Fuel compositions and methods and uses relating thereto

The present invention relates to diesel fuel compositions and to methods and uses relating thereto. In particular the invention relates to diesel fuel compositions having reduced emissions of nitrogen oxides.

The combustion of fossil fuels leads to the formation of nitrogen oxide species. The nitrogen oxides formed, commonly termed NO_x, include nitric oxide (NO) and nitrogen dioxide (NO_2).

NO_x are known to cause significant health and environmental problems. For example exposure to NO_x can trigger respiratory difficulties, especially asthma.

Currently attempts to reduce NO_x emissions are focused on treatment of exhaust gases after they have left the combustion chamber, by the inclusion of a selective catalytic reduction (SCR) unit. The SCR unit converts NO_x and other harmful gases in the exhaust stream into less harmful substances. The SCR unit commonly involves the use of urea as a reductant in the presence of a catalyst. The selective catalytic reduction unit comprises a porous ceramic support and a catalyst, typically comprising a metal or a zeolite. This unit is part of the post combustion system of a diesel engine which typically includes a series of components through which exhaust gases must flow before exiting the vehicle.

The SCR unit requires regular maintenance and may need to be treated with an additive. Some vehicles include means for dosing a separate additive into the exhaust stream specifically directed at regeneration of the catalyst. This adds costs and complexity to the vehicle maintenance procedure.

It would therefore be desirable to provide fuel compositions which on combustion provide reduced NO and NO_x emissions. The present inventors have surprisingly found the inclusion of certain additives in a diesel fuel can advantageously lead to a reduction in NO and NO_x emissions.

According to a first aspect of the present invention there is provided a method of reducing the emission of nitrogen oxide and/or nitrogen dioxide from a diesel engine combusting a diesel fuel composition, the method comprising dosing into the diesel fuel composition as an additive at least one ester compound; wherein the ester compound is the reaction product of:

a) an optionally substituted polycarboxylic acid or an anhydride thereof; and

b) an alcohol of formula H-$(OR)_n$-OR^1, wherein R is an optionally substituted alkylene group, R^1 is hydrogen or an optionally substituted hydrocarbyl group and n is 0 or a positive integer; provided that n is not 0 when R^1 is hydrogen.

According to a second aspect of the present invention there is provided the use of at least one ester compound as an additive to reduce the emission of nitrogen oxide and/or nitrogen dioxide from a diesel engine combusting a diesel fuel composition; wherein the ester compound is the reaction product of:

a) an optionally substituted polycarboxylic acid or an anhydride thereof; and

b) an alcohol of formula H-$(OR)_n$-OR^1, wherein R is an optionally substituted alkylene group, R^1 is hydrogen or an optionally substituted hydrocarbyl group and n is 0 or a positive integer; provided that n is not 0 when R^1 is hydrogen.

According to a third aspect of the present invention there is provided a diesel fuel composition comprising as an additive at least one ester compound; wherein the ester compound is the reaction product of:

a) an optionally substituted polycarboxylic acid or an anhydride thereof; and

b) an alcohol of formula H-$(OR)_n$-OR^1, wherein R is an optionally substituted alkylene group, R^1 is hydrogen or an optionally substituted hydrocarbyl group and n is 0 or a positive integer; provided that n is not 0 when R^1 is hydrogen;

wherein combustion of each unit volume of the diesel fuel composition in a diesel engine emits a reduced amount of nitrogen oxide and/or nitrogen dioxide from the exhaust of the diesel engine compared with combustion of each unit volume of an otherwise identical diesel fuel composition without the additive, in the same engine under identical conditions.

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 the use of an additive to reduce the emission of nitrogen oxide and/or nitrogen dioxide on combustion of a diesel fuel composition.

The present invention involves the use of at least one ester compound as an additive. By this we mean that the invention may include the use of one ester compound as an additive or the use of multiple ester compounds as multiple additives.

For the avoidance of doubt each additive used in the present invention may comprise a mixture of compounds and references to an additive or the additive include mixtures, unless otherwise stated. In particular mixtures of isomers and mixtures of homologues are within the scope of the invention. The skilled person will appreciate that commercial sources of some of the additive compounds and/or reactants used to form the additives described herein may comprise mixtures of isomers and/or mixtures of homologues. For example component a) may be a mixture of optionally substituted polycarboxylic acids or anhydrides thereof, and component b) may be a mixture of alcohols of formula $H-(OR)_n-OR^1$. Mixtures of already formed ester compounds are also within the scope of the invention.

The present invention relates to the use of one or more ester compounds which are the reaction product of an optionally substituted polycarboxylic acid or an anhydride thereof and an alcohol of formula $H-(OR)_n-OR^1$. The additive may be referred to herein as “the additive of the present invention”, “the ester compound” or as “the ester additive”.

The additive of the present invention is prepared from component a) an optionally substituted polycarboxylic acid or anhydride thereof. In some embodiments the polycarboxylic acid or anhydride is unsubstituted. Suitably the polycarboxylic acid or anhydride is substituted, suitably with a hydrocarbyl group. 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.

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

In some embodiments, the polycarboxylic acid or anhydride thereof is substituted with a 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_{14} to C_{36} alkyl or alkenyl group, suitably a C_{14} to C_{32} alkyl or alkenyl group, for example a C_{14} to C_{28} alkyl or alkenyl group, preferably said alkenyl groups.

In such embodiments, the substituted polycarboxylic acid or anhydride thereof may be formed by reacting the polycarboxylic acid or anhydride thereof with a suitable alkene to provide the alkenyl group as defined above. In some preferred embodiments the alkene is an internal olefin. The term internal olefin is used to refer to any alkene compound in which the alkene group is not terminal.

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 and Alphaplus C20-24.

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 one embodiment an internal olefin may be a β-olefin.

Internal olefins may be prepared by isomerisation of an α-olefin.

In some embodiments the polycarboxylic acid or anhydride thereof is substituted with a hydrocarbyl group derived from an α-olefin having 6 to 36 carbon atoms; preferably from 10 to 30 carbon atoms, suitably from 12 to 24 carbon atoms, for example from 14 to 18 carbon atoms.

In some embodiments the polycarboxylic acid or anhydride thereof is substituted with a hydrocarbyl group derived from an internal olefin having 6 to 36 carbon atoms preferably from 10 to 32 carbon atoms, suitably from 12 to 24 carbon atoms, for example 14 to 18 carbon atoms.

The optionally substituted polycarboxylic acid or anhydride thereof of component a) may be selected from 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, or anhydrides thereof.

In one embodiment, component a) is an optionally substituted polycarboxylic acid or anhydride thereof selected from pyromellitic acid, malonic acid, sebacic acid and succinic acid. Suitably the optionally substituted polycarboxylic acid or anhydride thereof is an optionally substituted succinic acid or an anhydride thereof. Suitably component a) is a succinic acid or an anhydride thereof substituted with a hydrocarbyl group.

In preferred embodiments, component a) is a polycarboxylic acid or anhydride thereof selected from pyromellitic acid, malonic acid, sebacic acid and succinic acid, substituted with a 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_{14} to C_{36} alkyl or alkenyl group, suitably a C_{14} to C_{32} alkyl or alkenyl group, for example a C_{14} to C_{28} alkyl or alkenyl group. Suitably component a) is an optionally substituted succinic acid or an anhydride thereof substituted with such an alkyl or alkenyl group, preferably a C_{14} to C_{28} alkyl or alkenyl group.

Preferred acids are dicarboxylic acids. Thus preferably the additive of the invention is the reaction product of a) a hydrocarbyl substituted dicarboxylic acid or hydrocarbyl substituted anhydride thereof and b) a polyhydric alcohol of formula $H\text{-}(OR)_n\text{-}OR^1$, as defined herein.

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.

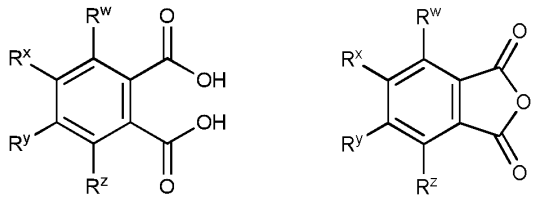
In some embodiments, component a) is a dimerised fatty acid. Such compounds are formed from the dimerization of unsaturated fatty acids, for example unsaturated fatty acids having 6 to

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 compounds 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, component a) is phthalic acid or an anhydride thereof, having the formula (A1) or (A2):



(A1) (A2)

wherein each of R^w, R^x, R^y and R^z 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^w, R^x, R^y and R^z 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_{14} to C_{32} alkyl or alkenyl group, suitably a C_{14} to C_{28} alkyl or alkenyl group. The alkyl or alkenyl group may be straight chain or branched. Preferably R^w, R^x and R^z are hydrogen and R^y is an optionally substituted alkyl or alkenyl group.

In some preferred embodiments, component a) is an optionally substituted succinic acid or anhydride thereof of formula (I):

$$R^2\text{-}(Suc)_x$$

wherein R^2 is hydrogen or an optionally substituted hydrocarbyl group;
Suc represents the succinic acid or anhydride thereof; and

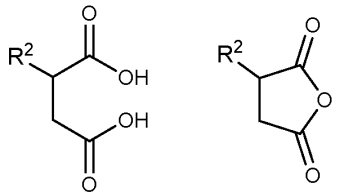
wherein $1 \leq x \leq 2$.

Suitably R^2 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_{14} to C_{36} alkyl or alkenyl group, suitably a C_{14} to C_{32} alkyl or alkenyl group, for example a C_{14} to C_{28} alkyl or alkenyl group.

Suitably R^2 is a C_{14} to C_{28} alkyl or alkenyl group.

The compound of formula (I) is suitably prepared by reacting maleic anhydride with a suitable alkene to provide the R^2 group as defined above. The product of this reaction also includes a double bond. The maleic anhydride is present in the resultant molecule as a succinic acid moiety. This initial product may be described as a monomaleated compound, which may be a compound according to formula (I) wherein $x = 1$.

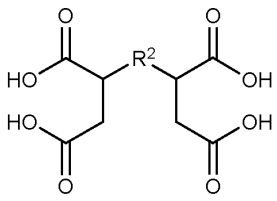
The monomaleated compound may comprise an optionally substituted succinic acid or anhydride thereof of formula (A3) or (A4):



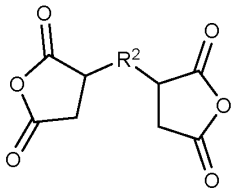
(A3) (A4)

wherein R^2 is hydrogen or an optionally substituted hydrocarbyl group. Preferably R^2 is an optionally substituted alkyl or alkenyl group.

The double bond in the monomaleated product, e.g. within the R^2 group of the compounds (A3) or (A4), can react with a further molecule of maleic anhydride to form a bismaleated compound, which may be a compound according to formula (I) wherein $x = 2$. Such bismaleated compounds may be represented by the structures (A5) or (A6):

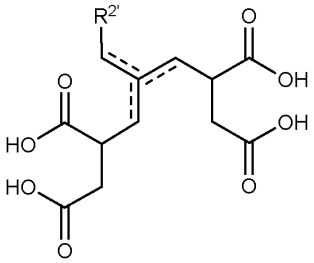


(A5)

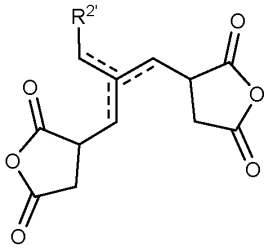


(A6)

The skilled person would understand that such bismaleated products may comprise compounds with different structures depending on the position of the double bond in the R^2 group of the monomaleated compound and the position on the R^2 group which the second succinic acid or anhydride moiety is bonded to. Structures (A7) and (A8) are examples of possible structures of such bismaleated compounds which may be formed by said reaction, wherein $R^{2'}$ is the remainder of the group R^2 as defined above, considering the four carbon atoms of the R^2 which are shown in the structures below linking the succinic acid moieties. The double bond remaining in the compound may have any one of the positions indicated by the dotted lines.



(A7)



(A8)

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

Depending on the extent of the bismaleation reaction discussed above, component a) may be a mixture of monomaleated and bismaleated compounds and therefore may be represented by formula (I) wherein x is greater than 1 and less than 2. In embodiments wherein component a) contains only monomaleated compounds, x is 1. In embodiments wherein component a) contains only bismaleated compounds, x is 2.

In some embodiments, component a) has the formula (I) wherein x is at least 1.2, suitably at least 1.5, at least 1.7 or at least 1.8. Suitably x is approximately 2.

In such embodiments, component a) suitably has the formula (I):

R^2-$(Suc)_x$

wherein R^2 is a C_{14} to C_{28} alkyl or alkenyl group;
Suc represents the succinic acid or anhydride thereof; and
wherein $1.2 \leq x \leq 2$.

The skilled person will appreciate that the ester compounds used in the present invention typically comprise mixtures of compounds and may be prepared from a mixture of monomaleated and bismaleated compounds.

The ester compounds may be defined in terms of their level of bismaleation.

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

A monomaleated compound has one succinic acid moiety per module.

A bismaleated compound has two succinic acid moieties per molecule.

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

Component a) comprises an optionally substituted polycarboxylic acid or an anhydride thereof. Preferably component a) comprises a hydrocarbyl substituted succinic acid or anhydride thereof. This may be referred to as a hydrocarbyl substituted succinic acid derived acylating agent.

The average number of succinic acid moieties per molecule of acylating agent is sometimes referred to in the art as “P value”, which can be calculated by known methods.

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

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

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

Preferably the hydrocarbyl substituted succinic acid derived acylating agent comprises on average at least 1.3 succinic acid moieties per molecule, more preferably at least 1.4 succinic acid moieties per molecule or at least 1.5.

Suitably the hydrocarbyl substituted succinic acid derived acylating agent comprises on average up to 2 succinic acid moieties per molecule, suitably up to 1.9, suitably up to 1.8 or up to 1.75 succinic acid moieties per molecule.

Suitably the hydrocarbyl substituted succinic acid derived acylating agent comprises on average from 1.2 to 2 succinic acid moieties per molecule, suitably from 1.3 to 1.8 or from 1.5 to 1.75 succinic acid moieties per molecule.

In some embodiments, the hydrocarbyl substituted succinic acid derived acylating agent comprises predominantly bismaleated compound.

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

In some embodiments R^2 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_{14} to C_{36} alkyl or alkenyl group, suitably a C_{14} to C_{32} alkyl or alkenyl group, for example a C_{14} to C_{28} alkyl or alkenyl group.

In the embodiments discussed above, R^2 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^2 is an unsubstituted alkyl or alkenyl group as defined above.

The substituted succinic acid or anhydrides may suitably be prepared by reacting maleic anhydride with an alkene.

In some preferred embodiments the alkene is an internal olefin.

In one embodiment the internal olefin may be a β-olefin.

Internal olefins may be prepared by isomerisation of an α-olefin.

In some embodiments, the R^2 group 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^2 of different lengths. In such embodiments any reference to the molecular weight of the group R^2 relates to the number average molecular weight for the mixture.

In some embodiments, R^2 is a polyisobutenyl group, preferably having a number average molecular weight of from 100 to 5000, preferably from 200 to 2400, suitably from 220 to 1400.

In some embodiments, R^2 is a polyisobutenyl group having a number average molecular weight of from 400 to 700.

In some embodiments, R^2 is a polyisobutenyl group having a number average molecular weight of from 180 to 400.

In some embodiments, R^2 is a polyisobutenyl group having a number average molecular weight of from 800 to 1200.

In some preferred embodiments, R^2 is an alkyl or alkenyl group having 6 to 40 carbon atoms, preferably 10 to 38 carbon atoms, more preferably 14 to 36 carbon atoms, suitably 18 to 26 carbon atoms, for example 20 to 24 carbon atoms.

In some preferred embodiments, R^2 is an alkyl or alkenyl group having 6 to 40 carbon atoms, preferably 10 to 38 carbon atoms, more preferably 14 to 36 carbon atoms, suitably 14 to 20 carbon atoms, for example 16 to 18 carbon atoms.

In some preferred embodiments, R^2 is an alkyl or alkenyl group having from 14 to 18 carbon atoms.

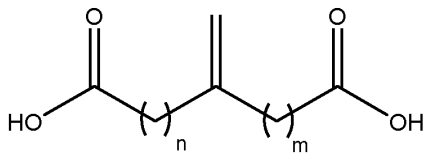
Suitably R^2 is the residue of an olefin. In such embodiments, component a) (of formula (A3) or (A4) is suitably obtained by the reaction of maleic acid with an olefin having 6 to 40 carbon atoms, suitably 10 to 38 carbon atoms, suitably 14 to 36 carbon atoms, preferably 14 to 28.

In some embodiments, R^2 is the residue of an α-olefin having 6 to 36 carbon atoms; preferably from 10 to 30 carbon atoms, suitably from 12 to 24 carbon atoms, for example from 14 to 18 carbon atoms.

In some embodiments, R^2 is the residue of an internal olefin having 6 to 36 carbon atoms preferably from 10 to 32 carbon atoms, suitably from 12 to 24 carbon atoms, for example 14 to 18 carbon atoms.

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 preferred embodiments, component (a) is not a dicarboxylic acid compound of formula (I):



(I)

or an anhydride thereof.

Suitably component (a) is not a dicarboxylic acid selected from itaconic acid, itaconic anhydride, 2-methylene glutaric acid, 2-methylene glutaric anhydride, 2-methylene adipic acid, 2-methylene adipic anhydride and isomers and/or mixtures thereof. Suitably component (a) is not itaconic acid.

In some preferred embodiments, the additive of the present invention is the reaction product of:

a) a succinic acid or anhydride having a C_{10} to C_{30} alkyl or alkenyl group, preferably a C_{14} to C_{28} alkyl or alkenyl group; and

b) an alcohol of formula $H\text{-}(OR)_n\text{-}OR^1$.

In some preferred embodiments, the additive of the present invention is the reaction product of:

a) a succinic acid or anhydride having polyisobutenyl substituent having a number average molecular weight of from 700 to 1300; and

b) an alcohol of formula H-(OR)$_n$-OR^1.

In some preferred embodiments, the additive of the present invention is the reaction product of:

a) a succinic acid or anhydride of formula (I):

$$R^2\text{-(Suc)}_x$$

wherein R^2 is a C_{14} to C_{28} alkyl or alkenyl group;
Suc represents the succinic acid or anhydride thereof; and
wherein $1.2 \leq x \leq 2$; and

b) an alcohol of formula H-(OR)$_n$-OR^1.

In some preferred embodiments, the additive of the present invention is the reaction product of:

a) a succinic acid or anhydride of formula (I):

$$R^2\text{-(Suc)}_x$$

wherein R^2 is polyisobutenyl substituent having a number average molecular weight of from 700 to 1300;
Suc represents the succinic acid or anhydride thereof; and
wherein $1.2 \leq x \leq 2$; and

b) an alcohol of formula H-(OR)$_n$-OR^1.

The alcohol of formula H(OR)$_n$OR^1 may take a number of forms.

In some embodiments, R is an unsubstituted alkylene group.

In such embodiments, R is suitably 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.

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

In some embodiments, R is suitably a group of formula $(CH_2)_x$ wherein x is from 2 to 12, preferably from 2 to 6.

In such embodiments, R is suitably an optionally substituted alkylene group. R is suitably 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.

In some preferred embodiments, R is preferably $CR^aR^bCR^cR^d$ and the alcohol has the formula $H\text{-}(OCR^aR^bCR^cR^d)_nOH$ wherein each of R^a, R^b, R^c and R^d is independently hydrogen or an optionally substituted alkyl group. Preferably each R^a, R^b, R^c and R^d 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^a, R^b, R^c and R^d 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^a, R^b, R^c and R^d are hydrogen, more preferably at least three of R^a, R^b, R^c and R^d are hydrogen.

In some embodiments, R^a, R^b, R^c and R^d are all hydrogen and R is an ethylene group CH_2CH_2.

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

In some embodiments, 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 $-CH(CH_3)CH_2$-.

In some embodiments, 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.

In some embodiments, n is from 18 to 26, suitably from 20 to 24, for example 22 to 23.

In embodiments in which n is more than 1 component b) may be a polyhydric alcohol or an ether thereof.

In some embodiments, n is 1 and R^1 is hydrogen. In such embodiments, the alcohol of component b) may be a diol. As R may be substituted, the alcohol may be a polyol. Suitably R is a straight chain or branched alkylene group, suitably having from 2 to 10 carbon atoms, suitably from 2 to 6 carbon atoms.

In such embodiments wherein n is 1 and R^1 is hydrogen, R may be a straight chain or branched alkylene group, suitably having from 2 to 10 carbon atoms, suitably from 2 to 6 carbon atoms. Therefore the alcohol of component b) may be 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 such embodiments wherein n is 1 and R^1 is hydrogen, the alcohol of formula $H(OR)_nOR^1$ may be an alkylene glycol, suitably wherein R is a straight chain or branched alkylene group, suitably having from 2 to 10 carbon atoms, suitably from 2 to 6 carbon atoms. Suitably the alcohol of component b) is ethylene glycol or propylene glycol, preferably ethylene glycol.

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

For example in some embodiments in which n is 1, the alcohol $H-(OR)_n-OR^1$ may be glycerol, pentaerythritol or trimethylolpropane.

In some preferred embodiments, in the alcohol of formula $H-(OR)_n-OR^1$, n is 1 or more and R^1 is an optionally substituted hydrocarbyl group. In such embodiments, component b) is a glycol ether or a polyglycol ether.

In such embodiments, component b) may be provided by an ether of a polyhydric alcohol. For example component b) may be an ether of: a polyethylene glycol, a polypropylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol or tripropylene glycol.

In such embodiments wherein R^1 is an optionally substituted hydrocarbyl group and n is a positive integer, R^1 is suitably an optionally substituted alkyl, alkenyl or aryl group, suitably an optionally substituted alkyl or alkenyl group. Preferably R^1 has from 4 to 50 carbon atoms, preferably 4 to 40 carbon atoms, more preferably from 10 to 30 carbon atoms. R^1 may be straight chain or branched. Preferably R^1 is straight chain.

In such embodiments, R^1 is suitably a substituted alkyl or alkenyl group, suitably a substituted alkyl group. Suitable substituents are hydroxy and ester groups. In some embodiments R^1 is a 2-hydroxy alkyl, alkenyl or aryl group.

Suitably R^1 is an unsubstituted alkyl or alkenyl group. Preferably R^1 is an alkyl group, preferably an unsubstituted alkyl group.

In some embodiments, n is greater than 1 and R^1 is hydrogen. In such embodiments, the alcohol of formula $H(OR)_nOR^1$ is suitably a polyalkylene glycol, with R as defined above. In such embodiments, n is suitably from 2 to 24, suitably from 2 to 10, from 2 to 6, preferably from 2 to 5, for example 3 or 4. In such embodiments, R is suitably a group of formula $(CH_2)_x$ wherein x is from 2 to 12, preferably from 2 to 6, suitably ethylene or propylene.

In such embodiments, component b) may be a polypropylene glycol having a number average molecular weight of 425.

In some embodiments, component b) may be selected from triethylene glycol, tetraethyelene glycol, propylene glycol, dipropylene glycol and tripropylene glycol.

In some embodiments, component b) is selected from ethylene glycol, propylene glycol and oligomers or polymers thereof.

In some embodiments, component b) may be a polypropylene glycol having a number average molecular weight of 725.

The skilled person will appreciate that commercial sources of such alcohols of formula H-$(OR)_n$-OH will often contain mixtures of compounds, for example in which n may be between 6 and 10.

In some preferred embodiments, R^1 is hydrogen.

In embodiments in which R^1 is hydrogen, each alcohol of formula $H(OR)_nOR^1$ can react with one or two acid or anhydride molecules to form the additive.

For example, in some embodiments component b) of formula $H(OR)_nOR^1$ is reacted with approximately 2 molar equivalents of polycarboxylic acid. Such additive products contain the residues of two acid moieties per molecule. The two acid moieties may be the same or different. In some embodiments both acid moieties are the same. In some embodiments the two acid moieties are different. Preferably, both acid moieties are the same.

In some embodiments, the additive of the present invention may be prepared from the reaction of a polyhydric alcohol of formula H-$(OR)_n$-OH with approximately one equivalent of a first polycarboxylic acid or anhydride thereof and approximately one equivalent of a second polycarboxylic acid or anhydride thereof.

For example, an additive of the present invention may be prepared from the reaction of a polyhydric alcohol of formula H-$(OR)_n$-OH with approximately one equivalent of a succinic acid or anhydride substituted with an alkyl or alkenyl group having 6 to 36 carbon atoms and one equivalent of a succinic acid or anhydride substituted with a polyisobutenyl group having a number average molecular weight of from 200 to 1300.

In some embodiments n is 0 and therefore component b) may be provided by an alcohol of formula R^1OH.

In such embodiments, R^1 is suitably an optionally substituted alkyl, alkenyl or aryl group, preferably having from 1 to 60, preferably from 10 to 40 carbon atoms. Preferably R^1 is an optionally substituted alkyl group.

In such embodiments, R^1 is suitably an unsubstituted alkyl group. The alkyl group may be straight chained or branched. In some embodiments R^1 is an optionally substituted alkyl group having 4 to 40, preferably 6 to 30, more preferably 10 to 20 carbon atoms.

One suitable alcohol for component b) is tetradecanol.

In such embodiments wherein component b) is provided by an alcohol of formula R^1OH, R^1 is suitably an alkyl or aryl group having 1 to 12, suitably 2 to 10 or 4 to 8 carbon atoms.

Suitable such alcohols for use herein include benzyl alcohol, tetradecanol, butanol, 2-butanol, isobutanol, octanol, 2-ethylhexanol, hexanol, cyclohexanol, cyclooctanol, 2-propylheptanol, isopropanol, 2-ethyl-1-butanol and mixtures thereof.

In one embodiment, the alcohol R^1OH is selected from benzyl alcohol, tetradecanol, butanol, octanol, 2-ethylhexanol, hexanol, cyclohexanol, cyclooctanol, 2-propylheptanol, 2-ethyl-1-butanol and mixtures thereof.

In such embodiments, R is preferably an unsubstituted alkyl or cycloalkyl group having 1 to 12, suitably 4 to 10 or 4 to 8 carbon atoms. R may be a straight chain, branched or cyclic alkyl group.

In such embodiments, component b) is preferably selected from butanol, octanol, 2-ethylhexanol, hexanol, cyclohexanol, cyclooctanol, 2-ethyl-1-butanol and mixtures thereof.

One especially preferred alcohol for component b) is 2-ethylhexanol.

Component b) may comprise a mixture of alcohols. Such a mixture may result from a source of alcohol comprising a mixture of isomers and/or a mixture of homologues. In some embodiments alcohols from different sources may be combined to provide a mixture.

In one embodiment component b) comprises a mixture of 2-ethylhexanol and isopropanol.

The skilled person will appreciate that commercial sources of alcohols of formula R^1OH will often contain mixtures of compounds.

In some preferred embodiments, the component b) is provided by an alcohol of formula H-(OR)$_n$-OR^1, wherein n is 0 or 1, R is a straight chain or branched alkylene group having from 2 to 10 carbon atoms and R^1 is hydrogen or an alkyl or aryl group having 4 to 12 carbon atoms; wherein when n is 1, R^1 is hydrogen.

In some preferred embodiments, the alcohol component b) is provided by an alcohol of formula H-(OR)$_n$-OR^1, wherein either:

n = 1, R is a straight chain or branched alkylene group, suitably having from 2 to 10 carbon atoms and R^1 is hydrogen; or

n = 0 and R^1 is an alkyl or aryl group having 4 to 12 carbon atoms.

In some preferred embodiments, the alcohol component b) is provided by an alcohol of formula H-(OR)$_n$-OR^1, wherein either:

n = 1, R is a straight chain or branched alkylene group, suitably having from 2 to 6 carbon atoms and R^1 is hydrogen; or

n = 0 and R^1 is a straight chain, branched or cyclic alkyl group having 4 to 12 carbon atoms;

suitably wherein the R and/or R^1 are unsubstituted.

In some preferred embodiments, the alcohol component b) is provided by either:

a diol selected from ethylene glycol, propylene glycol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol and neopentyl glycol; or

an alcohol selected from butanol, octanol, 2-ethylhexanol, hexanol, cyclohexanol, cyclooctanol and 2-ethyl-1-butanol.

In some preferred embodiments, the alcohol component b) is provided by ethylene glycol or 2-ethylhexanol.

In some preferred embodiments the additive of the present invention is the reaction product of:

a) an optionally substituted polycarboxylic acid or anhydride thereof selected from pyromellitic acid, malonic acid, sebacic acid and succinic acid; and

b) either:

a diol selected from ethylene glycol, propylene glycol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol and mixtures thereof; or

an alcohol selected from butanol, octanol, 2-ethylhexanol, hexanol, cyclohexanol, cyclooctanol, 2-ethyl-1-butanol and mixtures thereof.

In some preferred embodiments the additive of the present invention is the reaction product of:

a) a succinic acid or anhydride having a C_{10} to C_{30} alkyl or alkenyl group, preferably a C_{14} to C_{28} alkyl or alkenyl group; and

b) an alcohol of formula $H\text{-}(OR)_n\text{-}OR^1$, wherein n is 0 or 1, R is a straight chain or branched alkylene group having from 2 to 10 carbon atoms and R^1 is hydrogen or an alkyl or aryl group having 4 to 12 carbon atoms; wherein when n is 1, R^1 is hydrogen.

In some preferred embodiments the additive of the present invention is the reaction product of:

a) a succinic acid or anhydride having a C_{10} to C_{30} alkyl or alkenyl group, preferably a C_{14} to C_{28} alkyl or alkenyl group; and

b) an alcohol of formula $H\text{-}(OR)_n\text{-}OR^1$, wherein either:

n = 1, R is a straight chain or branched alkylene group, suitably having from 2 to 10 carbon atoms and R^1 is hydrogen; or

n = 0 and R^1 is an alkyl or aryl group having 4 to 12 carbon atoms;

suitably wherein the R and/or R^1 are unsubstituted.

In some preferred embodiments the additive of the present invention is the reaction product of:

a) a succinic acid or anhydride having a C_{10} to C_{30} alkyl or alkenyl group, preferably a C_{14} to C_{28} alkyl or alkenyl group; and

b) an alcohol of formula $H\text{-}(OR)_n\text{-}OR^1$, wherein either:

n = 1, R is a straight chain or branched alkylene group, suitably having from 2 to 6 carbon atoms and R^1 is hydrogen; or

n = 0 and R^1 is a straight chain, branched or cyclic alkyl group having 4 to 12 carbon atoms;

suitably wherein the R and/or R^1 are unsubstituted.

In some preferred embodiments the additive of the present invention is the reaction product of:

a) a succinic acid or anhydride having a C_{10} to C_{30} alkyl or alkenyl group, preferably a C_{14} to C_{28} alkyl or alkenyl group; and

b) either:

a diol selected from ethylene glycol, propylene glycol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol and mixtures thereof; or

an alcohol selected from butanol, octanol, 2-ethylhexanol, hexanol, cyclohexanol, cyclooctanol, 2-ethyl-1-butanol and mixtures thereof.

In some preferred embodiments the additive of the present invention is the reaction product of:

a) a succinic acid or anhydride having a C_{10} to C_{30} alkyl or alkenyl group, preferably a C_{14} to C_{28} alkyl or alkenyl group; and

b) ethylene glycol or 2-ethylhexanol.

In some preferred embodiments the additive of the present invention is the reaction product of:

a) a succinic acid or anhydride having a C_{14} to C_{18} alkenyl group; and

b) ethylene glycol;

suitably wherein the C_{14} to C_{18} alkenyl group is the residue of an internal olefin having from 14 to 18 carbon atoms.

In such embodiments, component a) is suitably obtained by the reaction of maleic acid with an internal olefin having from 14 to 18 carbon atoms.

In some preferred embodiments the additive of the present invention is the reaction product of:

a) a succinic acid or anhydride of formula (I):

R^2-$(Suc)_x$

wherein R^2 is a C_{10} to C_{30} alkyl or alkenyl group, preferably a C_{14} to C_{28} alkyl or alkenyl group; Suc represents the succinic acid or anhydride thereof; and
wherein $1.2 \leq x \leq 2$; and

b) an alcohol of formula H-$(OR)_n$-OR^1, wherein n is 0 or 1, R is a straight chain or branched alkylene group having from 2 to 10 carbon atoms and R^1 is hydrogen or an alkyl or aryl group having 4 to 12 carbon atoms; wherein when n is 1, R^1 is hydrogen.

In some preferred embodiments the additive of the present invention is the reaction product of:

a) a succinic acid or anhydride of formula (I):

R^2-$(Suc)_x$

wherein R^2 is a C_{10} to C_{30} alkyl or alkenyl group, preferably a C_{14} to C_{28} alkyl or alkenyl group; Suc represents the succinic acid or anhydride thereof; and
wherein $1.2 \leq x \leq 2$; and

b) an alcohol of formula H-$(OR)_n$-OR^1, wherein either:

n = 1, R is a straight chain or branched alkylene group, suitably having from 2 to 10 carbon atoms and R^1 is hydrogen; or

n = 0 and R^1 is an alkyl or aryl group having 4 to 12 carbon atoms;

suitably wherein the R and/or R^1 are unsubstituted.

In some preferred embodiments the additive of the present invention is the reaction product of:

a) a succinic acid or anhydride of formula (I):

R^2-$(Suc)_x$

wherein R^2 is a C_{10} to C_{30} alkyl or alkenyl group, preferably a C_{14} to C_{28} alkyl or alkenyl group; Suc represents the succinic acid or anhydride thereof; and
wherein $1.2 \leq x \leq 2$; and

b) an alcohol of formula $H\text{-}(OR)_n\text{-}OR^1$, wherein either:

n = 1, R is a straight chain or branched alkylene group, suitably having from 2 to 6 carbon atoms and R^1 is hydrogen; or

n = 0 and R^1 is a straight chain, branched or cyclic alkyl group having 4 to 12 carbon atoms;

suitably wherein the R and/or R^1 are unsubstituted.

In some preferred embodiments the additive of the present invention is the reaction product of:

a) a succinic acid or anhydride of formula (I):

$R^2\text{-}(Suc)_x$

wherein R^2 is a C_{10} to C_{30} alkyl or alkenyl group, preferably a C_{14} to C_{28} alkyl or alkenyl group; Suc represents the succinic acid or anhydride thereof; and
wherein $1.2 \leq x \leq 2$; and

b) either:

a diol selected from ethylene glycol, propylene glycol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol and mixtures thereof; or

an alcohol selected from butanol, octanol, 2-ethylhexanol, hexanol, cyclohexanol, cyclooctanol, 2-ethyl-1-butanol and mixtures thereof.

In some preferred embodiments the additive of the present invention is the reaction product of:

a) a succinic acid or anhydride of formula (I):

$R^2\text{-}(Suc)_x$

wherein R^2 is a C_{10} to C_{30} alkyl or alkenyl group, preferably a C_{14} to C_{28} alkyl or alkenyl group; Suc represents the succinic acid or anhydride thereof; and
wherein $1.2 \leq x \leq 2$; and

b) ethylene glycol or 2-ethylhexanol.

The ester additive of the present invention is the reaction product of:

a) an optionally substituted polycarboxylic acid or an anhydride thereof; and

b) an alcohol of formula $H\text{-}(OR)_n\text{-}OR^1$, wherein R is an optionally substituted alkylene group, R^1 is hydrogen or an optionally substituted hydrocarbyl group and n is 0 or a positive integer; provided that n is not 0 when R^1 is hydrogen.

In some embodiments component a) comprises a compound of formula (I) where x is approximately 1 and component a) and component b) are reacted in a molar ratio of from 5:1 to 1:20, preferably from 2:1 to 1:10, more preferably from 1:1 to 1:4 for example from 1.5:1 to 1:2.5.

In some embodiments component a) comprises a compound of formula (I) where x is approximately 1 and component a) and component b) 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.

Suitably component a) comprises a compound of formula (I) where x is approximately 1 and component a) and component b)are reacted in an approximately 1:1 molar ratio, for example from 1.2:1 to 1:1.2.

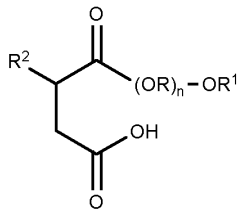
In such embodiments, component b) is suitably an alcohol selected from one or more of butanol, octanol, 2-ethylhexanol, hexanol, cyclohexanol, cyclooctanol and 2-ethyl-1-butanol, for example 2-ethylhexanol.

In some embodiments, component a) is reacted with an excess of component b), suitably wherein component b) is a diol selected from one or more of ethylene glycol, propylene glycol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol and neopentyl glycol, for example ethylene glycol.

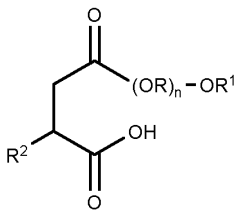
In some embodiments, component a) is reacted with from 0.5 to 1.5 molar equivalents of component b) per succinic acid or anhydride group present in component a). Suitably component a) is reacted with from 0.75 to 1.25 molar equivalents of component b) per succinic acid or

anhydride group present in component a), suitably from 0.9 to 1.1 molar equivalents of component b), suitably approximately 1 molar equivalent of component b), per succinic acid or anhydride group present in component a).

In some preferred embodiments, the ester additive is the reaction product of a substituted succinic acid or succinic anhydride and an alcohol of component b). In such embodiments, the additive preferably comprises compounds having the formula (C1) or (C2), suitably as major components:



(C1)



(C2)

wherein R and R^1 are as defined above in relation to component b) and R^2 is as defined above in relation to compounds (A3) and (A4). Therefore R is an optionally substituted alkylene group, R^1 is hydrogen or an optionally substituted hydrocarbyl group and n is 0 or a positive integer; provided that n is not 0 when R^1 is hydrogen; and R^2 is hydrogen or an optionally substituted hydrocarbyl group.

Preferably R^2 is an optionally substituted alkyl or alkenyl group. Suitably R^2 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_{14} to C_{32} alkyl or alkenyl group, for example a C_{14} to C_{28} alkyl or alkenyl group.

Preferably R^2 is an unsubstituted C_{14} to C_{28} alkyl or alkenyl group, which may be branched or straight chain.

Preferably, in the compounds of formula (C1) and (C2), either:

n = 1, R is a straight chain or branched alkylene group, suitably having from 2 to 10 carbon atoms and R^1 is hydrogen; or

n = 0 and R^1 is an alkyl or aryl group having 4 to 12 carbon atoms;

suitably wherein the R and/or R^1 are unsubstituted.

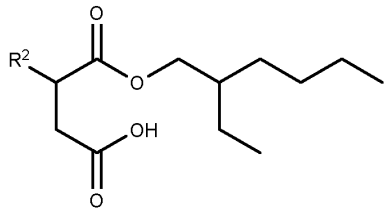
Preferably either:

n = 1, R is a straight chain or branched alkylene group, suitably having from 2 to 6 carbon atoms and R^1 is hydrogen; or

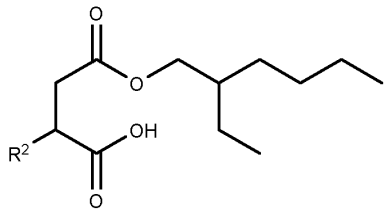
n = 0 and R^1 is a straight chain, branched or cyclic alkyl group having 4 to 12 carbon atoms;

suitably wherein the R and/or R^1 are unsubstituted.

In some embodiments, the ester additive comprises compounds having the formula (C3) or (C4), suitably as major components:



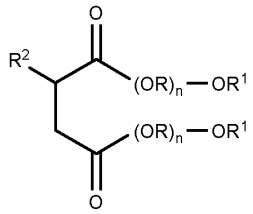
(C3)



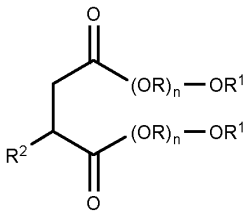
(C4)

wherein R^2 is a C_{14} to C_{28} alkyl or alkenyl group, preferably an unsubstituted C_{14} to C_{28} alkyl or alkenyl group.

In some embodiments, the ester additive comprises compounds having the formula (C5) or (C6):



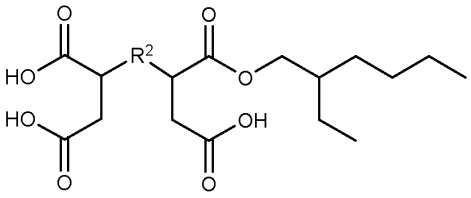
(C5)



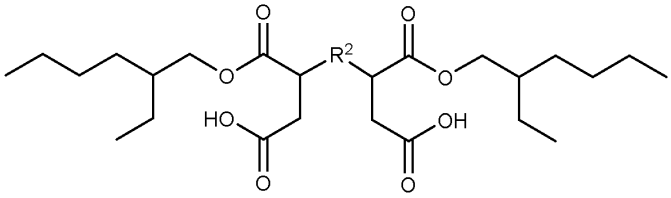
(C6)

wherein R, R^1 and R^2 are as defined above.

In some embodiments, the ester additive comprises compounds having the formula (C8) and/or (C9) and/or regioisomers of said compounds and/or anhydride analogues of said compounds, or mixtures thereof:



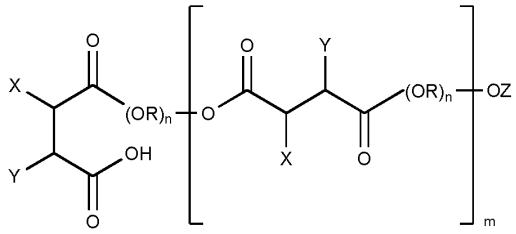
(C8)



(C9)

wherein R^2 is a C_{14} to C_{28} alkyl or alkenyl group, preferably an unsubstituted C_{14} to C_{28} alkyl or alkenyl group.

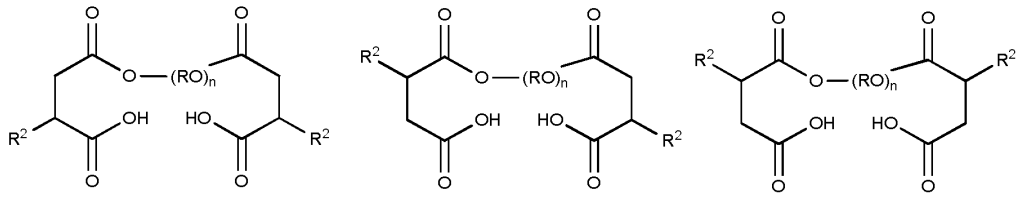
The additives may also include oligomers or polymers having a structure of formula (D):



(D)

wherein m is at least 1 and one of each X and Y is R^2 and the other is hydrogen, and Z is hydrogen or COCHXCHYCOOH.

In some embodiments in which R^1 is hydrogen the acid/anhydride are reacted with the alcohol in an approximate 2:1 molar ratio and the additive includes compounds of formula (E1), (E2) or (E3):



(E1) (E2) (E3)

and mixtures and/or isomers thereof; wherein R and R^2 are as defined above.

In some embodiments each acid residue in formulae (E1), (E2) or (E3) is the same. In some embodiments the acid residues are different.

The ester additive is suitably present in the diesel fuel composition in an amount of from 0.1 to 10000 ppm, preferably from 1 to 1000 ppm, preferably from 1 to 500 ppm. In preferred embodiments the ester additive is included in the diesel fuel composition in an amount of from 5 to 300 ppm, suitably 5 to 200 ppm, for example from 10 to 150 ppm.

In this specification, unless otherwise stated, ppm refers to parts per million by weight.

For the avoidance of doubt the above amounts refer to the amount of active ester compound present in the fuel composition, excluding any diluent, carrier, by-product or residual starting materials that may be present in the additive material added. In embodiments in which two or more ester compounds are present the above amounts refer to the total of all ester compounds defined according to the first and second aspects present in the fuel composition.

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

The ester additive may be added as part of an additive composition. The additive composition may comprise one or more diluents or carriers and optionally one or more further fuel additives. Suitably the additive composition comprises less than 10 wt% water, preferably less than 5 wt%, suitably less than 1 wt%, for example less than 0.1 wt%.

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

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.

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

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

In some embodiments the diesel fuel composition may be a blended diesel fuel comprising bio-diesel. In such blends the bio-diesel may be present in an amount of, for example up to 0.5%, up to 1%, up 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 GTL fuel or be 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.

In some embodiments the diesel fuel composition used in the present invention preferably comprises at least 5 wt% biodiesel and less than 50 ppm sulphur.

In some embodiments the diesel fuel composition is neat renewable diesel.

The diesel fuel composition may be suitably 100% derived from renewable sources. Such a fuel is referred to herein as a renewable diesel. A suitable renewable diesel is a renewable diesel obtained by the hydrodeoxygenation of fats and oils (the fats and oils being derived from renewable sources). For example, the renewable diesel may be a hydrotreated triglyceride oil such as a hydrogenated vegetable oil (HVO). The HVO suitably complies with EN15940 Class A. Such HVO fuels are available from Coryton and Neste.

Such renewable diesel fuels are suitably produced from raw materials of biological origin. These may suitably be selected from vegetable oils, animal fats, fish oils and mixtures thereof.

Examples include rapeseed oil, canola oil, tall oil, sunflower oil, soybean oil, hemp oil, olive oil, linseed oil, mustard oil, carinata oil, palm oil, palm kernel oil, peanut oil, castor oil, coconut oil, animal fats such as tallow or recycled food fats, raw materials resulting from genetic engineering, and biological raw materials produced from microorganisms such as algae and bacteria.

Preferably, the renewable diesel is provided by a process involving hydrodeoxygenation (HDO) and optionally isomerization steps. The hydrodeoxygenation (HDO) step results in the decomposition of the structures of the biological esters or of the triglyceride constituents, in the elimination of the oxygen-bearing, phosphorus-bearing and sulfur-bearing compounds and in the hydrogenation of olefinic bonds. The product resulting from the hydrodeoxygenation reaction may then be isomerized. A fractionation step may optionally follow the hydrodeoxygenation and isomerization steps.

Preferably the renewable diesel has a cetane number of between 50 and 90, preferably between 55 and 90, more preferably between 60 and 85. Cetane number is suitably measured by the standard test method set out in IP 498.

Preferably the renewable diesel has a cloud point of less than 25°C, more preferably less than 10°C. Suitably the paraffinic fuel has a cloud point of less than -5°C, for example less than -10°C. Cloud point may suitably be measured using the standard test method described in IP 219.

Preferably the renewable diesel has a kinematic viscosity at 40°C of 1 to 20 mm^2s^{-1}, preferably from 2 to 15 mm^2s^{-1}, more preferably from 2 to 10 mm^2s^{-1}, most preferably from 2 to 4.5 mm^2s^{-1}. Kinematic viscosity may be measured according to ASTM D445.

Preferably the renewable diesel has an initial boiling point (IBP) and a final boiling point (FBP) within the range 265 to 380°C, more preferably within the range 275 to 380°C and most preferably within the range 290 to 375°C.

Preferably the renewable diesel has a boiling range of less than 80°C, preferably less than 70°C, suitably less than 60°C, for example from 30 to 60°C. Boiling range is used to refer to the difference between the final boiling point and the initial boiling point.

The initial boiling point, final boiling point and boiling range can be determined according to the method set out in IP 123.

In preferred embodiments the renewable diesel comprises predominately straight chain alkanes and branched alkanes.

Preferably the renewable diesel comprises less than 20 wt% cycloalkanes, preferably less than 10 wt%, suitably less than 5 wt%, preferably less than 1 wt%, for example less than 0.1 wt%.

For the avoidance of doubt by the term cycloalkane or naphthene is used to refer to any saturated hydrocarbon compound which includes a non-aromatic cyclic moiety.

Preferably the weight of ratio n-paraffins to i-paraffins present in the renewable diesel is from 99:1 to 1:99, more preferably from 90:10 to 10:99, preferably from 75:25 to 25:75. Techniques for determining the ratio of n-paraffins to i-paraffins are known to the person skilled in the art and include gas chromatography.

Ratios of n-paraffins and i-paraffins present in a fuel typically depend on the hydrotreatment method used to prepare the fuel, which may also include an isomerisation step.

The renewable diesel may comprise greater than 4 wt%, preferably greater than 5 wt%, of C14 to C16 n-alkanes.

The renewable diesel may comprise less than 8 wt%, preferably less than 6 wt%, of C14 to C16 n-alkanes.

The renewable diesel may comprise from 4 to 8 wt%, preferably from 5 to 6 wt%, of C14 to C16 n-alkanes.

The renewable diesel may comprise greater than 5 wt%, preferably greater than 7 wt%, more preferably greater than 10 wt%, of C14 to C18 n-alkanes.

The renewable diesel may comprise less than 20 wt%, preferably less than 18 wt%, more preferably less than 16 wt%, of C14 to C18 n-alkanes.

The renewable diesel may comprise from 5 to 20 wt%, preferably from 7 to 18 wt%, more preferably from 10 to 16 wt%, of C14 to C18 n-alkanes.

The renewable diesel may comprise from 3 to 30 wt% of C6 to C24 n-alkanes (i.e. n-paraffin).

The renewable diesel suitably has an oxygen content of less than 1wt%, preferably less than 0.1wt% when measured according to EN 14078.

The renewable diesel suitably has an aromatic content of less than 5 wt%, preferably less than 1 wt%.

Preferably the renewable diesel is a hydrotreated triglyceride oil, suitably an HVO, having the contents and properties described above.

Suitably the renewable diesel complies with the standard specification set out in EN15940.

Preferably the renewable diesel is a hydrotreated triglyceride oil, suitably an HVO, having an aromatic content of less than 5 wt%, preferably less than 1 wt%.

Preferably the renewable diesel is a hydrotreated triglyceride oil, suitably an HVO, having cetane number of between 50 and 90, preferably between 55 and 90, more preferably between 60 and 85 (according to IP 498); a cloud point of less than 10°C, preferably less than -5°C (according to IP 219); and a kinematic viscosity at 40°C of from 1 to 20 mm^2s^{-1}, preferably from 2 to 10 mm^2s^{-1} (according to ASTM 445).

Preferably the renewable diesel is a hydrotreated triglyceride oil, suitably an HVO, having an initial boiling point and a final boiling point within the range 265 to 380°C, preferably 290 to 375°C and a boiling range of less than 80°C, preferably 30 to 60°C.

The diesel fuel composition used in the present invention suitably comprises at least 10 vol% renewable diesel as defined above, suitably at least 25 vol%, at least 50 vol% or at least 90 vol% renewable diesel, suitably wherein the renewable diesel is hydrotreated triglyceride oil, preferably HVO.

A fuel which comprises 100% renewable diesel is denoted as R100, a fuel which comprises 90% mineral diesel and 10% renewable diesel (by volume) is known as R10; fuel comprising 50% mineral diesel and 50% renewable diesel (by volume) is known as R50; and so on.

In some preferred embodiments, the fuel composition of the present invention comprises renewable diesel and one or more further components selected from biodiesel, mineral diesel and mixtures thereof.

In some embodiments the fuel composition comprises renewable diesel and at least 5 vol% biodiesel.

In some embodiments the fuel composition comprises renewable diesel and at least 20 vol% biodiesel.

In preferred embodiments the diesel fuel composition is neat (i.e. 100 vol%) renewable diesel as defined above, preferably neat hydrotreated triglyceride oil, preferably neat HVO. Such a fuel may be referred to as an R100 diesel fuel.

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

Other metal-containing species may also be present as a contaminant, for example through the 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.

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.

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

The diesel fuel composition preferably comprises less than 1 wt% water, preferably less than 0.1 wt%.

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

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

The present invention reduces the emission of nitrogen oxides from a diesel engine combusting a diesel fuel composition.
The diesel engine may be a direct injection diesel engine or an indirect injection diesel engine.

In some embodiments the engine may be an off road engine, for example a marine, rail or stationary engine. Stationary engines include engines for power generation and pumping.

Most preferably the engine is a direct injection diesel engine.

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

Suitably the present invention may be used to reduce the emission of nitrogen oxide and/or nitrogen dioxide from a diesel engine having a high pressure fuel system. Suitably the diesel engine has a fuel pressure in excess of 1350 bar (1.35×10^8 Pa). It may have a pressure of up to 2000 bar (2×10^8 Pa) or more.

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.

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.

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

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.

The present invention may also be used to reduce emissions of nitrogen oxide and/or nitrogen dioxide from a traditional diesel engine such as an indirect injection diesel engine.

The present invention reduces the emission of nitrogen oxide and/or nitrogen dioxide on combustion of a diesel fuel composition in a diesel engine.

In some embodiments the present invention reduces the emission of nitrogen oxide.

In some embodiments the present invention reduces the emission of nitrogen dioxide.

In some embodiments the present invention reduces the emission of nitrogen oxide and nitrogen dioxide.

The term "NO_x" is commonly used to refer to the combined emissions of nitrogen oxide (NO) and nitrogen dioxide (NO_2). Thus the method and use may reduce the emission of NO_x.

By reducing the emission of nitrogen oxide and/or nitrogen dioxide in the context of the present invention we mean that the amount of nitrogen oxide and/or nitrogen dioxide emitted from the exhaust of a diesel engine is lower when combusting a diesel fuel composition comprising as an additive at least one ester compound as defined in relation to the first and second aspects compared with when an otherwise identical diesel fuel composition without the additive is combusted.

The amount of nitrogen oxide and/or nitrogen dioxide emitted from the engine may be measured by any suitable means. Such means will be known to the person skilled in the art. One suitable method is described in example 2.

The reduction in emissions may be measured by comparing emissions per unit volume of fuel combusted and/or by comparing emissions per unit volume of exhaust gas emitted.

Suitably the present invention reduces the emission of nitrogen oxide and/or nitrogen dioxide in the exhaust gas directly emitted from the engine, before it enters the post combustion system.

Preferably the method and use of the present invention reduces the emission of nitrogen oxide by at least 2%, preferably at least 5%.

Preferably the method and use of the present invention reduces the emission of nitrogen dioxide by at least 2%, preferably at least 5%.

Preferably the method and use of the present invention reduces the total emissions of nitrogen oxide and nitrogen dioxide by at least 2%, preferably at least 5%.

The method of the first aspect of the present invention may further involve a step of measuring the amount of nitrogen oxide and/or nitrogen dioxide emitted per unit volume of exhaust gas from an engine combusting a fuel composition comprising as an additive at least one ester compound as defined in relation to the first and second aspects and comparing the amount of nitrogen oxide and/or nitrogen dioxide emitted per unit volume of exhaust gas from the same engine combusting an otherwise identical diesel fuel composition without the additive.

Preferably the method and use of the present invention reduces the total emission of nitrogen oxide and/or nitrogen dioxide by at least 2%, preferably at least 5% measured by comparing the amount of nitrogen oxide and/or nitrogen dioxide emitted per unit volume of exhaust gas from an engine combusting a fuel composition comprising as an additive at least one ester compound as defined in relation to the first and second aspects with the amount of nitrogen oxide and/or nitrogen dioxide emitted per unit volume of exhaust gas from the same engine combusting an otherwise identical diesel fuel composition without the additive.

The amount of nitrogen oxide and/or nitrogen dioxide emitted per unit volume of exhaust gas is suitably measured as parts per million. The amount of nitrogen oxide and/or nitrogen dioxide emitted is suitably measured by FTIR, as described herein.

Because the present invention reduces the levels of nitrogen oxide and/or nitrogen dioxide emitted from a diesel engine, there are lower amounts of these gases that need to be treated by the selective catalytic reduction (SCR) unit. As a result the SCR unit may need less frequent maintenance and/or the SCR additive may need topping up less frequently.

Thus the method and use of the present invention advantageously increase maintenance intervals for a vehicle fitted with a selective catalytic reduction (SCR) unit.

Further the method and use of the present invention may reduce the consumption of additive by a selective catalytic reduction (SCR) unit.

The third aspect of the invention provides a diesel fuel composition comprising as an additive at least one ester compound as defined herein wherein combustion of the diesel fuel composition in a diesel engine emits a reduced amount of nitrogen oxide and/or nitrogen dioxide from the exhaust of the diesel engine compared with combustion of an otherwise identical diesel fuel composition without the additive.

By emitting a reduced amount of nitrogen oxide and/or nitrogen dioxide it is meant that when the same volume of fuel is combusted under identical conditions in the same engine the total mass of nitrogen oxide and/or nitrogen dioxide is reduced when the additive is present compared with when the additive is not present.

Preferably on combustion of a diesel fuel composition of the third aspect of the present invention comprising an ester additive the total mass of nitrogen oxide and/or nitrogen dioxide emitted per unit volume of fuel combusted is reduced by at least 1.0% compared with combustion of an otherwise identical diesel fuel composition without the additive in the same engine under identical conditions.

Preferably on combustion of a diesel fuel composition of the third aspect of the present invention comprising an ester additive the total mass of nitrogen oxide and/or nitrogen dioxide emitted per unit volume of fuel combusted is reduced by at least 5% compared with combustion of an otherwise identical diesel fuel composition without the additive in the same engine under identical conditions.

Preferably on combustion of a diesel fuel composition of the third aspect of the present invention comprising an ester additive the total mass of nitrogen oxide emitted per unit volume of fuel combusted is reduced by at least 1.0%, preferably at least 1.5%, compared with combustion of an otherwise identical diesel fuel composition without the additive in the same engine under identical conditions.

Preferably on combustion of a diesel fuel composition of the third aspect of the present invention comprising an ester additive the total mass of nitrogen dioxide emitted per unit volume of fuel combusted is reduced by at least 2%, preferably at least 15%, compared with combustion of an otherwise identical diesel fuel composition without the additive in the same engine under identical conditions.

Preferably on combustion of a diesel fuel composition of the third aspect of the present invention comprising an ester additive the total mass of nitrogen oxide and nitrogen dioxide emitted per

unit volume of fuel combusted is reduced by at least 2%, preferably at least 5%, compared with combustion of an otherwise identical diesel fuel composition without the additive in the same engine under identical conditions.

The reference to identical conditions suitably includes the use of the same engine, the same fuel type and composition (apart from the additive defined herein) and the same operating conditions of the engine as discussed herein.

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

Example 1

Additive A is the reaction product of a C16 to C18 alkenyl substituted succinic acid with at least 2 molar equivalents of ethylene glycol, wherein the C16 to C18 alkenyl substituted succinic acid is formed from a C16 to C18 internal olefin.

Additive B was prepared as follows:

Alphaplus C20-24 olefin (642.1 g, 2.08mol) was heated to 185°C and maleic anhydride (407.9 g, 4.16 mol, 2 equivalents) was added over a period of 3 hours. The mixture was then reacted for a further 9 hours at 215°C, then distilled under vacuum to provide 953.5 g of a deep brown liquid. Acid value was measured at 6.88 mmolH+/g, as determined by titration with lithium methoxide. This corresponds to approximately 67% bismaleation of the olefin.

The product obtained by the above process (bismaleated C20-24 ASA) (473.5 g, AV 6.88 mmolH+/g,) was heated to 80°C. 2-ethylhexanol (211.9 g, 1 equivalent based on anhydride groups present) was added and stirred at 80°C for 15 mins. The temperature was increased to 165°C and mixture stirred at this temperature for approximately 4 hrs. The infra-red spectra was monitored until the anhydride absorption band was absent and then the temperature of the mixture was reduced to 80°C. Aromatic 150 solvent (289.7g) was added to provide the product additive B (953.4 g) having 70% w/w active material.

Diesel fuel compositions were prepared comprising the following components:

Table 1

Composition	Additive	Treat rate (ppm active)
1	None	-
2	A	75
3	B	70

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

Feature	Units	Results	Minimum	Maximum	Method
Density 15°C	kg/m³	836.0	833.0	837.0	ASTM D4052
Marker (Red)	-	Pass	-	-	VISUAL
Cetane Number		53.9	52.0	54.0	ASTM D613
I.B.Pt.	°C	214.3			ASTM D86
10% v/v Recovered at	°C	232.6			ASTM D86
50% v/v Recovered at	°C	275.5	245.0	-	ASTM D86
90% v/v Recovered at	°C	330.2			ASTM D86
95% v/v Recovered at	°C	348.0	345.0	350.0	ASTM D86
F.B.Pt.	°C	356.2	-	370.0	ASTM D86
Aromatics by FIA	%(V/V)	19.8	Corrected for		ASTM D1319
Olefins by FIA	%(V/V)	5.5			
Flash Point, Pensky Closed	°C	92.0	55.0	-	ASTM D93
Sulphur Content	mg/kg	< 3.0	-	10.0	ASTM D5453
Viscosity at 40°C	mm2/s	3.062	2.300	3.300	ASTM D445
Cloud Point	°C	-18			ASTM D2500
CFPP	°C	-20	-	-15	EN 116
Lubricity (WSD 1.4) at 60°C	µm	180	-	400	ISO 12156-1
Carbon Residue (on 10% Dist. Res)	%(m/m)	< 0.10	-	0.20	ASTM D4530
Ash	%(m/m)	< 0.001	-	0.010	ASTM D482
FAME Content: None Detected	-	Pass	-	-	EN 14078
Polycyclic Aromatic Hydrocarbons	%(m/m)	5.8	3.0	6.0	EN 12916
Total Aromatic Hydrocarbons	%(m/m)	22.2			EN 12916
Water Content	mg/kg	50	-	200	IP 438
Water & Sediment	%(V/V)	< 0.010			ASTM D2709
Strong Acid Number	mg	0 KOH/g	-	0.02	ASTM D974
Oxidation Stability	mg	< 0.1 per 100ml	-	2.5	ASTM D2274
Copper Corrosion, 3hrs at 100°C	-	1B	-	-	ASTM D130
Oxygen Content	%(m/m)	< 0.04	ELEMENTAL		Elemental Analysis
Carbon Content	%(m/m)	86.89	ASTM D5291		ASTM D5291
Hydrogen Content	%(m/m)	13.11	ASTM D5291		ASTM D5291
Carbon Weight Fraction		0.8689	CALCULATION		Calculation
C/H Mass Ratio		6.63	CALCULATION		Calculation
Atomic H/C Ratio		1.7979	CALCULATION		Calculation
Atomic O/C Ratio		< 0.0003	CALCULATION		Calculation
Gross Heat of Combustion	MJ/kg	45.72	IP 12		IP 12
Net Heat of Combustion	MJ/kg	42.94	IP 12		IP 12
Net Heat of Combustion	btu/lb	18480	CALCULATION		Calculation

Example 2

Engine testing was carried out as described below to assess the performance of the ester additives of the present invention in the reduction of the emission of NO and NO_x from the exhausts of diesel engines.

Engine Details

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

Modifications / Test Setup

1. No SCR Catalyst or associated components were present in the exhaust system.
2. High pressure EGR cooler is artificially controlled to 40°C for the duration of the test.
3. An FTIR (AVL SESAM i60 FTIR analyser) was connected and the sample point is located pre-aftertreatment on the exhaust outlet of the turbocharger, for measuring the NO and NO_2 emissions.

Diesel fuel compositions 1 to 8 of example 9 (table 2) were tested.

Test Procedure

No cleaning of the injectors was conducted between each test run.

- Engine Start + Warm-Up
- Passive DPF Regeneration by varying the engine speed and load until the regeneration is complete. The differential pressure across the DPF is used to monitor the regeneration progress.
- Engine Stop
- Change to test fuel
- Engine restarted and warmed
- 8-Hour Steady-State Test Cycle
- 1200RPM
- 60Nm
- Engine Stop

The emissions outputs were measured by FTIR and recorded as an average over the 8h steady state test cycle and the results are provided in table 2. The emission of nitrogen oxide (NO) was measured, as was the total emission of nitrogen oxide and nitrogen dioxide (NO_x).

Table 2

Composition	NO_2 (ppm by volume)	NO (ppm by volume)	NO_x (ppm by volume)
1 [base fuel]	4.84	24.86	29.69
2	2.69	24.44	27.13
3	3.48	23.08	26.56

These results demonstrate that the use of the ester additives described herein in a diesel fuel composition may provide a significant reduction in the emission of nitrogen oxide and nitrogen dioxide on combustion of said fuel in a diesel engine.

Claims

1. A method of reducing the emission of nitrogen oxide and/or nitrogen dioxide from a diesel engine combusting a diesel fuel composition, the method comprising dosing into the diesel fuel composition as an additive at least one ester compound; wherein the ester compound is the reaction product of:

a) an optionally substituted polycarboxylic acid or an anhydride thereof; and

b) an alcohol of formula $H\text{-}(OR)_n\text{-}OR^1$, wherein R is an optionally substituted alkylene group, R^1 is hydrogen or an optionally substituted hydrocarbyl group and n is 0 or a positive integer; provided that n is not 0 when R^1 is hydrogen.

2. The use of at least one ester compound as an additive to reduce the emission of nitrogen oxide and/or nitrogen dioxide from a diesel engine combusting a diesel fuel composition; wherein the ester compound is the reaction product of:

a) an optionally substituted polycarboxylic acid or an anhydride thereof; and

b) an alcohol of formula $H\text{-}(OR)_n\text{-}OR^1$, wherein R is an optionally substituted alkylene group, R^1 is hydrogen or an optionally substituted hydrocarbyl group and n is 0 or a positive integer; provided that n is not 0 when R^1 is hydrogen.

3. A diesel fuel composition comprising as an additive at least one ester compound; wherein the ester compound is the reaction product of:

a) an optionally substituted polycarboxylic acid or an anhydride thereof; and

b) an alcohol of formula $H\text{-}(OR)_n\text{-}OR^1$, wherein R is an optionally substituted alkylene group, R^1 is hydrogen or an optionally substituted hydrocarbyl group and n is 0 or a positive integer; provided that n is not 0 when R^1 is hydrogen;

wherein combustion of each unit volume of the diesel fuel composition in a diesel engine emits a reduced amount of nitrogen oxide and/or nitrogen dioxide from the exhaust of the diesel engine compared with combustion of each unit volume of an otherwise identical diesel fuel composition without the additive, in the same engine under identical conditions.

4. The method, use or composition according to any preceding claim wherein component a) is a hydrocarbyl substituted succinic acid or a hydrocarbyl substituted succinic anhydride.

5. The method, use or composition according to any preceding claim wherein component a) is an optionally substituted succinic acid or anhydride thereof of formula (I):

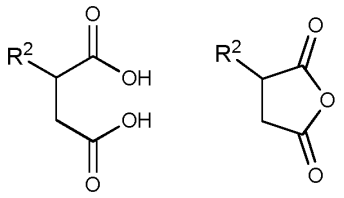
R^2-$(Suc)_x$

wherein R^2 is hydrogen or an optionally substituted hydrocarbyl group;
Suc represents the succinic acid or anhydride thereof; and
wherein $1 \leq x \leq 2$.

6. The method, use or composition according to claim 5, wherein R^2 is a C_{14} to C_{28} alkyl or alkenyl group.

7. The method, use or composition according to claim 5 or claim 6 wherein x is at least 1.2.

8. The method, use or composition according to any one of claims 1 to 6 wherein component a) is an optionally substituted succinic acid or anhydride thereof of formula (A3) or (A4):



(A3) (A4)

wherein R^2 is hydrogen or an optionally substituted hydrocarbyl group.

9. The method, use or composition according to any preceding claim, wherein in component b) 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 30.

10. The method, use or composition according to any preceding claim wherein in component b) n is 1, R^1 is hydrogen and R is a straight chain or branched alkylene group, preferably wherein component b) is ethylene glycol or propylene glycol, preferably ethylene glycol.

11. The method, use or composition according to any one of claims 1 to 9 wherein in component b) n is 0 and R^1 is an optionally substituted alkyl, alkenyl or aryl group having from 1 to 60 carbon atoms.

12. The method, use or composition according to claim 11, wherein R^1 is an alkyl or aryl group having 1 to 12 carbon atoms, preferably selected from benzyl alcohol, tetradecanol, butanol, 2-butanol, isobutanol, octanol, 2-ethylhexanol, hexanol, cyclohexanol, cyclooctanol, 2-propylheptanol, isopropanol, 2-ethyl-1-butanol and mixtures thereof.

13. The method, use or composition according to any one of claims 1 to 9 wherein in component b) either:

n = 1, R is a straight chain or branched alkylene group, preferably having from 2 to 10 carbon atoms and R^1 is hydrogen; or

n = 0 and R^1 is an alkyl or aryl group having 4 to 12 carbon atoms.

14. The method or use according to any one of claims 1 to 9, wherein component b) is either:

a diol selected from ethylene glycol, propylene glycol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol and mixtures thereof; or

an alcohol selected from butanol, octanol, 2-ethylhexanol, hexanol, cyclohexanol, cyclooctanol, 2-ethyl-1-butanol and mixtures thereof.

15. The method, use or composition according to any preceding claim wherein component a) and component b) are reacted in a molar ratio of from 2:1 to 1:2, preferably wherein component b) is selected from benzyl alcohol, tetradecanol, butanol, 2-butanol, isobutanol, octanol, 2-ethylhexanol, hexanol, cyclohexanol, cyclooctanol, 2-propylheptanol, isopropanol, 2-ethyl-1-butanol and mixtures thereof.

16. The method, use or composition according to any one of claims 1 to 14 wherein component a) is reacted with an excess of component b), preferably wherein component b) is a diol selected from ethylene glycol, propylene glycol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol and mixtures thereof.

17. The method, use or composition according to any preceding claim wherein the one or more ester compounds are the reaction product of:

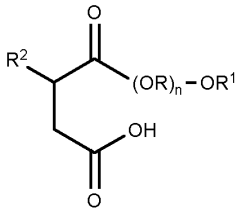
a) a succinic acid or anhydride having a C_{10} to C_{30} alkyl or alkenyl group, preferably a C_{14} to C_{28} alkyl or alkenyl group; and

b) an alcohol of formula $H\text{-}(OR)_n\text{-}OR^1$, wherein either:

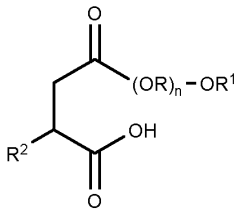
n = 1, R is a straight chain or branched alkylene group, suitably having from 2 to 10 carbon atoms and R^1 is hydrogen; or

n = 0 and R^1 is an alkyl or aryl group having 4 to 12 carbon atoms.

18. The method, use or composition according to any preceding claim wherein the one or more ester compounds include compounds having the formula (C1) or (C2):



(C1)



(C2)

wherein R is an optionally substituted alkylene group; R^1 is hydrogen or an optionally substituted hydrocarbyl group; n is 0 or a positive integer; provided that n is not 0 when R^1 is hydrogen; R^2 is hydrogen or an optionally substituted hydrocarbyl group, preferably wherein R^2 is a C_{14} to C_{28} alkyl or alkenyl group.

19. The method, use or composition according to any preceding claim wherein the one or more ester compounds are present in the fuel in an amount of from 5 to 200 ppm.

20. The method, use or composition according to any preceding claim which reduces the emission of nitrogen oxide.

21. The method, use or composition according to any preceding claim which reduces the emission of nitrogen dioxide.

22. The method, use or composition according to any preceding claim which reduces the emission of nitrogen oxide and nitrogen dioxide.

23. The method, use or composition according to any preceding claim which reduces the emission of nitrogen oxide and/or nitrogen dioxide by at least 5%.

24. The method or use according to any of claims 1, 2 or 4 to 23 which reduces the emission of nitrogen oxide and/or nitrogen dioxide from a direct injection diesel engine.