Method and Use

The present invention relates to methods and uses for improving the performance of diesel engines using fuel additives. In particular the invention relates to additives for diesel fuel compositions for use in 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. Furthermore, the timing, quantity and control of fuel injection has become increasingly precise. This precise fuel metering must be maintained to achieve optimal performance.

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.

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, lacquers 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. In recent years the need to reduce emissions has led to the continual redesign of injection systems to help meet lower targets. This has led to increasingly complex injectors and lower tolerance to deposits.

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 and those containing metallic species may lead to increased deposits.

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 and increased exhaust emissions and poor fuel economy.

Deposits are known to occur in the spray channels of the injector, leading to reduced flow and power loss. As the size of the injector nozzle hole is reduced, the relative impact of deposit build up becomes more significant. Deposits are also known to occur at the injector tip. Here they affect the fuel spray pattern and cause less effective combustion and associated higher emissions and increased fuel consumption.

In addition to these “external” injector deposits in the nozzle hole and at the injector tip which lead to reduced flow and power loss, deposits may occur within the injector body causing further problems. These deposits may be referred to as internal diesel injector deposits (or IDIDs). IDIDs occur further up inside the injector on the critical moving parts. They can hinder the movement of these parts affecting the timing and quantity of fuel injection. Since modern diesel engines operate under very precise conditions these deposits can have a significant impact on performance.

IDIDs cause a number of problems, including power loss and reduced fuel economy due to less than optimal fuel metering and combustion. Initially the engine may experience cold start problems and/or rough engine running. These deposits can lead to more serious injector sticking. This occurs when the deposits stop parts of the injector from moving and thus the injector stops working. When several or all of the injectors stick the engine may fail completely.

IDIDs are recognised as a serious problem by those working in the field and a new engine test has been developed by the industry based organisation, the Coordinating European Council (CEC). The IDID DW10C test was developed to be able to discriminate between a fuel that produces no measurable deposits and one which produces deposits that cause startability issues considered unacceptable. The objective of the test is to discriminate between fuels that differ in their ability to produce IDIDs in direct injection common rail diesel engines.

The present inventors have studied internal diesel injector deposits and have found that they contain a number of components. As well as carbonaceous deposits the presence of lacquers and/or carboxylate residues can lead to injector sticking.

Lacquers are varnish-like deposits which are insoluble in fuel and common organic solvents. Some occurrences of lacquers have been found by analysis to contain amide functionality and it has been suggested that they form due to the presence of low molecular weight amide containing species in the fuel.

Carboxylate residues may be present from a number of sources. By carboxylate residues we mean to refer to salts of carboxylic acids. These may be short chain carboxylic acids but more commonly long chain fatty acid residues are present. The carboxylic residues may be present as ammonium and/or metal salts. Both carboxylic acids and metals may be present in diesel fuel from a number of sources. Carboxylic acids may occur due to oxidation of the fuel, may form during the combustion process and are commonly added into fuel as lubricity additives and/or corrosion inhibitors. Residual fatty acids may be present in the fatty acid methyl esters included as biodiesel and they may also be present as byproducts in other additives. Derivatives of fatty acids may also be present and these may react or decompose to form carboxylic acids.

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

The present inventors believe that one of the many causes of injector sticking occurs when metal or ammonium species react with carboxylic acid species in the fuel. One example of injector sticking has arisen due to sodium contamination of the fuel. Sodium contamination may occur for a number of reasons. For example, sodium hydroxide may be used in a washing step in the hydrodesulfurisation process and could lead to contamination. Sodium may also be present due to the use of sodium-containing corrosion inhibitors in pipelines. Another example can arise from the presence of calcium from, for example, interaction with or contamination with a lubricant or from calcium chloride used in salt drying processes in refineries. Other metal contamination may occur for example during transportation due to water bottoms.

Metal contamination of diesel fuel and the resultant formation of carboxylate salts is believed to be a significant cause of injector sticking. The formation of lacquers is yet another major cause of injector sticking.

One approach to combatting IDIDs and injector sticking resulting from carboxylate salts is to try to eliminate the source of metal contamination and/or carboxylic acids or to try to ensure that particularly problematic carboxylic acids are eliminated. This has not been entirely successful and there is a need for additives to provide control of IDIDs.

Deposit control additives are often included in fuel to combat deposits in the injector nozzle or at the injector tip. These may be referred to herein as “external injector deposits”. Additives are also used to control deposits on vehicle fuel filters. However additives which have been found to be useful to control “external deposits” and fuel filter deposits are not always effective at controlling IDIDs. A challenge for the additive formulator is to provide more effective detergents.

It is an aim of the present invention to provide methods and uses which improve the performance of a diesel engine, especially a diesel engine having a high pressure fuel system. This may be achieved for example by preventing or reducing the formation of IDIDs and/or by reducing or removing existing IDIDs. The invention provides methods and uses which control “external injector deposits” and/or fuel filter deposits.

Reducing or preventing the formation of deposits may be regarded as providing “keep clean” performance. Reducing or removing existing deposits may be regarded as providing “clean up” performance. It is an aim of the present invention to provide “keep clean” and/or “clean up” performance.

Many different types of compounds are known in the art for use as detergent additives in fuel oil compositions, for the control of deposits in engines. Examples of common detergents include hydrocarbyl-substituted amines; hydrocarbyl substituted succinimides; Mannich reaction products and quaternary ammonium salts. All of these known detergents are nitrogen-containing compounds.

The present invention relates in particular to detergent compounds for diesel fuel that do not contain nitrogen. Such compounds are much less commonly used as detergents.

US2013/0192124 discloses the use of diacid compounds as detergents. The exemplified detergent is a polyolefin acid derived from a polyisobutylene having a number average

molecular weight of 1000 and a dicarboxylic acid. However, the inventors have surprisingly found that certain esters of polycarboxylic acids and polyhydric alcohols are particularly effective as detergents, especially in modern diesel engines having a high pressure fuel system.

According to a first aspect of the present invention there is provided a diesel fuel composition comprising as an additive an ester compound which is the reaction product of an optionally substituted polycarboxylic acid or an anhydride thereof and a polyhydric alcohol of formula H-$(OR)_n$-OH, wherein R is an optionally substituted alkylene group and n is at least 1.

According to a second aspect of the present invention there is provided a method of combatting deposits in a diesel engine, the method comprising combusting in the engine a diesel fuel composition comprising as an additive an ester compound which is the reaction product of an optionally substituted polycarboxylic acid or an anhydride thereof and a polyhydric alcohol of formula H-$(OR)_n$-OH, wherein R is an optionally substituted alkylene group and n is at least 1.

According to a third aspect of the present invention there is provided the use of an ester compound as a detergent additive in a diesel fuel composition in a diesel engine; wherein the ester compound is the reaction product of an optionally substituted polycarboxylic acid or an anhydride thereof and a polyhydric alcohol of formula H-$(OR)_n$-OH, wherein R is an optionally substituted alkylene group and n is at least 1.

The method of the second aspect preferably involves combusting in the engine a composition of the first aspect.

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

The present invention relates to a composition, a method and a use involving a fuel additive. This additive is the reaction product of an optionally substituted polycarboxylic acid or an anhydride thereof and a polyhydric alcohol of formula H-$(OR)_n$-OH. The additive may be referred to herein as “the additive of the present invention” or as “the ester additive”.

Compounds of this type are known in the art and are described, for example in US2993773. However, they have not previously been used as detergents in diesel fuels.

The additive of the present invention is the reaction product of an optionally substituted polycarboxylic acid or anhydride thereof. In some embodiments the polycarboxylic acid or anhydride is unsubstituted. In preferred embodiments the additive is prepared from a hydrocarbyl substituted polycarboxylic acid or an anhydride thereof.

As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

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

(ii) substituted hydrocarbon groups, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent (e.g., halo (e.g. chloro, fluoro or bromo), hydroxy, alkoxy (e.g. C_1 to C_4 alkoxy), keto, acyl, cyano, mercapto, amino, amido, nitro, nitroso, sulfoxy, nitryl and carboxy);

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

The additive of the present invention is the reaction product of an optionally substituted polycarboxylic acid or anhydride thereof. Suitable polycarboxylic acids include pyromellitic acid, maleic acid, fumaric acid, oxalic acid, malonic acid, pimelic acid, suberic acid, glutaric acid, adipic acid, phthalic acid, succinic acid, citric acid, azelaic acid, sebacic acid and dimerised fatty acids.

In one embodiment the additive of the present invention is the reaction product of an optionally substituted polycarboxylic acid or anhydride thereof selected from pyromellitic acid, malonic

acid, sebacic acid and succinic acid. Suitably the additive is an optionally substituted pyromellitic or succinic acid, or an anhydride thereof.

Preferred acids are dicarboxylic acids. Thus preferably the ester additive of the invention is the reaction product of a hydrocarbyl substituted dicarboxylic acid or hydrocarbyl substituted anhydride thereof and a polyhydric alcohol of formula $H-(OR)_n-OH$.

Suitable dicarboxylic acids include maleic acid, glutaric acid, fumaric acid, oxalic acid, malonic acid, pimelic acid, suberic acid, adipic acid, phthalic acid, succinic acid, azelaic acid, sebacic acid and dimerised fatty acids.

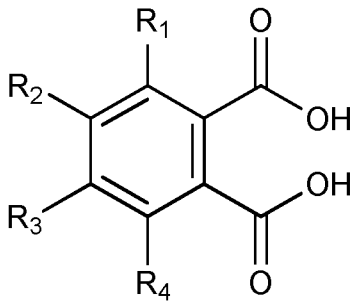
In some embodiments the ester may be prepared from a carboxylic acid of formula $HOOC(CH_2)_nCOOH$ wherein n is from 1 to 20, preferably from 2 to 16, more preferably from 4 to 12, for example from 6 to 10. In one embodiment n is 8 and the ester is prepared from sebacic acid.

In some embodiments the ester is prepared from a dimerised fatty acid. Such compounds are formed from the dimerization of unsaturated fatty acids, for example unsaturated fatty acids having 6 to 50, suitably 8 to 40, preferably 10 to 36, for example 10 to 20 carbon atoms, or 16 to 20 carbon atoms.

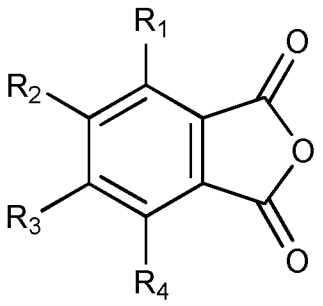
Such dimerised fatty acids may have 12 to 100 carbon atoms, preferably 16 to 72 carbon atoms such as 20 to 40 carbon atoms, for example 32 to 40 carbon atoms.

These compound are well known in the art, particularly for their use as corrosion inhibitors. Particularly preferred dimerised fatty acids are mixtures of C36 dimer acids such as those prepared by dimerising oleic acid, linoleic acid and mixtures comprising oleic and linoleic acid, for example, tall oil fatty acids.

In some embodiments the additive is prepared from phthalic acid or an anhydride thereof, having the formula (A1) or (A2):



(A1)

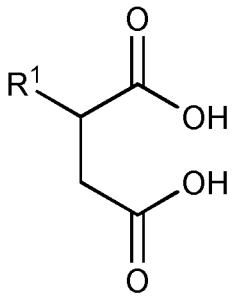


(A2)

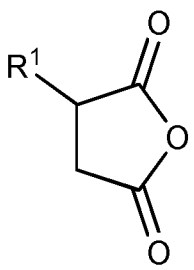
wherein each of R^1, R^2, R^3 and R^4 is independently hydrogen or an optionally substituted hydrocarbyl group.

Preferably each is hydrogen or an optionally substituted alkyl or alkenyl group. Preferably three of R^1, R^2, R^3 and R^4 are hydrogen and the other is an optionally substituted C_1 to C_{500} alkyl or alkenyl group, preferably a C_2 to C_{100} alkyl or alkenyl group, preferably a C_6 to C_{50} alkyl or alkenyl group, preferably a C_8 to C_{40} alkyl or alkenyl group, more preferably a C_{10} to C_{36} alkyl or alkenyl group, preferably a C_{12} to C_{22} alkyl or alkenyl group, suitably a C_{16} to C_{28} alkyl or alkenyl group, for example a C_{20} to C_{24} alkyl or alkenyl group. The alkyl or alkenyl group may be straight chain or branched. Preferably R^1, R^2 and R^4 are hydrogen and R^3 is an optionally substituted alkyl or alkenyl group.

Preferably the additive of the present invention is the reaction product of an alcohol of formula $H-(OR)_n-OH$ and an optionally substituted succinic acid or anhydride thereof of formula (A3) or (A4):



(A3)



(A4)

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

In some embodiments R^1 is hydrogen. Thus in some embodiments the additive of the present invention is the reaction product of an alcohol of formula H-$(OR)_n$-OH and succinic acid or succinic anhydride.

In some embodiments R^1 is an optionally substituted C_1 to C_{500} alkyl or alkenyl group, preferably a C_2 to C_{100} alkyl or alkenyl group, preferably a C_6 to C_{50} alkyl or alkenyl group, preferably a C_8 to C_{40} alkyl or alkenyl group, more preferably a C_{10} to C_{38} alkyl or alkenyl group, preferably a C_{16} to C_{36} alkyl or alkenyl group, suitably a C_{18} to C_{32} alkyl or alkenyl group.

In some embodiments R^1 has at least 20 carbon atoms.

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

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

In some embodiments R^1 has a molecular weight of from 100 to 5000, preferably from 300 to 4000, suitably from 450 to 2500, for example from 500 to 2000 or from 600 to 1500.

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

In some embodiments R^1 is a polyisobutenyl group, preferably having a number average molecular weight of from 100 to 5000, preferably from 200 to 2000, suitably from 220 to 1300, for example from 240 to 900.

In some embodiments R^1 is a polyisobutenyl group having a number average molecular weight of from 400 to 700.

In some embodiments R^1 is a polyisobutenyl group having a number average molecular weight of from 180 to 400.

In some embodiments R^1 is a polyisobutenyl group having a number average molecular weight of from 800 to 1200.

In some embodiments R^1 has less than 30 carbon atoms. Preferably less than 28 carbon atoms, suitably less than 26 carbon atoms.

In some preferred embodiments R^1 is an alkyl or alkenyl group having 6 to 40 carbon atoms, preferably 10 to 38 carbon atoms.

In some preferred embodiments R^1 is an alkyl or alkenyl group having 16 to 36 carbon atoms, suitably 18 to 26 carbon atoms, preferably 19 to 25 carbon atoms, for example 20 to 24 carbon atoms.

In some embodiments R^1 is an alkyl or alkenyl group having 10 to 20 carbon atoms, for example 12 or 18 carbon atoms.

In some embodiments R^1 may be the residue of an internal olefin. In such embodiments the compound of formula (A3) or (A4) is suitably obtained by the reaction of maleic acid with an internal olefin.

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.

In some embodiments the additive of the present invention is the reaction product of a succinic acid or anhydride of formula (A3) or (A4) and an alcohol of formula $H-(OR)_n-OH$; wherein R^1 is an alkyl or alkenyl group having 6 to 36 carbon atoms or a polyisobutenyl group having a number average molecular weight of from 200 to 1300.

In some especially preferred embodiments the additive of the present invention is the reaction product of a succinic acid or anhydride having a C_{10} to C_{30}, preferably a C_{20} to C_{24} alkyl or alkenyl group and an alcohol of formula $H-(OR)_n-OH$.

R is an optionally substituted alkylene group.

In some embodiments the alcohol of formula H-$(OR)_n$-OH has more than 2 hydroxy groups and the group R is a hydroxy substituted alkylene group. Such a group may have 1, 2 or more hydroxyl groups.

In some embodiments the alcohol of formula H-$(OR)_n$-OH may be a sugar derived unit in which R includes one or more hydroxy residues.

R may be substituted to form a cyclic alkylene unit. One or more heteroatoms may be present in the cyclic alkylene unit. For example the unit may contain an ether linkage.

In some embodiments R may be one or more saccharide units or may be substituted with one or more saccharide units.

In some embodiments H-$(OR)_n$-OH may be selected from glycerol, pentaerythritol and trimethylolpropane.

In some embodiments H-$(OR)_n$-OH may be a sugar component for example, trehalose or sorbitol.

Preferably R is an unsubstituted alkylene group.

Preferably R is an optionally substituted alkylene group having 1 to 50 carbon atoms, preferably 1 to 40 carbon atoms, preferably 1 to 30 carbon atoms, more preferably 1 to 20 carbon atoms, suitably 1 to 10 carbon atoms, for example 2 to 6 or 2 to 4 carbon atoms.

Preferably R is an unsubstituted alkylene group having 1 to 50 carbon atoms, preferably 1 to 20, more preferably 1 to 10, suitably 2 to 6, for example 2 to 4 carbon atoms. R may be straight chained or branched.

Suitably R may be an ethylene, propylene, butylene, pentylene, or hexylene group. When R has more than 2 carbon atoms any isomer may be present. In some preferred embodiments R is an ethylene or a propylene group, most preferably a propylene group.

In some embodiments in which n is 1, R may be a group of formula $(CH_2)_x$ wherein x is from 2 to 12, preferably from 2 to 6.

In some embodiments in which n is 1, R is a straight chain or branched alkylene group and the polyhydric alcohol is selected from ethylene glycol, propylene glycol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol and neopentyl glycol.

In some preferred embodiments in which n is 1, R is a straight chain or branched alkylene group having 2 to 6, preferably 3 to 5 carbon atoms.

Suitable compounds of this type include propylene glycol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol and neopentyl gycol.

In some preferred embodiments R is preferably $CR^1R^2CR^3R^4$ and the polyhydric alcohol has the formula $H-(OCR^1R^2CR^3R^4)_nOH$ wherein each of R^1, R^2, R^3 and R^4 is independently hydrogen or an optionally substituted alkyl group. Preferably each R^1, R^2, R^3 and R^4 is independently selected from hydrogen or an optionally substituted alkyl group having 1 to 20, preferably 1 to 12, more preferably 1 to 4, for example 1 to 2 carbon atoms.

Preferably each of R^1, R^2, R^3 and R^4 is independently selected from hydrogen and an unsubstituted alkyl group, preferably having 1 to 20 carbon atoms, suitably 1 to 12 carbon atoms, preferably 1 to 4 atoms, for example 1 or 2 carbon atoms. Preferably at least two of R^1, R^2, R^3 and R^4 is hydrogen, more preferably at least three of R^1, R^2, R^3 and R^4 is hydrogen.

In some embodiments R^1, R^2, R^3 and R^4 are all hydrogen and R is an ethylene group CH_2CH_2.

In some embodiments three of R^1, R^2, R^3, and R^4 is hydrogen and the other is an unsubstituted alkyl group having 1 to 12, preferably 1 to 4, suitably 1 to 2, and most preferably 1 carbon atoms.

In some embodiments the polyhydric alcohols used to prepare the additive of the present invention are prepared from epoxides, preferably terminal epoxides.

R may comprise a mixture of isomers. For example when R is propylene, the polyhydric alcohol may include moieties $-CH_2CH(CH_3)-$ and $-CH(CH_3)CH_2-$ in any order within the chain.

R may comprise a mixture of different groups for example ethylene, propylene or butylene units. Block copolymer units are preferred in such embodiments.

R is preferably an ethylene, propylene or butylene group. R may be an n-propylene or n-butylene group or an isopropylene or isobutylene group. For example R may be $–CH_2CH_2-$, $-CH_2CH(CH_3)-$, $-CH_2C(CH_3)_2$, $-CH(CH_3)CH(CH_3)-$ or $-CH_2CH(CH_2CH_3)-$.

Preferably R is ethylene or propylene. More preferably R is $-CH_2CH_2-$ or $-CH(CH_3)CH_2-$. Most preferably R is $-CH(CH_3)CH_2-$.

n is at least 1. Preferably n is from 1 to 100, preferably from 1 to 50, more preferably from 1 to 30, more preferably from 1 to 24, preferably from 1 to 20, suitably from 1 to 16, preferably from 1 to 14.

In some embodiments n is from 4 to 10, for example from 6 to 8.

In some embodiments n is from 1 to 6, suitably from 2 to 5, for example 3 or 4.

In some embodiments n is from 8 to 16, for example from 11 to 14.

Preferably the polyhydric alcohol has a number average molecular weight of from 60 to 6000, preferably from 60 to 3000, more preferably from 60 to 2000, more preferably from 60 to 1500, preferably from 60 to 1200, suitably from 60 to 1000, preferably from 60 to 850.

In some embodiments, the number average molecular weight is from 190 to 600, for example from 280 to 490

In some embodiments the number average molecular weight is from 60 to 370, suitably from 110 to 320, for example 190 to 260 or 140-200

In some embodiments the number average molecular weight is from 360 to 950, for example 500 to 840.

In some embodiments the polyhydric alcohol may be a polypropylene glycol having a number average molecular weight of 425.

In some embodiments the polyhydric alcohol may be a polypropylene glycol having a number average molecular weight of 725.

In some embodiments the polyhydric alcohol may be a polypropylene glycol having a number average molecular weight of 1000.

In some embodiments the polyhydric alcohol may be a polyethylene glycol having a number average molecular weight of 400.

In some embodiments the polyhydric alcohol may be a polyethylene glycol having a number average molecular weight of 950-1050.

In some embodiments the polyhydric alcohol may be selected from triethylene glycol, tetraethyelene glycol, propylene glycol, dipropylene glycol and tripropylene glycol.

In some embodiments the polyhydric alcohol is selected from ethylene glycol, propylene glycol and oligomers or polymers thereof.

The skilled person will appreciate that commercial sources of alcohols of formula $H-(OR)_n-OH$ will often contain mixtures of compounds, for example in which n may be between 6 and 10. Commercial sources of substituted succinic acids and anhydrides may also contain mixtures of compounds, for example including different compounds with substituents having 20 to 24 carbon atoms.

In some embodiments the ester additive of the present invention is the reaction product of an optionally substituted polycarboxylic acid or anhydride thereof selected from pyromellitic acid, malonic acid, sebacic acid and succinic acid; and a polyhydric alcohol of formula $H-(OR)_n-OH$ selected from ethylene glycol, propylene glycol and oligomers or polymers thereof; alkane diols having 1 to 12, preferably 3 to 6 carbon atoms and sugar alcohols.

In some embodiments the ester additive of the present invention is the reaction product of an optionally substituted polycarboxylic acid or anhydride thereof selected from pyromellitic acid and succinic acid; and a polyhydric alcohol of formula $H-(OR)_n-OH$ selected from ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, trehalose, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol and a polyethylene or polypropylene glycol having a number average molecular weight of 300 to 1200.

In some embodiments the ester additive of the present invention is the reaction product of a succinic acid or anhydride of formula (A3) or (A4) and an alcohol of formula $H-(OR)_n-OH$; wherein R^1 is an alkyl or alkenyl group having 6 to 36 carbon atoms or a polyisobutenyl group having a number average molecular weight of from 200 to 1300; wherein the alcohol of formula $H-(OR)_n-OH$ is selected from ethylene glycol, diethylene glycol, triethylene glycol,

tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, trehalose, sorbitol, glycerol, pentaerythritol, trimethylolpropane, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol and a polyethylene or polypropylene glycol having a number average molecular weight of 300 to 1200.

In some embodiments the ester additive of the invention is the reaction product of a succinic acid or anhydride thereof having an alkyl or alkenyl substituent having 6 to 36 carbon atoms and a polypropylene glycol having a number average molecular weight of 300 to 800.

In some embodiments the ester additive of the invention is the reaction product of a succinic acid or anhydride thereof having an alkyl or alkenyl substituent having 6 to 36 carbon atoms and a polyhydric alcohol selected from ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol and tetrapropylene glycol.

In some embodiments the ester additive of the invention is the reaction product of a succinic acid or anhydride thereof having an alkyl or alkenyl substituent having 6 to 36 carbon atoms and a polyhydric alcohol selected from glycerol, pentaerythritol and trimethyolpropane.

In some especially preferred embodiments the ester additive of the present invention is the reaction product of a succinic acid or anhydride having a C_{10} to C_{30}, preferably a C_{20} to C_{24} alkyl or alkenyl substituent and a polyethylene or polypropylene glycol having 4 to 16, preferably 6 to 8 alkoxy groups.

In some embodiments the ester additive of the invention is the reaction product of a succinic acid or anhydride thereof having an alkyl or alkenyl substituent having 6 to 36 carbon atoms and an alcohol selected from propylene glycol, dipropylene glycol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1-4-butanediol and neopentyl glycol.

In some embodiments the ester additive of the invention is the reaction product of a succinic acid or anhydride thereof having an alkyl or alkenyl substituent having 6 to 36 carbon atoms and a polyethylene or polypropylene glycol having a number average molecular weight of 800 to 1200.

In some embodiments the ester additive of the present invention is the reaction product of a succinic acid or anhydride having a C_{10} to C_{30}, preferably a C_{20} to C_{24} alkyl or alkenyl substituent and a polyethylene or polypropylene glycol having a number average molecular weight of 800 to 1200.

In some embodiments the ester additive of the present invention is the reaction product of a succinic acid or anhydride having a C_{10} to C_{30}, preferably a C_{20} to C_{24} alkyl or alkenyl substituent and an alcohol selected from propylene glycol, dipropylene glycol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1-4-butanediol and neopentyl glycol.

In some embodiments the ester additive of the present invention is the reaction product of a succinic acid or anhydride of formula (A3) or (A4) and an alcohol of formula H-$(OR)_n$-OH; wherein R^1 is an alkyl or alkenyl group having 6 to 36 carbon atoms or a polyisobutenyl group having a number average molecular weight of from 200 to 1300; and an alcohol selected from from ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, polypropylene glycol, polyethylene glycol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, trehalose, 1,6-hexanediol and neopentyl glycol.

In some preferred embodiments the ester additive of the invention is the reaction product of a succinic acid or anhydride thereof having an alkyl or alkenyl substituent having less than 30 carbon atoms, preferably less than 26 carbon atoms and an alcohol selected from from ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, polypropylene glycol, polyethylene glycol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol and neopentyl glycol.

In some especially preferred embodiments the ester additive of the present invention is the reaction product of a succinic acid or anhydride having a C_{20} to C_{24} alkyl or alkenyl substituent and an alcohol selected from 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, tripropylene glycol and polypropylene glycols having a number average molecular weight of from 300 to 600.

The ester additive of the present invention is the reaction product of a hydrocarbyl substituted polycarboxylic acid or an anhydride thereof and an alcohol of formula H-$(OR)_n$-OH wherein R is an optionally substituted alkylene group and n is at least 1.

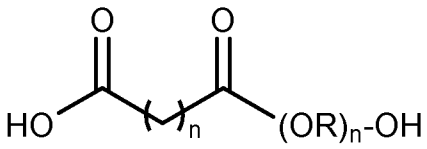
Preferably the acid/anhydride and the alcohol are reacted in a molar ratio of from 10:1 to 1:10, preferably from 5:1 to 1:5, more preferably from 2:1 to 1:2, for example from 1.5:1 to 1:1.5.

Most preferably the acid/anhydride and the alcohol are reacted in an approximately 1:1 molar ratio, for example from 1.2:1 to1:1.2.

In some embodiments the ester additive is the reaction product of an acid of formula $HOOC(CHR^x)_nCOOH$ wherein each R^x is independently hydrogen or an optionally substituted hydrocarbyl group.

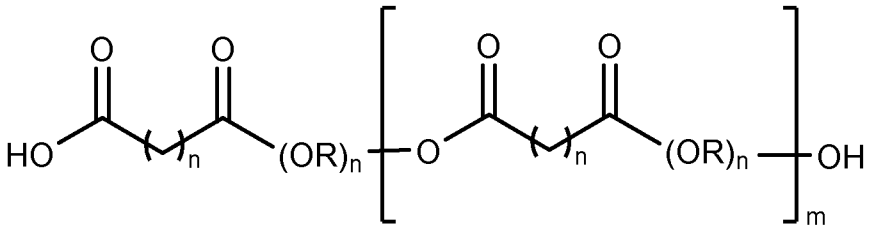
n may be from 1 to 50, preferably from 1 to 30, more preferably from 1 to 20, suitably from 2 to 16, preferably from 4 to 12, more preferably from 6 to 10. Preferably 0 or 1 R^x group is an optionally substituted hydrocarbyl group and all other R^x groups are hydrogen. When R^x is an optionally substituted hydrocarbyl it is suitably a group R^1 as previously defined herein in relation to compounds (A3) and (A4).

Most preferably each R^x is hydrogen and the ester additive has the structure of formula (E):



(E)

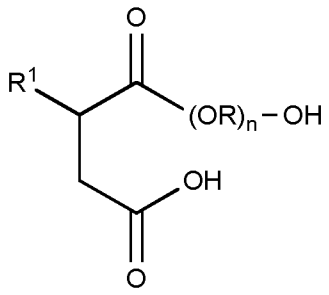
Oligomers or polymers of formula (F) may also be provided:



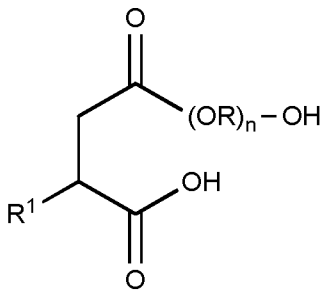
(F)

In an especially preferred embodiment n is 8 and the ester additive is the reaction product of sebacic acid and an alcohol of formula $H\text{-}(OR)_n\text{-}OH$.

In preferred embodiments the ester additive is the reaction product of a substituted succinic acid or succinic anhydride. In such embodiments, the additive preferably includes compounds having the formula (C1) or (C2):

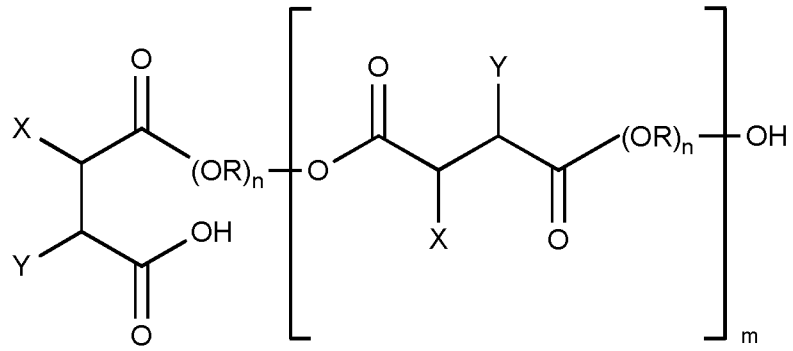


(C1)



(C2)

The additive may also include oligomers or polymers having a structure of formula (D):



(D)

wherein m is at least 1 and one of each X and Y is R^1 and the other is hydrogen.

Suitably the ester additive is present in the diesel fuel composition in an amount of at least 0.1ppm, preferably at least 1 ppm, more preferably at least 5 ppm, suitably at least 10 ppm, preferably at least 20 ppm, for example at least 30ppm or at least 50 ppm.

Suitably the ester additive is present in the diesel fuel composition in an amount of less than 10000 ppm, preferably less than 1000 ppm, preferably less than 500 ppm, preferably less than 300 ppm, for example less than 250 ppm.

In some embodiments the ester additive is present in the diesel fuel composition in an amount of suitably less than 200 ppm, for example less than 150 ppm.

Suitably the ester additive is present in the diesel fuel in an amount of from 80 to 130 ppm.

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

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

For avoidance of doubt mixtures of ester additive compounds that may be present include mixtures formed by reacting a mixture of different polyhydric alcohols with a polycarboxylic acid and/or mixtures formed by reacting a polyhydric alcohol with a mixture of polycarboxylic acids and/or compounds formed by reacting a mixture of polyhydric alcohols with a mixture of carboxylic acids. Such mixtures may also include mixtures of initially pure fully formed ester compounds.

The use of mixtures may arise due to the availability of starting materials or a particular mixture may be deliberately selected to use in order to achieve a benefit. For example, a particular mixture may lead to improvements in handling, a general improvement in performance or a synergistic improvement in performance.

In this specification any reference to “an additive” or “the additive” of the invention includes embodiments in which a single additive compound is present and embodiments in which two or more additive compounds are present. In embodiments in which two or more compounds are present the mixtures may be present due to a mixture of starting materials being used to prepare the additive compounds (e.g. a mixture of polyhydric alcohols and/or a mixture of polycarboxylic acids). Alternatively and/or additionally two or more pre-formed ester compounds may be mixed into a fuel composition.

The present invention relates to improving the performance of diesel engines by combusting diesel fuel compositions comprising an ester additive.

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

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 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 110ºC to 500ºC, e.g. 150ºC to 400ºC. 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 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 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, 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.

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 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-liquid) fuels. Third generation biodiesel does not differ widely from some second generation biodiesel, but aims to exploit the whole plant (biomass) and thereby widens the feedstock base.

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

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

In some embodiments the fuel composition may comprise neat biodiesel.

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

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

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 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%.

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.

The diesel fuel composition of the present invention preferably comprises at least 5 wt% biodiesel and less than 50 ppm sulphur.

The second aspect of the present invention relates to a method of combatting deposits in a diesel engine.

The method is achieved by combusting in the engine an ester additive which functions as a detergent. Various non-nitrogen containing ester compounds are known for use in diesel fuel as corrosion inhibitors or lubricity improvers but such compounds have not previously been used as detergents to combat deposits in diesel engines.

The third aspect of the present invention relates to the use of the ester additive as a detergent.

Suitably the use of the third aspect of the invention improves the performance of the invention. This improvement in performance may, for example, be achieved by combatting deposits in the engine.

References herein to improving performance and/or combating deposits may apply to either the second and/or the third aspect of the invention.

The ester additives used in the present invention have been found to be particularly effective in modern diesel engines having a high pressure fuel system. Some features of engines of this type have been previously described herein.

Suitably the present invention combats deposits and/or improves performance of a diesel engine having a high pressure fuel system. Suitably the diesel engine has a 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.

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 100ºC, 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, lacquers 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. In recent years the need to reduce emissions has led to the continual redesign of injection systems to help meet lower targets. This has led to increasingly complex injectors and lower tolerance to deposits.

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 and those containing metallic species may lead to increased deposits.

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.

Deposits are known to occur in the spray channels of the injector, leading to reduced flow and power loss. As the size of the injector nozzle hole is reduced, the relative impact of deposit build up becomes more significant. Deposits are also known to occur at the injector tip. Here, they affect the fuel spray pattern and cause less effective combustion and associated higher emissions and increased fuel consumption.

In addition to these “external” injector deposits in the nozzle hole and at the injector tip which lead to reduced flow and power loss, deposits may occur within the injector body causing further problems. These deposits may be referred to as internal diesel injector deposits (or IDIDs). IDIDs occur inside the injector on the critical moving parts. They can hinder the movement of these parts affecting the timing and quantity of fuel injection. Since modern diesel engines operate under very precise conditions these deposits can have a significant impact on performance.

IDIDs cause a number of problems, including power loss and reduced fuel economy due to less than optimal fuel metering and combustion. Initially the user may experience cold start problems and/or rough engine running. These deposits can lead to more serious injector

sticking. This occurs when the deposits stop parts of the injector from moving and thus the injector stops working. When several or all of the injectors stick the engine may fail completely.

The CEC have recently introduced an Internal Diesel Injector Deposit Test, CEC F-110-16, to discriminate between fuels that differ in their ability to produce IDIDs in direct injection common rail diesel engines.

As mentioned above, the problem of injector fouling may be more likely to occur when using fuel compositions comprising metal species. Various metal species may be present in fuel compositions. This may be due to contamination of the fuel during manufacture, storage, transport or use or due to contamination of fuel additives. Metal species may also be added to fuels deliberately. For example, transition metals are sometimes added as fuel borne catalysts, for example to improve the performance of diesel particulate filters.

Problems of injector sticking may occur when metal or ammonium species, particularly sodium species, react with carboxylic acid species in the fuel.

Sodium contamination of diesel fuel and the resultant formation of carboxylate salts is believed to be a major cause of injector sticking.

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

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

The presence of metal containing species may give rise to fuel filter deposits and/or external injector deposits including injector tip deposits and/or nozzle deposits.

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 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 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.

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

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.

It is advantageous to provide a diesel fuel composition which prevents or reduces the occurrence of deposits in a diesel engine. In some embodiments such deposits may include “external” injector deposits such as deposits in and around the nozzle hole and at the injector tip. In some preferred embodiments the deposits include “internal” injector deposits or IDIDs. Such fuel compositions may be considered to perform a “keep clean” function i.e. they prevent or inhibit fouling. It is also be desirable to provide a diesel fuel composition which would help clean up deposits of these types. 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 in 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 is useful to provide compositions that prevent or inhibit the occurrence of fuel filter deposits i.e. provide a "keep clean" function. It is 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 are especially useful.

The method of the present invention is particularly effective at combatting deposits in a modern diesel engine having a high pressure fuel system.

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.

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.

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 250ºC.

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

The method of the present invention preferably combats deposits in an engine having one or more of the above-described characteristics.

The use of the present invention preferably improves the performance of an engine. This improvement in performance is suitably achieved by reducing deposits in the engine.

The first aspect of the present invention relates to a method of combating deposits in a diesel engine. Combating deposits may involve reducing or the preventing of the formation of deposits in an engine compared to when running the engine using unadditised fuel. Such a method may be regarded as achieving “keep clean” performance.

Combating deposits may involve the removal of existing deposits in an engine. This may be regarded as achieving “clean up” performance.

In especially preferred embodiments the method of the first aspect and the use of the second aspect of the present invention may be used to provide “keep clean” and “clean up” performance.

As explained above deposits may occur at different places within a diesel engine, for example a modern diesel engine.

The present invention is particularly useful in the prevention or reduction or removal of internal deposits in 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.

The present invention may also provide improved performance in modern diesel engines having a high pressure fuel system by controlling external injector deposits, for example those occurring in the injector nozzle and/or at the injector tip. The ability to provide control of

internal injector deposits and external injector deposits is a useful advantage of the present invention.

Suitably the present invention may reduce or prevent the formation of external injector deposits. It may therefore provide “keep clean” performance in relation to external injector deposits.

Suitably the present invention may reduce or remove existing external injector deposits. It may therefore provide “clean up” performance in relation to external injector deposits.

Suitably the present invention may reduce or prevent the formation of internal diesel injector deposits. It may therefore provide “keep clean” performance in relation to internal diesel injector deposits.

Suitably the present invention may reduce or remove existing internal diesel injector deposits. It may therefore provide “clean up” performance in relation to internal diesel injector deposits.

The present invention may also combat deposits on vehicle fuel filters. This may include reducing or preventing the formation of deposits (“keep clean” performance) or the reduction or removal of existing deposits (“clean up” performance).

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

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.

An improvement in “keep clean” performance may be measured by comparison with a base fuel. “Clean up” performance can be observed by an improvement in performance of an already fouled engine.

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

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 test for additives for modern diesel engines such as HSDI engines. The CEC F-98-08 test is used 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 is commonly referred to as the DW10B test. This test measures power loss in the engine due to deposits on the injectors, and is further described in example 4.

Preferably the use of the fuel composition of the present invention leads to reduced deposits in the DW10B 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 DW10B test is used to measure the power loss in modern diesel engines having a high pressure fuel system.

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 in 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 DW10B 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 16 hours, preferably 12 hours, more preferably 8 hours as measured in the DW10B test.

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

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

The CEC have also developed a new test, commonly known as the DW10C which assesses the ability of a fuel composition to prevent the formation of IDIDs that lead to injector sticking. This test is described in example 5. A modified version of this test adapted to measure clean up, is described in example 6.

The DW10C test may be used to measure the “keep clean” or “clean up” performance of an engine.

In some embodiments the present invention provides a “keep clean” performance in relation to the formation of IDIDs. Such performance may be illustrated by achieving a merit score of at least 7 as measured by the DW10C test, preferably at least 8, more preferably at least 9.

In some embodiments a merit score of at least 9.3 may be achieved, for example at least 9.4, at least 9.5, at least 9.6 or at least 9.7.

In some embodiments the present invention provides a “clean-up” performance in relation to IDIDs, whereby existing IDIDs may be removed. Such a performance is illustrated in the examples.

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.

For older engines an improvement in performance may be measured using the XUD9 test. This test is described in relation to example 7.

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 reduced by 10% or more within 10 hours as measured in the XUD-9 test.

The benefits provided by the present invention mean that engines need to be serviced less frequently, leading to cost savings and an increase in maintenance intervals.

Preferably the method and use of the present invention provide an improvement in the performance of a diesel engine. This improvement in performance is suitably selected from one or more of:

- a reduction in power loss of the engine;
- a reduction in external diesel injector deposits;
- a reduction in internal diesel injector deposits;
- an improvement in fuel economy;
- a reduction in fuel filter deposits;
- a reduction in emissions; and
- an increase in maintenance intervals.

The additives of the present invention may provide a further benefit in addition to those listed above. For example the additive may provide lubricity benefits and/or corrosion inhibition and/or cold flow improvement.

The diesel fuel composition used in the present invention may include one or more further additives such as those which are commonly found in diesel fuels. These include, for example, antioxidants, 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 embodiments the combination of an additive of the invention and a further additive may provide synergistic improvement in performance.

For example the use of an ester additive of the invention in combination with a cold flow improver may provide an unexpected improvement in detergency and/or cold flow performance compared with the performance of the individual additives used alone.

In some embodiments the use of an ester additive of the present invention may enable a lower treat rate of cold flow improver to be used.

For example the use of an ester additive of the invention in combination with a corrosion inhibitor may provide an unexpected improvement in detergency and/or corrosion inhibition compared with the performance of the individual additives used alone.

In some embodiments the use of an ester additive of the present invention may enable a lower treat rate of corrosion inhibitor to be used.

For example the use of an ester additive of the invention in combination with a lubricity improver may provide an unexpected improvement in detergency and/or lubricity compared with the performance of the individual additives used alone.

In some embodiments the use of an ester additive of the present invention may enable a lower treat rate of lubricity improver to be used.

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

The one or more further detergents may provide a synergistic benefit such that an improved performance is observed when using the combination of an ester additive of the invention and a nitrogen-containing detergent compared to the use of an equivalent amount of either additive alone.

The use of a combination of an ester additive and a nitrogen-containing detergent may also combat deposits and improve performance in a traditional diesel engine.

The one or more further detergents may be 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;

(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.

Preferably one or more further 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 ester additive to the nitrogen containing detergent is suitable 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.

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.

An especially preferred additonal 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.

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 quaternary ammonium compounds described in the applicants copending applications WO2011095819, 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 500 ppm, preferably 50 to 250 ppm of the ester additive and from 1 to 500 ppm, preferably 50 to 250ppm of a quaternary ammonium additive (i).

In some embodiments the diesel fuel composition comprises further (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.

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

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

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

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

In some embodiments the diesel fuel composition of the present invention comprises from 1 to 500 ppm, preferably 50 to 250ppm of the ester additive and from 1 to 500 ppm, preferably 50 to 250ppm 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.

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

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

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

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

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

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

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

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

In some embodiments the diesel fuel composition of the present invention comprises from 1 to 500 ppm, preferably 50 to 250ppm of the ester additive and 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 C_8-C_{36} group, preferably a C_8-C_{18} 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 NH_2-NH_2. 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 hydrocarbon 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.

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.

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.

Further preferred features of these detergents are described in EP1884556.

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

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

Example 1

Additive A1, an ester additive of the invention was prepared as follows:

A mixture of alkenes having 20 to 24 carbon atoms was heated with 1.2 molar equivalents of maleic anhydride. On completion of the reaction excess maleic anhydride was removed by distillation. The anhydride value of the substituted succinic anhydride product was measured as 2.591 $mmolg^{-1}$.

This product was then heated with one molar equivalent of polypropylene glycol having a number average molecular weight of 425, and the reaction was monitored by FTIR.

Compounds A2 to A31 detailed in table 1 were prepared by an analogous method.

In each case the reaction product is believed to comprise the following compounds:

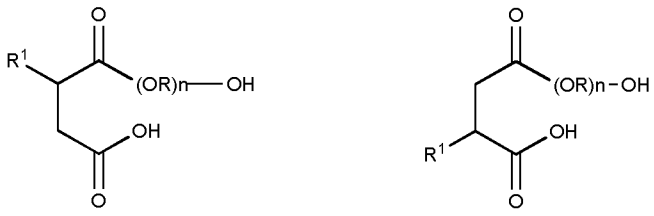


Table 1

Compound	R^1	H-(OR)n-OH
A1	C20-24	polypropylene glycol Mn425
A2	C20-24	triethyleneglycol
A3	C20-24	polypropylene glycol Mn725
A4	C18	polypropylene glycol Mn425
A5	C12	polypropylene glycol Mn425
A6	PIB550	polypropylene glycol Mn425

A7	C30+	polypropylene glycol Mn425
A8	C20-24	tetraethyleneglycol
A9	C20-24	polyethyleneglycol Mn400
A10	C20-24	tripropylene glycol
A11	C20-24	polyethylene glycol Mn 950-1050
A12	C20-24	propylene glycol
A13	C20-24	dipropylene glycol
A14	C20-24	1,3 propanediol
A15	C20-24	1,2 butanediol
A16	C20-24	1,3 butanediol
A17	C20-24	1,4 butanediol
A18	C20-24	neopentyl glycol
A19	PIB550	polypropylene glycol Mn1000
A20	H	tripropylene glycol
A21	C20-24	polypropylene glycol Mn1000
A22	C20-24	trehalose
A23	C20-24	di(ethylene glycol)
A24	C20-24	ethylene glycol
A25	C30+	propylene glycol
A26	C18	tri(propylene glycol)
A27	PIB1000	poly(propylene glycol) Mn725
A28	PIB260	tri(propylene glycol)
A29	PIB260	poly(propylene glycol) Mn425
A30	PIB550	1,3-butanediol
A31	PIB550	1,4-butanediol

Additive A32 was prepared by analogous route by heating with two molar equivalents of polypropylene glycol having a number average molecular weight of 425 with pyromellitic dianhydride.

Example 2

Diesel fuel compositions were prepared by dosing additives to aliquots all drawn from a common batch of RF06 base fuel, and containing 1 ppm zinc (as zinc neodecanoate).

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 3

The compositions were tested in a screening test which correlates with performance at combatting IDIDs as measured in the DW10C test.

In this test a fuel composition is tested using a Jet Fuel Thermal Oxidation Test equipment. In this modified test 800ml of fuel is flowed over a heated tube at pressures of approximately 540psi. The test duration is 2.5 hours. At the end of the test the amount of deposit obtained on the tube is compared to a reference value.

The value shown in table 2 is the percentage reduction in deposit thickness compared to base fuel.

Table 3

Compound	ppm active	Average thickness % reduction
A1 (inventive)	120	99
A2 (inventive)	120	98
A3 (inventive)	120	91
A6 (inventive)	120	93
A7 (inventive)	120	94
A8 (inventive)	120	91
A9 (inventive)	120	97
A10 (inventive)	120	95
A11 (inventive)	120	98
A12 (inventive)	120	87
A13 (inventive)	120	100
A14 (inventive)	120	97
A15 (inventive)	120	99
A16 (inventive)	120	97
A18 (inventive)	120	100
A19 (inventive)	120	75
A20 (inventive)	120	81
A22 (inventive)	120	92
A23 (inventive)	120	100
A24 (inventive)	120	99
A25 (inventive)	120	100
C1 (comparative)	120	0
C2 (comparative)	120	2

Comparative additive C1 is dodecenyl substituted succinic acid.

Comparative additive C2 is a polyisobutenyl (PIB) substituted succinic acid wherein the PIB has a number average molecular weight of 1000.

Example 4

The performance of fuel compositions of example 2 in modern diesel engines having a high pressure fuel system may be tested according to the CECF-98-08 DW 10 method. This is referred to herein as the DW10B test.

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 (minutes)**	**Engine Speed (rpm)**	**Torque (Nm)**
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.

Example 5

Diesel fuel compositions comprising: (i) additive A1 (53 ppm active); and (ii) additive A16 (50 ppm active) were tested according to the CECF-98-08 DW10B test method described in example 3, modified to measure clean up performance as outlined below.

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 was then 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 additive.

Figure 1 shows the power output of the engine when running the fuel composition comprising additive A1 over the test period.

Figure 2 shows the power output of the engine when running the fuel composition comprising additive A16 over the test period.

Example 6

The ability of additives of the invention to remove 'Internal Diesel Injector Deposits' (IDIDs) may be measured according to he test method CEC F-110-16, available from the Co-ordinating European Council. The test uses the PSA DW10C engine.

The engine characteristics as follows:

Design:	Four cylinders in line, overhead camshaft, variable geometry turbocharger with EGR
Capacity:	1997 cm^3
Combustion chamber:	Four valves, bowl in piston, direct injection
Power:	120 kW @ 3750 rpm
Torque:	340 Nm @ 2000 rpm
Injection system:	Common rail with solenoid type injectors Delphi Injection System
Emissions control:	Conforms to Euro V limit values when combined with exhaust gas post-treatment system.

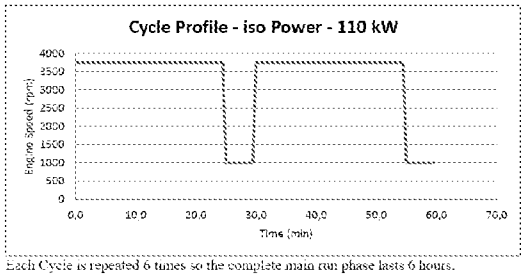
The test fuel (RF06) is dosed with 0.5mg/kg Na in the form of Sodium Naphthenate + 10mg/kg Dodecyl Succinic Acid (DDSA).

The test procedure consists of main run cycles followed by soak periods, before cold starts are carried out.

The main running cycle consist of two speed and load set points, repeated for 6hrs, as seen below.

Step	Speed (rpm)	Torque (N.m)	Duration (s)
1	3750	280	1470
1 - Ramp →2	-	-	30
2	1000	10	270
2 - Ramp →1	-	-	30

The ramp times of 30 seconds are included in the duration of each step.



Each Cycle is repeated 6 times so the complete main run phase lasts 6 hours.

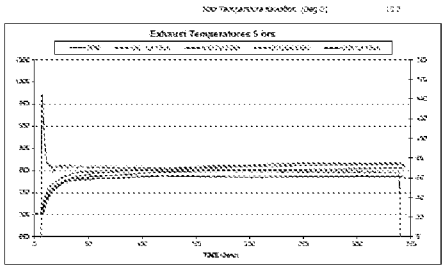
During the main run, parameters including, Throttle pedal position, ECU fault codes, Injector balance coefficient and Engine stalls are observed and recorded.

The engine is then left to soak at ambient temperature for 8hrs.

After the soak period the engine is re-started. The starter is operated for 5 seconds; if the engine fails to start the engine is left for 60 seconds before a further attempt. A maximum of 5 attempts are allowed.

If the engine starts the engine is allowed to idle for 5 minutes. Individual exhaust temperatures are monitored and the maximum Temperature Delta is recorded. An increased variation in Cylinder-to-Cylinder exhaust temperatures is a good indication that injectors are suffering from IDID. Causing them to either open slowly or stay open to long.

An example below of all exhaust temperatures with <30°C deviation, indicating no sticking caused by IDID.



The complete test comprises of 6x Cold Starts, although the Zero hour Cold Start does not form part of the Merit Rating and 5x 6hr Main run cycles, giving a total of 30hrs engine running time.

The recorded data is inputted into the Merit Rating Chart. This allows a Rating to be produced for the test. Maximum rating of 10 shows no issues with the running or operability of the engine for the duration of the test.

An example below:

Cold start										Main run										
		Starting				Exhaust temperature consistency				Operability										
Cold Start	Start Y/N	Maximum Starter	Number of Attempts (1 = first start)	Deduction	Merits	Maximum Starter	Exhaust Temperature Max Dev. Deviation (°C)	Deduction	Merits	Main run	Maximum Starter	Number of Fault Codes	Deduction	Stall (Y/N)	Deduction	Max Pedal Position at 1000 rpm / 10 Nm (%)	Deduction	Max Injec. Balancing Coeff. (rpm)	Deduction	Merits
#0					not rated					#1	5	0	5	N	0	10.4	0	15	0	5
#1	Y	0	1	0	5	1	21.5	0	5	#2	5	0	5	N	0	10.5	0	15	0	5
#2	Y	0	1	0	5	1	20.1	0	5	#3	5	0	0	N	0	10.6	0	15	0	5
#3	Y	0	1	0	5	1	15.1	0	5	#4	5	0	0	N	0	10.0	0	15	0	5
#4	Y	0	1	0	5	1	20.2	0	5	#5	5	0	5	N	0	10.3	0	15	0	5
#5	Y	0	1	0	5	1	22.5	0	5											25
Total merits					25				25											

Global Rating - Summary (Merit / 10)	10

Example 7

The ability of additives of the invention to clean up IDIDs was assessed according to a modification of the DW10C test described in example 6.

The In-House Clean-Up Method developed starts by running the engine using reference diesel (RF06) dosed with 0.5mg/kg Na + 10mg/Kg DDSA until an exhaust temperature Delta of >50°C is observed on the Cold Start. This has repeatedly been seen on the 3rd Cold Start which follows the second main run, 12hrs total engine run time.

Once the increased Exhaust temperature Delta is observed, the engine fuel supply is swapped to reference diesel, dosed with 0.5mg/kg Na (as sodium naphthenate) + 10mg/kg DDSA + the Candidate sample. The fuel is flushed through to the engine and allowed to commence with the next Main run.

The ability of the Candidate additive to prevent any further increase in deposits or to remove the deposits can then be determined as the test continues.

A diesel fuel composition comprising additive A1 (53 ppm active) was tested according to the test method outlined above. A final De-Merit rating of 8.5 was achieved. The full results are provided in table 3.

Table 3

Cold start										
		Starting					Exhaust temperature consistency			
Cold Start	Start Y/N	Maximum Merits	Number of Attempts (1 = first start)	Deduction	Merits		Maximum Merits	Exhaust Temperature Max Cyl. Deviation (°C)	Deduction	Merits
#0	Y						Initial Value:	[illegible]	Not Rated	
#1	Y	5	[illegible]	0	5		5	[illegible]	3	2
#2	Y	5	[illegible]	0	5		5	[illegible]	5	0
#3	Y	5	[illegible]	0	5		5	[illegible]	0	5
#4	Y	5	[illegible]	0	5		5	[illegible]	3	2
#5	Y	5	[illegible]	0	5		5	[illegible]	0	5
Total merits					25					14

Main run										
Operability										
Main run	Maximum Merits	Number of ECU Fault resets	Deduction	Stall (Y/N)	Deduction	Max Pedal Position at 1000 rpm / 10 N.m (%)	Deduction	Max Inject. Balancing Coeff. (rpm)	Deduction	Merits
#1	5	0	0	N	0	17.3	0	14.9	0	5
#2	5	0	0	N	0	14.4	0	15.2	0	5
#3	5	0	0	N	0	15.3	0	15.6	0	5
#4	5	0	0	N	0	16.1	0	15.4	0	5
#5	5	0	0	N	0	17.0	0	15.2	0	5
										25
									Global Rating - Summary (Merit / 10)	8.5333

A diesel fuel composition comprising additive A16 (50 ppm active) was also tested according to the method of example 6. A final demerit rating of 7.47 was achieved. The full results are provided in table 4.

Table 4

Cold start									
		Starting				Exhaust temperature consistency			
Cold Start	Start Y/N	Maximum Merits	Number of Attempts (1 = first start)	Dedu-ction	Merits	Maximum Merits	Exhaust Tempera-ture Max Cyl. Deviation (°C)	Dedu-ction	Merits
#0	not rated								
#1	Y	5	1	0	5	5	32.3	3	2
#2	Y	5	1	0	5	5	139.3	5	0
#3	Y	5	1	0	5	5	59.1	5	0
#4	Y	5	1	0	5	5	49.9	3	2
#5	Y	5	1	0	5	5	47.7	3	2
Total merits					25				6

Main run										
Operability										
Main run	**Maximum Merits**	**Number of ECU Fault resets**	Deduc-tion	**Stall (Y/N)**	Dedu-ction	**Max Pedal Position at 1000 rpm / 10 N.m (%)**	Dedu-ction	**Max Inject. Balancing Coeff. (rpm)**	Dedu-ction	**Merits**
#1	5	**0**	0	**N**	0	**15.9**	0	**11.8**	0	**5**
#2	5	**0**	0	**N**	0	**18.7**	0	**11.8**	0	**5**
#3	5	**0**	0	**N**	0	**19.9**	0	**10.4**	0	**5**
#4	5	**0**	0	**N**	0	**19.7**	0	**10.6**	0	**5**
#5	5	**0**	0	**N**	0	**19.1**	0	**10.4**	0	**5**
										25
Global Rating - Summary (Merit / 10)										7.466667

A diesel fuel composition comprising additive A10 (50 ppm active) was also tested according to the method of example 6. A final demerit rating of 8.67 was achieved. The full results are provided in table 5.

Table 5

Cold start									
		Starting				Exhaust temperature consistency			
Cold Start	**Start Y/N**	**Maximum Merits**	**Number of Attempts (1 = first start)**	Deduction	**Merits**	**Maximum Merits**	**Exhaust Temperature Max Cyl. Deviation (°C)**	Deduction	**Merits**
#0	not rated								
#1	**Y**	5	**1**	0	**5**	5	**32.6**	3	**2**
#2	**Y**	5	**1**	0	**5**	5	**162.8**	5	**0**
#3	**Y**	5	**2**	1	**4**	5	**17.8**	0	**5**
#4	**Y**	5	**1**	0	**5**	5	**19.7**	0	**5**
#5	**Y**	5	**1**	0	**5**	5	**23.4**	0	**5**
Total					**24**				**17**

Main run										
Operability										
Main run	Maximum Merits	Number of ECU Fault resets	Deduction	Stall (Y/N)	Deduction	Max Pedal Position at 1000 rpm / 10 N.m (%)	Deduction	Max Inject. Balancing Coeff. (rpm)	Deduction	Merits
#1	5	0	0	N	0	14.4	0	11.6	0	5
#2	5	0	0	N	0	17.8	0	10.7	0	5
#3	5	1	1	N	0	18.2	0	10.8	0	4
#4	5	0	0	N	0	16.9	0	9.8	0	5
#5	5	0	0	N	0	16.1	0	9.7	0	5
										24
									Global Rating - Summary (Merit / 10)	8.666667

Example 8

The effectiveness of the additives of the invention in older traditional diesel engine types maybe 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.

5

Claims

1. A diesel fuel composition comprising as an additive an ester compound which is the reaction product of an optionally substituted polycarboxylic acid or an anhydride thereof and a polyhydric alcohol of formula $H-(OR)_n-OH$, wherein R is an optionally substituted alkylene group and n is at least 1.

2. A method of combatting deposits in a diesel engine, the method comprising combusting in the engine a diesel fuel composition comprising as an additive the reaction product of an optionally substituted polycarboxylic acid or an anhydride thereof and a polyhydric alcohol of formula $H-(OR)_n-OH$, wherein R is an optionally substituted alkylene group and n is at least 1.

3. Use of an ester compound as a detergent additive in a diesel fuel composition in a diesel engine; wherein the ester compound is the reaction product of an optionally substituted polycarboxylic acid or an anhydride thereof and a polyhydric alcohol of formula $H-(OR)_n-OH$, wherein R is an optionally substituted alkylene group and n is at least 1.

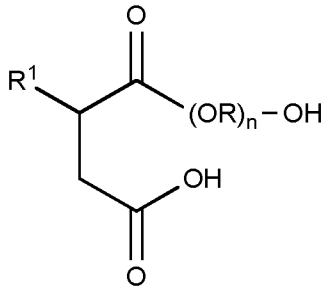
4. A composition, method or use according to any preceding claim wherein the optionally substituted polycarboxylic acid or anhydride thereof is a hydrocarbyl substituted succinic acid or a hydrocarbyl substituted succinic anhydride.

5. A composition, method or use according to any preceding claim wherein each R is ethylene or propylene, preferably $-CH_2CH_2-$ or $-CH(CH_3)CH_2-$, more preferably $-CH(CH_3)CH_2-$; and n is from 1 to 20.

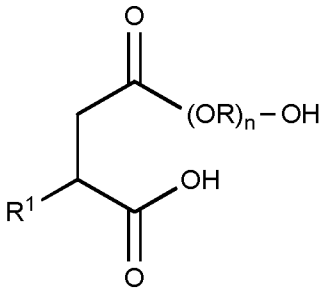
6. A composition, method or use according to any preceding claim wherein the polycarboxylic acid or anhydride thereof includes an optionally substituted alkyl or alkenyl group having 6 to 100 carbon atoms, preferably 6 to 50 carbon atoms.

7. A composition, method or use according to any preceding claim wherein the optionally substituted polycarboxylic acid or hydrocarbyl substituted anhydride and alcohol of formula H-(OR)n-OH are reacted in a ratio of from 1.5:1 to 1:1.5.

8. A composition, method or use according to any preceding claim wherein the additive includes compounds having the formula (C1) or (C2):

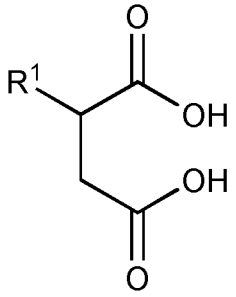


(C1)

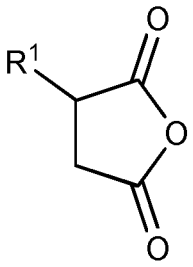


(C2)

9. A composition, method or use according to any preceding claim wherein the additive comprises the reaction product of a succinic acid or anhydride of formula (A3) or (A4):



(A3)

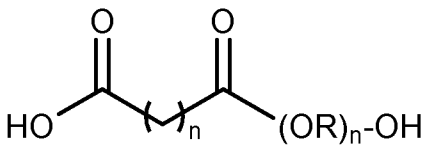


(A4)

and an alcohol of formula H-$(OR)_n$-OH; wherein R^1 is an alkyl or alkenyl group having 6 to 36 carbon atoms or a polyisobutenyl group having a number average molecular weight of from 200 to 1300; wherein the alcohol of formula H-$(OR)_n$-OH is selected from ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, trehalose, sorbitol, glycerol, pentaerythritol, trimethylolpropane, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol and a polyethylene or polypropylene glycol having a number average molecular weight of 300 to 1200.

10. A composition, method or use according to any preceding claim wherein the additive comprises the reaction product of a succinic acid or anhydride having a C_{20} to C_{24} alkyl or alkenyl substituent and an alcohol selected from 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, tripropylene glycol and polypropylene glycols having a number average molecular weight of from 300 to 600.

11. A composition, method or use according to any preceding claim wherein the additive includes compounds having the formula (E):



(E)

12. A composition, method or use according to any preceding claim wherein the diesel engine is a modern diesel engine having a high pressure fuel system.

13. A method or use according to any of claims 2 to 12 which achieves “keep clean” performance.

14. A method or use according to any of claims 2 to 13 which achieves “clean up” performance.

15. A method or use according to any of claims 2 to 14 wherein the deposits are injector deposits.

16. A method or use according to claim 15 wherein the deposits are internal diesel injector deposits.

17. A composition, method or use according to any preceding claim wherein the diesel fuel composition comprises less than 50 ppm sulphur by weight.

18. A composition, method or use according to any preceding claim wherein the diesel fuel composition comprises biodiesel.

19. A composition, method or use according to any preceding claim wherein the diesel fuel composition comprises one or more further detergents 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;

(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.

20. A composition, method or use according to any preceding claim wherein the diesel fuel composition comprises a mixture of two or more ester additives.

21. A method or use according to any of claims 2 to 20 which achieves an improvement in performance selected from one or more of:

- a reduction in power loss of the engine;
- a reduction in external diesel injector deposits;
- a reduction in internal diesel injector deposits;
- an improvement in fuel economy;
- a reduction in fuel filter deposits;
- a reduction in emissions; and
- an increase in maintenance intervals.

22. A method or use according to claim 21 which provides an improvement in performance in modern diesel engines having a high pressure fuel system and provides an improvement in performance in traditional diesel engines.

23. Use according to any of claims 3 to 22 which provides one or more further benefits selected from lubricity benefits, corrosion inhibition and cold flow improvement.

24. A composition according to any of claims 1 and 4 to 20 which further comprises one or more further additives selected from lubricity improvers, corrosion inhibitors and cold flow improvers.

25. Use of an ester additive as defined in any preceding claim to reduce the treat rate of one or more further additives selected from lubricity improvers, corrosion inhibitors and cold flow improvers whilst maintaining performance.