-6) alkyl moiety.

In particularly preferred compounds each of R^1, R^2, R^3, R^4 and R^5 is hydrogen and R^6 is an optionally substituted alkyl, alkenyl, alkynyl, aryl, alkylaryl or arylalkyl substituent. Preferably R^6 is an optionally substituted C(1-6) alkyl moiety.

Such an alkyl moiety may be substituted with one or more groups selected from hydroxyl, amino (especially unsubstituted amino; -NH-, $-NH_2$), sulpho, sulphoxy, C(1-4) alkoxy, nitro, halo (especially chloro or fluoro) and mercapto.

There may be one or more heteroatoms incorporated into the alkyl chain, for example O, N or S, to provide an ether, amine or thioether.

Especially preferred substituents R^1, R^2, R^3, R^4, R^5 or R^6 are hydroxy-C(1-4)alkyl and amino-(C(1-4)alkyl, especially $HO\text{-}CH_2\text{-}CH_2\text{-}$ and $H_2N\text{-}CH_2\text{-}CH_2\text{-}$.

Suitably the polyamine includes only amine functionality, or amine and alcohol functionalities.

The polyamine may, for example, be selected from ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylene-hexamine, hexaethyleneheptamine, heptaethyleneoctamine, propane-1,2-diamine, 2(2-amino-ethylamino)ethanol, and N',N'-bis (2-aminoethyl) ethylenediamine ($N(CH_2CH_2NH_2)_3$). Most preferably the polyamine comprises tetraethylenepentamine or ethylenediamine.

Commercially available sources of polyamines typically contain mixtures of isomers and/or oligomers, and products prepared from these commercially available mixtures fall within the scope of the present invention.

The polyamines used to form the Mannich additives of the present invention may be straight chained or branched, and may include cyclic structures.

Phenol component (c) used to prepare the Mannich additives of the present invention may be substituted with 1 to 4 groups on the aromatic ring (in addition to the phenol OH). For example it may be a tri- or di- substituted phenol. Most preferably component (c) is a mono-substituted phenol. Substitution may be at the ortho, and/or meta, and/or para position(s).

Each phenol moiety may be ortho, meta or para substituted with the aldehyde/amine residue. Compounds in which the aldehyde residue is ortho or para substituted are most commonly formed. Mixtures of compounds may result. In preferred embodiments the starting phenol is para substituted and thus the ortho substituted product results.

The phenol may be substituted with any common group, for example one or more of an alkyl group, an alkenyl group, an alkynl group, a nitryl group, a carboxylic acid, an ester, an ether, an alkoxy group, a halo group, a further hydroxyl group, a mercapto group, an alkyl mercapto group, an alkyl sulphoxy group, a sulphoxy group, an aryl group, an arylalkyl group, a substituted or unsubstituted amine group or a nitro group.

As mentioned above the phenol includes at least one branched hydrocarbyl substituent. The hydrocarbyl substituent may be optionally substituted with, for example, hydroxyl, halo, (especially chloro and fluoro), alkoxy, alkyl, mercapto, alkyl sulphoxy, aryl or amino residues. Preferably the hydro carbyl group consists essentially of carbon and hydrogen atoms. The substituted phenol may include an alkenyl or alkynyl residue including one or more double and/or triple bonds.

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. Most preferably they contain no more than one carbon-to-carbon unsaturated bond for every 50 carbon-to-carbon bonds present.

Preferably component (c) is a monoalkyl phenol, especially a para-substituted monoalkyl phenol in which the alkyl chain of the substituent is branched.

In preferred embodiments phenol component (c) used to prepare Mannich reaction product additive (ii) includes a predominantly or completely saturated branched hydrocarbyl substituent. Preferably this predominantly or completely saturated hydrocarbyl substituent is branched along the length of the chain. By branched along the length of the chain we mean that there are multiple branches from the main (or longest) chain. Preferably there is a branch at least every 10 carbon atoms along the main chain, preferably at least every 6 carbons, suitably at least every 4 carbons, for example every 3 carbon atoms or every 2 carbon atoms.

A particular carbon atom in the main hydrocarbyl chain (which is preferably an alkylene chain) may have one or two branching hydrocarbyl groups. By branching hydrocarbyl groups we mean hydrocarbyl groups not forming part of the main chain but directly attached thereto. Thus the main hydrocarbyl chain may include the moiety $-CHR^1-$ or $-CR^1R^2-$ wherein R^1 and R^2 are branching hydrocarbyl groups.

Preferably each branching hydrocarbyl group is an alkyl group, preferably a C_1 to C_4 alkyl group, for example propyl, ethyl or most preferably methyl.

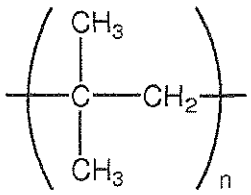
In some preferred embodiments phenol component (c) used to prepare Mannich reaction product additive (ii) includes a hydrocarbyl substituent which is substituted with methyl groups along the main chain thereof. Suitably there are a plurality of carbon atoms which each have two methyl substituents.

Preferably the branching points are substantially equally spaced along the main chain of the hydrocarbyl group of phenol component (c).

Component (c) used to prepare additive (ii) includes at least one branched hydrocarbyl substituent. Preferably this is an alkyl substituent. In especially preferred embodiments the hydrocarbyl substituent is derived from a polyalkene, suitably a polymer of a branched alkene, for example polyisobutene or polypropene.

In especially preferred embodiments component (c) used in the preparation of Mannich reaction product additive (ii) includes a poly(isobutene) derived substituent.

Thus the Mannich reaction product additives (ii) used in the present invention preferably include a hydrocarbyl chain having the repeating unit:



Poly(isobutenes) are prepared by the addition polymerisation of isobutene, $(CH_3)_2C=CH_2$. Each molecule of the resulting polymer will include a single alkene moiety.

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

Methods of preparing polyalkylene substituted phenols, for example polyisobutene substituted phenols are known to the person skilled in the art, and include the methods described in EP831141.

The hydrocarbyl substituent of component (c) has an average molecular weight of 200 to 3000. Preferably it has a molecular weight of at least 225, suitably at least 250, preferably at least 275, suitably at least 300, for example at least 325 or at least 350. In some embodiments the hydrocarbyl substituent of component (c) has an average molecular weight of at least 375, preferably at least 400, suitably at least 475, for example at least 500.

In some embodiments component (c) may include a hydrocarbyl substituent having an average molecular weight of up to 2800, preferably up to 2600, for example up to 2500 or up to 2400.

In some embodiments the hydrocarbyl substituent of component (c) has an average molecular weight of from 400 to 2500, for example from 450 to 2400, preferably from 500 to 1500, suitably from 550 to 1300.

In some embodiments the hydrocarbyl substituent of component (c) has an average molecular weight of from 200 to 600.

In some embodiments the hydrocarbyl substituent of component (c) has an average molecular weight of from 500 to 1000.

In some embodiments the hydrocarbyl substituent of component (c) has an average molecular weight of from 700 to 1300.

In some embodiments the hydrocarbyl substituent of component (c) has an average molecular weight of from 1000 to 2000.

In some embodiments the hydrocarbyl substituent of component (c) has an average molecular weight of from 1700 to 2600, for example 2000 to 2500.

Unless otherwise mentioned all average molecular weights referred to herein are number average molecular weights.

Components (a), (b) and (c) used to prepare the Mannich product additives (ii) may each comprise a mixture of compounds and/or a mixture of isomers.

The Mannich additive is preferably the reaction product obtained by reacting components (a), (b) and (c) in a molar ratio of from 5:1:5 to 0.1:1:0.1, more preferably from 3:1:3 to 0.5:1:0.5.

To form the Mannich additive of the present invention components (a) and (b) are preferably reacted in a molar ratio of from 6:1 to 1:4 (aldehyde:amine), preferably from 4:1 to 1:2, more preferably from 3:1 to 1:1.

In preferred embodiments the molar ratio of component (a) to component (b) (aldehyde:amine) in the reaction mixture is preferably greater than 1:1, preferably at least 1.1:1, more preferably at least 1.3:1, suitably at least 1.5:1, for example at least 1.6:1.

Preferably, the molar ratio of component (a) to component (b) (aldehyde:amine) in the reaction mixture is less than 3:1, preferably up to 2.7:1, more preferably up to 2.3:1, for example up to 2.1:1, or up to 2:1.

Preferably, the molar ratio of component (a) to component (b) (aldehyde:amine) in the reaction mixture used to prepare the Mannich additive of the present invention is from 1.1:1 to 2.9:1, preferably from 1.3:1 to 2.7:1, preferably from 1.4:1 to 2.5:1, more preferably from 1.5:1 to 2.3:1, suitably from 1.6:1 to 2.2:1, for example from 1.7:1 to 2.1:1.

To form a preferred Mannich additive of the present invention the molar ratio of component (a) to component (c) (aldehyde:phenol) in the reaction mixture is preferably from 5:1 to 1:4, preferably from 3:1 to 1:2, for example from 2:1 to 1:1.

In preferred embodiments the molar ratio of component (a) to component (c) (aldehyde:phenol) in the reaction mixture used to prepare the Mannich additive of the present invention is greater than 1:1; preferably at least 1.1:1; preferably at least 1.2:1 and more preferably at least 1.3:1.

Preferably the molar ratio of component (a) to component (c) (aldehyde:phenol) is less than 2:1, preferably up to 1.9:1; more preferably up to 1.8:1 for example up to 1.7:1; more preferably up to 1.6:1.

Suitably the molar ratio of component (a) to component (c) (aldehyde:phenol) in the reaction mixture used to prepare the Mannich additive is from 1.05:1 to 1.95:1, preferably from 1.1:1 to 1.85:1, more preferably from 1.2:1 to 1.75:1, suitably from 1.25:1 to 1.65:, most preferably from 1.3:1 to 1.55 :1.

To form the Mannich additive of the present invention components (c) and (b) are preferably reacted in a molar ratio of from 6:1 to 1:4 (phenol : amine), preferably from 4:1 to 1:2, more preferably from 3:1 to 1:2 and more preferably from 2:1 to 1:2.

Suitably the molar ratio of component (c) to component (b) (phenol:amine) in the reaction mixture is 0.7:1 to 1.9: 1, preferably 0.8:1 to 1.8:1, preferably 0.9:1 to 1.7:1, preferably 1:1 to 1.6:1 preferably 1.1:1 to 1.5:1, preferably 1.2:1 to 1.4:1.

In preferred embodiments, the molar ratio of component (c) to component (b) (phenol : amine) in the reaction mixture is greater than 0.5:1; preferably at least 0.8:1; preferably at least 0.9:1 and more preferably at least 1:1 for example at least 1.1:1.

Preferably the molar ratio of component (c) to component (b) (phenol:amine) in the reaction mixture is less than 2:1, preferably up to 1.9:1; more preferably up to 1.7:1 for example up to 1.6:1; more preferably up to 1.5:1.

In some preferred embodiments in the Mannich reaction used to form the additive the molar ratio of component (a) to component (b) is 2.2-1.01:1; the molar ratio of component (a) to component (c) is 1.99-1.01:1 and the molar ratio of component (b) to component (c) is 1:1.01-1.99.

In some preferred embodiments in the reaction used to make the Mannich additive the molar ratio of component (a) to component (b) is 2-1.6:1, the molar ratio of component (a) to component (c) is 1.6-1.2:1 and the molar ratio of component (b) to component (c) is 1:1.1-1.5.

Some preferred compounds used in the present invention are typically formed by reacting components (a), (b) and (c) in a molar ratio of 1.8 parts (a) ± 0.3 parts (a), to 1 part (b), to 1.3 parts (c) ± 0.3 parts (c); preferably 1.8 parts (a) ± 0.1 parts (a), to 1 part (b), to 1.3 parts (c) ± 0.1 parts (c); preferably approximately 1.8:1:1.3 (a : b : c).

Suitable treat rates of the quaternary ammonium salt additive and when present the Mannich additive will depend on the desired performance and on the type of engine in which they are used. For example different levels of additive may be needed to achieve different levels of performance.

Suitably the quaternary ammonium salt additive is present in the diesel fuel composition in an amount of from 1 to 10000ppm, preferably from 1 to 1000 ppm, more preferably from 5 to 500 ppm, suitably from 5 to 250 ppm, for example from 5 to 150ppm.

Suitably the Mannich additive when used is present in the diesel fuel composition in an amount of from 1 to 10000ppm, preferably from 1 to 1000 ppm, more preferably from 5 to 500 ppm, suitably from 5 to 250 ppm, for example from 5 to 150ppm.

The weight ratio of the quaternary ammonium salt additive to the Mannich additive is preferably from 1:10 to 10:1, preferably from 1:4 to 4:1, for example from 1:3 to 3:1.

As stated previously, fuels containing biodiesel or metals are known to cause fouling. Severe fuels, for example those containing high levels of metals and/or high levels of biodiesel may require higher treat rates of the quaternary ammonium salt additive and/or Mannich additive than fuels which are less severe.

The diesel fuel composition of 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.

In some preferred embodiments the composition additionally comprises a dehazer/demulsifier.

Dehazer/demulsifiers are commercially available, for example from Nalco or Baker Hughes. Suitable compounds include, but are not limited to alkoxylated phenol formaldehyde polymers, alkylated phenols and resins derived therefrom, oxylated alkylphenolic resins, polyglycol esters, epoxides such as diepoxides, polyols, polyamines and ethylene oxide / propylene oxide block copolymers . Particularly preferred demulsifier/dehazers are a mixture of 2-4 different components comprising at least one alkoxylated phenol formaldehyde

The dehazer/demulsifier is suitably present in an amount of from 0.01 to 1000ppm, preferably from 0.1 to 500ppm, more preferably from 0.5 to 100ppm, for example from 1 to 50ppm.

In some preferred embodiments the composition additionally comprises an antifoam additive. Suitable antifoam additives are known to the person skilled in the art and include for example organomodified siloxanes, organo modified poly dimethyl siloxanes or polysilicone polyether copolymers. Examples of such compounds are available under the trade name SAG™ TP-317 or TP-325 from Momentive Perfomance Materials or Dow Corning® 2-2617 .

The antifoam additive is suitably present in an amount of from 0.01 to 1000ppm, preferably from 0.1 to 500ppm, more preferably from 0.5 to 100ppm, for example from 1 to 50ppm.

In some preferred embodiments the compositon additionally 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.

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

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

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

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

The diesel fuel composition may comprise 1st generation biodiesel. First generation biodiesel contains esters of, for example, vegetable oils, animal fats and used cooking fats. This form of biodiesel may be obtained by transesterification of oils, for example rapeseed oil, soybean oil, safflower oil, palm 25 oil, corn oil, peanut oil, cotton seed oil, tallow, coconut oil, physic nut oil (Jatropha), sunflower seed oil, used cooking oils, hydrogenated vegetable oils or any mixture thereof , with an alcohol, usually a monoalcohol, in the presence of a catalyst.

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

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

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

In some preferred embodiments the diesel fuel composition comprises a Fischer Tropsch fuel and/or biodiesel.

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

In some preferred embodiments the composition comprises from 1 to 20 wt%, biodiesel, preferably from 5 to 10 wt%.

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

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

However in preferred embodiments the diesel fuel has a sulphur content of at most 0.05% by weight, more preferably of at most 0.035% by weight, especially of at most 0.015%. Fuels with even lower levels of sulphur are also suitable such as, fuels with less than 50 ppm sulphur by weight, preferably less than 20 ppm, for example 10 ppm or less.

Commonly when present, metal-containing species will be present as a contaminant, for example through the corrosion of metal and metal oxide surfaces by acidic species present in the fuel or from lubricating oil. In use, fuels such as diesel fuels routinely come into contact with metal surfaces for example, in vehicle fuelling systems, fuel tanks, fuel transportation means etc. Typically, metal-containing contamination may comprise transition metals such as zinc, iron and copper; group I or group II metals such as sodium; and other metals such as lead.

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. Such catalysts are often based on metals such as iron, cerium, Group I and Group II metals e.g., calcium and strontium, either as mixtures or alone. Also used are platinum and manganese. The presence of such catalysts may also give rise to injector deposits when the fuels are used in diesel engines having high pressure fuel 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 compounds or complexes or colloidal species.

In some embodiments, the metal-containing species comprises a fuel-borne catalyst.

In some embodiments, the metal-containing species comprises zinc.

In one preferred embodiment the diesel fuel composition of the invention comprises a fuel-borne catalyst which includes a metal selected from iron, cerium, group I and group II metals,

platinum, manganese and mixtures thereof. Preferred group I and group II metals include calcium and strontium.

Typically, the amount of 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 10 ppm by weight, based on the weight of the diesel fuel.

The fuel compositions of the present invention show improved performance when used in diesel engines having high pressure fuel systems compared with diesel fuels of the prior art.

According to a second aspect of the present disclosure there is provided an additive package which upon addition to a diesel fuel provides a composition as disclosed herein.

The additive package may comprise a mixture of the quaternary ammonium salt additive, the Mannich additive and optionally further additives, for example those described above. Alternatively the additive package may comprise a solution of additives, suitably in a mixture of hydrocarbon solvents for example aliphatic and/or aromatic solvents; and/or oxygenated solvents for example alcohols and/or ethers.

According to a third aspect of the present disclosure there is provided a method of operating a diesel engine, the method comprising combusting in the engine a composition as disclosed herein.

According to a fourth aspect of the present disclosure there is provided the use of a quaternary ammonium salt additive (i) and a Mannich reaction product additive (ii) in a diesel fuel composition as defined herein to improve the engine performance of a diesel engine when using said diesel fuel composition.

Preferred features of the second, third and fourth aspects are as defined in relation to the first aspect.

The improvement in performance may be achieved by the reduction or the prevention of the formation of deposits in a diesel engine. This may be regarded as an improvement in "keep clean" performance. Thus the present invention may provide a method of reducing or preventing the formation of deposits in a diesel engine by combusting in said engine a composition of the first aspect.

The improvement in performance may be achieved by the removal of existing deposits in a diesel engine. This may be regarded as an improvement in "clean up" performance. Thus the

present invention may provide a method of removing deposits from a diesel engine by combusting in said engine a composition of the first aspect.

In especially preferred embodiments the composition of the first aspect of the present invention may be used to provide an improvement in "keep clean" and "clean up" performance.

In some preferred embodiments the use of the third aspect may relate to the use of a quaternary ammonium salt additive, optionally in combination with a Mannich additive, in a diesel fuel composition to improve the engine performance of a diesel engine when using said diesel fuel composition wherein the diesel engine has a high pressure fuel system.

Modern diesel engines having a high pressure fuel system may be characterised in a number of ways. Such engines are typically equipped with fuel injectors having a plurality of apertures, each aperture having an inlet and an outlet.

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

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.

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.

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

Such modern diesel engines may be characterised by a fuel pressure of more than 1350 bar, preferably more than 1500 bar, more preferably more than 2000 bar.

The use of the present invention preferably improves the performance of an engine having one or more of the above-described characteristics.

The present invention is particularly useful in the prevention or reduction or removal of deposits on injectors of engines operating at high pressures and temperatures in which fuel may be recirculated and which comprise a plurality of fine apertures through which the fuel is delivered to the engine. The present invention finds utility in engines for heavy duty vehicles and passenger vehicles. Passenger vehicles incorporating a high speed direct injection (or HSDI) engine may for example benefit from the present invention.

Within the injector body of modern diesel engines having a high pressure fuel system, clearances of only 1-2 μm may exist between moving parts and there have been reports of engine problems in the field caused by injectors sticking and particularly injectors sticking open. Control of deposits in this area can be very important.

The diesel fuel compositions of the present invention may also provide improved performance when used with traditional diesel engines. Preferably the improved performance is achieved when using the diesel fuel compositions in modern diesel engines having high pressure fuel systems and when using the compositions in traditional diesel engines. This is important because it allows a single fuel to be provided that can be used in new engines and older vehicles.

The improvement in performance of the diesel engine system may be measured by a number of ways. Suitable methods will depend on the type of engine and whether "keep clean" and/or "clean up" performance is measured.

One of the ways in which the improvement in performance can be measured is by measuring the power loss in a controlled engine test. An improvement in "keep clean" performance may be measured by observing a reduction in power loss compared to that seen in a base fuel. "Clean up" performance can be observed by an increase in power when diesel fuel compositions of the invention are used in an already fouled engine.

The improvement in performance of the diesel engine having a high pressure fuel system may be measured by an improvement in fuel economy.

The use of the third aspect may also improve the performance of the engine by reducing, preventing or removing deposits in the vehicle fuel filter.

The level of deposits in a vehicle fuel filter may be measured quantitatively or qualitatively. In some cases this may only be determined by inspection of the filter once the filter has been removed. In other cases, the level of deposits may be estimated during use.

Many vehicles are fitted with a fuel filter which may be visually inspected during use to determine the level of solids build up and the need for filter replacement. For example, one such system uses a filter canister within a transparent housing allowing the filter, the fuel level within the filter and the degree of filter blocking to be observed.

Using the fuel compositions of the present invention may result in levels of deposits in the fuel filter which are considerably reduced compared with fuel compositions not of the present invention. This allows the filter to be changed much less frequently and can ensure that fuel filters do not fail between service intervals. Thus the use of the compositions of the present invention may lead to reduced maintenance costs.

In some embodiments the occurrence of deposits in a fuel filter may be inhibited or reduced. Thus a "keep clean" performance may be observed. In some embodiments existing deposits may be removed from a fuel filter. Thus a "clean up" performance may be observed.

Improvement in performance may also be assessed by considering the extent to which the use of the fuel compositions of the invention reduce the amount of deposit on the injector of an engine. For "keep clean" performance a reduction in occurrence of deposits would be observed. For "clean up" performance removal of existing deposits would be observed.

Direct measurement of deposit build up is not usually undertaken, but is usually inferred from the power loss or fuel flow rates through the injector.

The use of the third aspect may improve the performance of the engine by reducing, preventing or removing deposits including gums and lacquers within the injector body.

In Europe the Co-ordinating European Council for the development of performance tests for transportation fuels, lubricants and other fluids (the industry body known as CEC), has developed a new test, named CEC F-98-08, to assess whether diesel fuel is suitable for use in engines meeting new European Union emissions regulations known as the "Euro 5" regulations. The test is based on a Peugeot DW10 engine using Euro 5 injectors, and will hereinafter be referred to as the DW10 test. It will be further described in the context of the examples (see example 9).

Preferably the use of the fuel composition of the present invention leads to reduced deposits in the DW10 test. For "keep clean" performance a reduction in the occurrence of deposits is preferably observed. For "clean up" performance removal of deposits is preferably observed. The DW10 test is used to measure the power loss in modern diesel engines having a high pressure fuel system.

For older engines an improvement in performance may be measured using the XUD9 test. This test is described in relation to example 10.

Suitably the use of a fuel composition of the present invention may provide a "keep clean" performance in modern diesel engines, that is the formation of deposits on the injectors of these engines may be inhibited or prevented. Preferably this performance is such that a power loss of less than 5%, preferably less than 2% is observed after 32 hours as measured by the DW10 test.

Suitably the use of a fuel composition of the present invention may provide a "clean up" performance in modern diesel engines, that is deposits on the injectors of an already fouled engine may be removed. Preferably this performance is such that the power of a fouled engine may be returned to within 1% of the level achieved when using clean injectors within 32 hours as measured in the DW10 test.

Preferably rapid "clean-up" may be achieved in which the power is returned to within 1% of the level observed using clean injectors within 10 hours, preferably within 8 hours, suitably within 6 hours, preferably within 4 hours, more preferably within 2 hours.

Clean injectors can include new injectors or injectors which have been removed and physically cleaned, for example in an ultrasound bath.

Suitably the use of a fuel composition of the present invention may provide a "keep clean" performance in traditional diesel engines, that is the formation of deposits on the injectors of these engines may be inhibited or prevented. Preferably this performance is such that a flow loss of less than 50%, preferably less than 30% is observed after 10 hours as measured by the XUD-9 test.

Suitably the use of a fuel composition of the present invention may provide a "clean up" performance in traditional diesel engines, that is deposits on the injectors of an already fouled engine may be removed. Preferably this performance is such that the flow loss of a fouled engine may be increased by 10% or more within 10 hours as measured in the XUD-9 test.

In addition to achieving the improvement in performance of diesel engines as described herein the composition of the present invention has also been found to be stable on storage.

In particular the compositions of the present invention have been found to have a reduced tendency to form emulsions compared with similar compositions of the prior art.

According to a fifth aspect of the present invention there is provided the use of a first additive (i) comprising a quaternary ammonium salt and a second additive (ii) comprising a Mannich reaction product as defined herein to inhibit the formation of an emulsion in a diesel fuel composition.

By inhibit the formation of an emulsion we mean that an emulsion forms less readily and/or separates more easily compared to when similar engine performance additives of the prior art are used.

In another aspect, the present disclosure further provides the use of a Mannich reaction product (ii) as defined herein to improve the demulsification performance of a diesel fuel composition comprising a dehazer/demulsifier and a quaternary ammonium salt additive (i) as defined herein.

The tendency of water and fuels to separate rather than form an emulsion may be measured by using the standard test method ASTM D7451 which is described in example 8.

In this test, fuel and water are shaken under prescribed conditions and the time taken for the fuel water to separate and the quality of that separation are assessed.

The time taken for fuel and water to separate once mixed, is particularly important in ensuring the quality of fuel taken from storage tanks. When fresh fuel is added to a storage tank, if there is any emulsified fuel/water, then it would be unacceptable to supply that fuel to an end user until the fuel and water had separated. Similarly, the fuel clarity must be acceptable to the end user.

The interface condition and fuel water separation rating are particularly important for ensuring that microbial growth is minimised at the fuel / water interface.

This test is a common requirement for fuel companies when assessing fuel additive performance.

Any feature of any aspect of the invention may be combined with any other feature, where appropriate.

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

Example 1

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

A mixture of succinic anhydride prepared from 1000 Mn polyisobutylene (21425g) and diluent oil – pilot 900 (3781g) were heated with stirring to 110°C under a nitrogen atmosphere. Dimethylaminopropylamine (DMAPA, 2314g) was added slowly over 45 minutes maintaining batch temperature below 115°C. The reaction temperature was increased to 150°C and held for a further 3 hours. The resulting compound is a DMAPA succinimide.

This DMAPA succinimide was heated with styrene oxide (12.5g), acetic acid (6.25g) and methanol (43.4g) under reflux (approx 80°C) with stirring for 5 hours under a nitrogen atmosphere. The mixture was purified by distillation (30°C, -1 bar) to give the styrene oxide quaternary ammonium salt as a water white distillate.

Example 2 (comparative)

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

A reactor was charged with dodecylphenol (170.6g, 0.65 mol), ethylenediamine (30.1g, 0.5 mol) and Caromax 20 (123.9g). The mixture was heated to 95°C and formaldehyde solution, 37 wt% (73.8g, 0.9 mol) charged over 1 hour. The temperature was increased to 125°C for 3 hours and water removed. In this example the molar ratio of aldehyde (a) : amine (b) : phenol (c) was approximately 1.8:1:1.3.

Example 3

A polyiosbutene-substituted phenol was prepared as follows:

Polyisobutene having an average molecular wieght of 750 (450.3g, 0.53mol, 1 equiv) was heated to 45-50ºC and then phenol (150.0g, 1.59mol, 3equivs) was added. The turbid mixture was stirred and boron trifluoride dietherate (15.0g , 0.10mol , 0.18equivs) was added in 2-3ml aliquots over approx two hoursto provide a clear orange liquid which was stirred at 45-50ºC for 5 hours. Aqueous ammonia 35% (10.5g , 0.22moles) was then added and the reaction mixture stirred for 30mins. Vacuum distillation provided 81.3g of distillate. This was stirred at 70ºC in toluene (250.3g) for 5 mins, before adding 250.4g of water. The layers were separated and the toluene extract was washed twice more with water. Residual water and toluene removed under vacuum to provide the product as a viscous pale yellow liquid. (510.9g) having a toluene content of 2 wt% and a phenol content of less than 0.2wt%.

Example 4

Additive C, a Mannich additive of the present invention was prepared as follows:

PIB 750 Phenol (a phenol having a polyisobutenyl substituent of average molecular weight 750) with a residual PIB content of 5 wt% (447.8g, 425.4g "active" PIB phenol, 0.50moles, 1.3equivs) was mixed with ethylenediamine (25.3g, 0.38moles, 1equiv) and Caromax 20 solvent (225.6g). The homogenous mixture was heated to 90-95ºC. 36.7% formalin (57.12g, 0.69moles, 1.8equivs) was then added over 1hr and the reaction mixture was then held at 95ºC for 1hr. Water was removed using a Dean-Stark apparatus. Following distillation 708.3g of product was collected.

Example 5

Three Diesel Additive Formulations were prepared according to Table 1

Table 1

	% weight		
	Composition 1 (Comparative)	Composition 2 (Comparative)	Composition 3
Additive A	57.93	28.20	28.20
Additive B		29.73	
Additive C			29.73
Demulsifier / Dehazer(1)	2.67	2.67	2.67
Antifoam (2)	1.67	1.67	1.67
Solvent (3)	37.73	37.73	37.73

Demulsifier(1) A commercially available demulsifier/dehazer comprising a mixture of phenolic resins in aromatic solvent.

Antifoam (2) A commercially available antifoam additive comprising organomodified siloxanes in aromatic solvent.

Solvent (3) A commercially available blend of aromatic and aliphatic solvents

Example 6

Diesel fuel compositions were prepared by adding the additive compositions listed in table 1 to aliquots all drawn from a common batch of RF06 base fuel, and containing 1 ppm zinc (as zinc neodecanoate). In each case a total additive treat rate of 350ppm was used.

Table 2 below shows the specification for RF06 base fuel.

Table 2

Property	Units	Limits		Method
		Min	Max	
Cetane Number		52.0	54.0	EN ISO 5165
Density at 15°C	kg/m^3	833	837	EN ISO 3675
Distillation				
50% v/v Point	°C	245	-	
95% v/v Point	°C	345	350	
FBP	°C	-	370	
Flash Point	°C	55	-	EN 22719
Cold Filter Plugging Point	°C	-	-5	EN 116
Viscosity at 40°C	mm^2/sec	2.3	3.3	EN ISO 3104
Polycyclic Aromatic Hydrocarbons	% m/m	3.0	6.0	IP 391
Sulphur Content	mg/kg	-	10	ASTM D 5453
Copper Corrosion		-	1	EN ISO 2160
Conradson Carbon Residue on 10% Dist. Residue	% m/m	-	0.2	EN ISO 10370
Ash Content	% m/m	-	0.01	EN ISO 6245
Water Content	% m/m	-	0.02	EN ISO 12937
Neutralisation (Strong Acid) Number	mg KOH/g	-	0.02	ASTM D 974
Oxidation Stability	mg/mL	-	0.025	EN ISO 12205
HFRR (WSD1,4)	µm	-	400	CEC F-06-A-96
Fatty Acid Methyl Ester		prohibited		

Example 7

Diesel fuel compositions were prepared comprising the additive compositions listed in Table 1, added to aliquots all drawn from a common batch of a B7 reference fuel prepared from 93% RF06 base fuel and 7% of a biodiesel comprising rapeseed oil methyl ester. Again, a total additive treat rate of 350ppm was used.

Example 8

The fuel compositions prepared in examples 6 and 7 were tested using a modified version of ASTM D7451 Water Separation Properties of Light and Middle Distillate, and Compression and Spark Ignition Fuels.

This test is designed to evaluate the tendency of water and fuels to separate rather than form emulsions when they contain potential emulsion forming additives or components. In this test, 80ml of fuel and 20ml of water are shaken together under controlled conditions and then allowed to stand for a period of time. After 5 minutes, the volume of the aqueous layer, the fuel clarity, the fuel water separation and the interface condition are rated according to standard definitions.

The test was performed in accordance with the ASTM D7451 - 08 method with the exception of :-

6.1) Stoppered 100ml measuring cyclinders as specified in ASTM D1094 were used instead of the tubes specified in D7451.

10.1) The aqueous phase was added to the tube first, rather than the fuel

11.1) The time taken to reach 20ml clear water was also recorded.

Please note: the numbered sections above refer to the numbered sections of the D7451 test method.

This test is a common requirement for fuel companies when assessing fuel additive performance.

The results of the ASTM D 7451 tests in the two fuels are given in tables 3 to 6.

In these tests, the time taken for 20ml water to return and the volume of aqueous layer at 5 minutes each give an indication of how quickly a fuel / water emulsion will separate back into two distinct phases. The interface condition rating, fuel clarity rating and fuel –water separation rating all give an indication of how well the separation has taken place

The results of duplicate ASTM D7451 tests on fuel compositions of example 6 using aqueous phases at pH4, pH7 and pH 9 are given in tables 3-5.

The results of duplicate ASTM D7451 tests on fuel compositions of example 7 using aqueous phases at pH4 are given in table 6.

Table 3 – Aqueous Phase pH7 (RF06 base fuel and 350ppm total additive):

Additive Composition	T20 (Time taken for 20ml of water to return in (mins))	Volume of Aqueous Layer at 5 mins (ml)	Interface Condition Rating at 5 mins	Fuel Clarity Rating at 5 mins	Fuel- Water Separation Rating at 5 mins
Composition 1 (Comparative)	10:00	14	4	6	3
	10:00	14	4	6	3
Composition 2 (Comparative)	4:45	20	2	6	2
	4:45	20	2	6	2
Composition 3	3:15	20	1b-2	6	2
	3:15	20	1b-2	6	2

Table 4 – Aqueous Phase pH4 (RF06 base fuel and 350ppm total additive):

Additive Composition	T20 (Time taken for 20ml of water to return in (mins))	Volume of Aqueous Layer at 5 mins (ml)	Interface Condition Rating at 5 mins	Fuel Clarity Rating at 5 mins	Fuel- Water Separation Rating at 5 mins
Composition 1 (Comparative)	10:00	18	3	6	2
	10:00	17	3	6	2
Composition 2 (Comparative)	4:15	20	2	6	2
	5:30	19	2	6	2
Composition 3	2:45	20	1b	6	2
	3:45	20	1b	6	2

Table 5 Aqueous Phase pH9 (RF06 base fuel and 350ppm total additive):

Additive Composition	T20 (Time taken for 20ml of water to return in (mins))	Volume of Aqueous Layer at 5 mins (ml)	Interface Condition Rating at 5 mins	Fuel Clarity Rating at 5 mins	Fuel- Water Separation Rating at 5 mins
Composition 1 (Comparative)	6:30	19	2	6	2
	9:00	17	2-3	6	2
Composition 2 (Comparative)	4:10	20	2	6	2
	3:55	20	2	6	2
Composition 3	3:15	20	2	6	2
	3:30	20	2	6	2

Table 6 - Aqueous Phase pH4 (B7 base fuel and 350ppm total additive):

Additive Composition	T20 (Time taken for 20ml of water to return in (mins))	Volume of Aqueous Layer at 5 mins (ml)	Interface Condition Rating at 5 mins	Fuel Clarity Rating at 5 mins	Fuel- Water Separation Rating at 5 mins
Composition 1 (Comparative)	>30	0	4	6	3
	>30	0	4	6	3
Composition 2 (Comparative)	20:00	11	4	6	3
	20:00	10	4	6	3
Composition 3	10:00	19	2	6	2
	10:30	19	2	6	2

In the above tests, Fuel Clarity and Fuel – Water Separation ratings after 5 minutes were fairly similar. However, as evidenced by the volume of the aqueous layer after 5 minutes, the interface condition rating and the time taken for 20ml of water to return, composition 3 gave significantly better performance than compositions 1 or 2.

Example 9

The performance of diesel fuel compositions of the present invention in modern diesel engines may be tested according to the CECF-98-08 DW 10 method.

The engine of the injector fouling test is the PSA DW10BTED4. In summary, the engine characteristics are:

Design: Four cylinders in line, overhead camshaft, turbocharged with EGR
Capacity: 1998 cm^3
Combustion chamber: Four valves, bowl in piston, wall guided direct injection
Power: 100 kW at 4000 rpm
Torque: 320 Nm at 2000 rpm
Injection system: Common rail with piezo electronically controlled 6-hole injectors.
Max. pressure: 1600 bar (1.6 x 10^8 Pa). Proprietary design by SIEMENS VDO
Emissions control: Conforms with Euro IV limit values when combined with exhaust gas post-treatment system (DPF)

This engine was chosen as a design representative of the modern European high-speed direct injection diesel engine capable of conforming to present and future European emissions requirements. The common rail injection system uses a highly efficient nozzle design with rounded inlet edges and conical spray holes for optimal hydraulic flow. This type of nozzle, when combined with high fuel pressure has allowed advances to be achieved in combustion efficiency, reduced noise and reduced fuel consumption, but are sensitive to influences that can disturb the fuel flow, such as deposit formation in the spray holes. The presence of these deposits causes a significant loss of engine power and increased raw emissions.

The test is run with a future injector design representative of anticipated Euro V injector technology.

It is considered necessary to establish a reliable baseline of injector condition before beginning fouling tests, so a sixteen hour running-in schedule for the test injectors is specified, using non-fouling reference fuel.

Full details of the CEC F-98-08 test method can be obtained from the CEC. The coking cycle is summarised below.

1. A warm up cycle (12 minutes) according to the following regime:

Step	Duration	Engine Speed	Torque (Nm)

	(minutes)	(rpm)	
1	2	idle	<5
2	3	2000	50
3	4	3500	75
4	3	4000	100

2. 8 hrs of engine operation consisting of 8 repeats of the following cycle

Step	Duration (minutes)	Engine Speed (rpm)	Load (%)	Torque (Nm)	Boost Air After IC (°C)
1	2	1750	(20)	62	45
2	7	3000	(60)	173	50
3	2	1750	(20)	62	45
4	7	3500	(80)	212	50
5	2	1750	(20)	62	45
6	10	4000	100	*	50
7	2	1250	(10)	20	43
8	7	3000	100	*	50
9	2	1250	(10)	20	43
10	10	2000	100	*	50
11	2	1250	(10)	20	43
12	7	4000	100	*	50

* for expected range see CEC method CEC-F-98-08

3. Cool down to idle in 60 seconds and idle for 10 seconds

4. 4 hrs soak period

The standard CEC F-98-08 test method consists of 32 hours engine operation corresponding to 4 repeats of steps 1-3 above, and 3 repeats of step 4. ie 56 hours total test time excluding warm ups and cool downs.

In each case, a first 32 hour cycle was run using new injectors and RF-06 base fuel having added thereto 1ppm Zn (as neodecanoate). This resulted in a level of power loss due to fouling of the injectors.

A second 32 hour cycle may then be run as a 'clean up' phase. The dirty injectors from the first phase were kept in the engine and the fuel changed to RF-06 base fuel having added thereto 1ppm Zn (as neodecanoate) and the test additives.

Example 10

The effectiveness of the additives of the present invention in older engine types may be assessed using a standard industry test - CEC test method No. CEC F-23-A-01.

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

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

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

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

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

Example 11

A diesel fuel composition was prepared by adding 350 ppm of additive composition 3 described in example 5 to a base fuel having the specification defined in example 6. This fuel

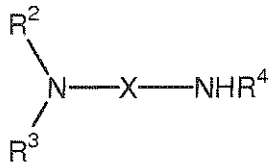
and a base fuel were tested in a Peugeot XUD9 A/L Engine according to the method described in example 10. The results are shown in table 7.

Table 7

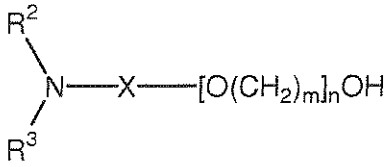
Additive Composition	Treat rate, mg/kg	% Flow Loss
Basefuel	-	76.8
Composition 3	350	2.3

Claims:

1. A diesel fuel composition comprising a first additive (i) comprising a quaternary ammonium salt and a second additive (ii) comprising a Mannich reaction product; wherein the quaternary ammonium salt additive (i) is formed by the reaction a quaternising agent which is not an ester and a compound formed by the reaction of a hydrocarbyl-substituted acylating agent and an amine of formula (B1) or (B2):



(B1)



(B2)

wherein R^2 and R^3 are the same or different alkyl, alkenyl or aryl groups having from 1 to 22 carbon atoms; X is a bond or alkylene group having from 1 to 20 carbon atoms; n is from 0 to 20; m is from 1 to 5; and R^4 is hydrogen or a C_1 to C_{22} alkyl group; and wherein the Mannich reaction product additive (ii) is the product of a Mannich reaction between:

(a) an aldehyde;

(b) an amine; and

(c) a substituted phenol;

wherein the phenol is substituted with at least one branched hydrocarbyl group having a molecular weight of between 200 and 3000.

2. A diesel fuel composition according to claim 1 wherein the quaternising agent is selected from selected from dialkyl sulfates, benzyl halides, hydrocarbyl substituted carbonates, hydrocarbyl susbsituted epoxides in combination with an acid, alkyl halides, alkyl sulfonates, sultones, hydrocarbyl substituted phosphates, hydrocarbyl substituted borates, alkyl nitrites, alkyl nitrates, N-oxides or mixtures thereof.

3. A diesel fuel composition according to claim 2 wherein the quaternising agent is selected from selected from dialkyl sulfates, benzyl halides, hydrocarbyl substituted carbonates and hydrocarbyl susbsituted epoxides in combination with an acid.

4. A diesel fuel composition according to any preceding claim wherein the hydrocarbyl substituted acylating agent is reacted with a diamine compound of formula (B1).

5. A diesel fuel composition according to any preceding claim wherein additive (i) is a salt of tertiary amine prepared from dimethylamiropropylamine and a polyisobutylene-substituted succinic anhydride.

6. A diesel fuel composition according to any preceding claim wherein component (a) used to prepare additive (ii) is formaldehyde.

7. A diesel fuel composition according to any preceding claim wherein component (b) used to prepare additive (ii) is a (poly)ethylene polyamine.

8. A diesel fuel composition according to any preceding claim wherein component (c) used to prepare additive (ii) is a polyisobutylene-substituted phenol.

9. A diesel fuel composition according to any preceding claim wherein in the Mannich reaction used to form additive (ii) the molar ratio of component (a) to component (b) is 2.2-1.01:1; the molar ratio of component (a) to component (c) is 1.99-1.01:1 and the molar ratio of component (b) to component (c) is 1:1.01-1.99.

10. A diesel fuel composition according to claim 9 wherein in the reaction used to make the Mannich additive the molar ratio of component (a) to component (b) is 2-1.4:1, the molar ratio of component (a) to component (c) is 1.7-1.1:1 and the molar ratio of component (b) to component (c) is 1:1.1-1.7.

11. A diesel fuel composition according to any preceding claim wherein the diesel fuel comprises a non-renewable Fischer Tropsch fuel and/or biodiesel.

12. A diesel fuel composition as claimed in any preceding claim which further comprises a fuel-borne catalyst which includes a metal selected from iron, cerium, group I and group II metals, platinum, manganese and mixtures thereof.

13. An additive package which upon addition to a diesel fuel provides a composition as claimed in any preceding claim.

14. A method of operating a diesel engine, the method comprising combusting in the engine a composition as claimed in any of claims 1 to 12.

15. Use of a quaternary ammonium salt additive (i) and a Mannich reaction product additive (ii) in a diesel fuel composition as defined in any preceding claim to improve the engine performance of a diesel engine when using said diesel fuel composition.

16. The use according to claim 15 to provide "keep clean" performance and/or "clean up" performance.

17. A use according to claim 15 or claim 16 to improve the performance of a modern diesel engine having a high pressure fuel system and/or to improve the performance of a traditional diesel engine.

18. Use of a quaternary ammonium salt additive (i) and a Mannich reaction product additive (ii) as defined in any preceding claim in a diesel fuel composition to inhibit the formation of an emulsion.

19. The use of a Mannich reaction product (ii) as defined in any preceding claim to improve the demulsification performance of a diesel fuel composition comprising a demulsifier/dehazer and a quaternary ammonium salt additive (i) as defined in any preceding claim.