

Improvements in fuels

5 The present invention relates to improvements in fuel compositions, and in particular to improving the properties of blended fuel compositions comprising renewable diesel and biodiesel.

10 Due to environmental considerations significant efforts have been made in developing alternative hydrocarbon fuels to fossil fuels to power internal combustion engines. The present invention relates in particular to alternatives to mineral diesel fuel.

15 One alternative fuel suitable for use in diesel engines is biodiesel. Biodiesel is produced by the transesterification of lipids obtained from plants or animals, for example tallow oil, soybean oil or other vegetable oil. Transesterification of the triglycerides obtained from these plant or animal sources with an alcohol such as methanol, ethanol or propanol produces a mono alkyl ester as the biodiesel fuel.

20 Renewable diesel is produced from biomass sources through biological, thermal and chemical processes. Typically renewable diesels are obtained by hydrotreatment of vegetable oils with hydrogen at elevated temperatures and pressures in the presence of a catalyst. Renewable diesel is sometimes referred to as hydrogenated vegetable oil.

25 Renewable diesel contains mainly saturated, straight chain or branched, aliphatic hydrocarbons. Biodiesel consists primarily of mono alkyl esters. Mineral diesel often contains aromatic and sulfated species as well as aliphatic hydrocarbons.

Due to the different chemical components of the fuels, new challenges can arise when mineral diesel is replaced partially or fully with renewable diesel and/or biodiesel.

30 The present invention attempts to solve some problems that may occur when blends of renewable diesel and biodiesel are used. Due to the different chemical nature of the renewable and biodiesel components of a blended fuel, problems can occur when storing the fuel, particularly if storage is at low temperatures.

35 Three measurements are commonly taken to assess the low temperature performance of diesel fuel. Standardised tests have been devised to measure the temperature at which the fuel hazes (the cloud point - CP), the lowest temperature at which a fuel can flow (the pour point - PP) and the lowest temperature at which fuel flows through a filter, the cold filter plugging point - CFPP); and the changes thereto caused by additives (Δ CP, Δ PP, Δ CFPP).

The present invention is not about the use of additives to change the cloud point, pour point or cold filter plugging point of a fuel. Rather the present invention seeks to address problems that can occur in a fuel when it is above the cloud point.

- 5 Diesel vehicle fuel systems are fitted with a filter to prevent particulate matter reaching the final injection system. If such particulates are not removed, failure of the fuel injection system could result.

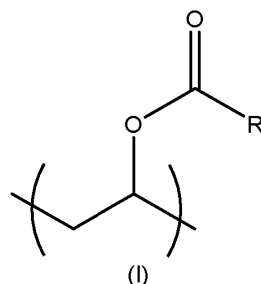
Problems can arise when the filter becomes blocked as this affects the rate at which fuel is delivered to the engine. This issue is different to the problems which occur during cold filter plugging where wax forms under very low temperatures and blocks the filter until the wax re-dissolves. Filter blocking can occur due to the formation of particulates within the fuel, particularly during storage. In recent years the problems with filter blocking have become more prominent. This is because in an effort to reduce emissions and improve engine performance,
10 more sophisticated injection systems have been developed. Since these fuel injection systems operate at high temperature and pressures they are more susceptible to wear and damage if exposed to particulates in the fuel. Fuel filter pore sizes have therefore decreased and in some cases may be as low as 2 to 5 microns in diameter. The reduction in pore size of the filter has inevitably led to increased issues with filter blocking. A blocked filter will restrict or prevent fuel
15 from reaching an engine. This can cause problems with starting the engine and a loss of power. In some instances a blocked filter can cause an engine to shut down altogether until the filter has been replaced, in order to protect the injection system, causing huge inconvenience to the user.

- 25 The present invention seeks to reduce the filter blocking tendency of fuels containing a blend of renewable diesel and biodiesel fuels. These fuels are different in nature to mineral diesel fuels and blends containing mineral diesel.

According to a first aspect of the present invention there is provided the use of one or more
30 additives to reduce the filter blocking tendency of a fuel composition having a tendency to block filters, wherein the fuel composition comprises a renewable diesel component and a biodiesel component; and wherein the one or more additives are selected from:

- (a) a copolymer comprising units of formula (I):

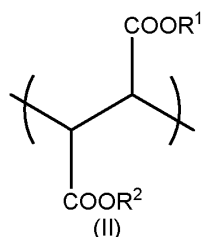
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(I)

and units of formula (II):

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(II)

wherein R is an alkyl group and each of R¹ and R² is an alkyl or alkenyl group having 6 to 22 carbon atoms;

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(b) the reaction product of a polycarboxylic acid having at least one tertiary amino group and a primary or secondary amine; and

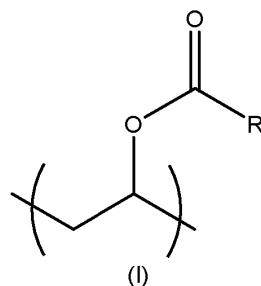
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(c) the reaction product of secondary amines and a copolymer of maleic anhydride and an α -olefin.

According to a second aspect of the present invention there is provided a method of reducing the filter blocking tendency of a fuel composition having a tendency to block filters and which comprises a biodiesel component and a renewable diesel component, the method comprising dosing into the fuel one or more additives selected from:

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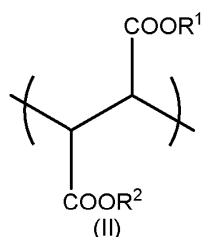
(a) a copolymer comprising units of formula (I):



(I)

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and units of formula (II):



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wherein R is an alkyl group and each of R¹ and R² is an alkyl or alkenyl group having 6 to 22 carbon atoms;

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(b) the reaction product of a polycarboxylic acid having at least one tertiary amino group and a primary or secondary amine; and

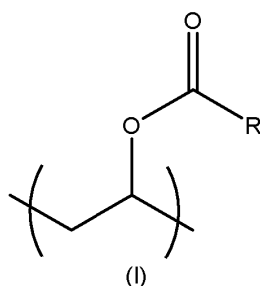
(c) the reaction product of secondary amines and a copolymer of maleic anhydride and an α -olefin.

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According to a third aspect of the present invention there is provided a fuel composition comprising a renewable diesel component, a biodiesel component and one or more additives; wherein the fuel composition has a reduced filter blocking tendency compared with an otherwise identical fuel composition which does not comprise the one or more additives and has a tendency to block filters; and wherein the one or more additives are selected from:

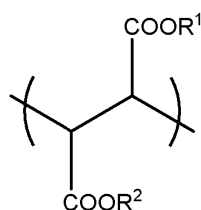
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(a) a copolymer comprising units of formula (I):



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and units of formula (II):



(II)

wherein R is an alkyl group and each of R¹ and R² is an alkyl or alkenyl group having 6 to 22 carbon atoms;

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(b) the reaction product of a polycarboxylic acid having at least one tertiary amino group and a primary or secondary amine; and

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(c) the reaction product of secondary amines and a copolymer of maleic anhydride and an α -olefin.

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

15 The first, second and third aspects of the present invention relate to one or more additives selected from components (a), (b), and (c). The invention can involve the use of one such additive or a mixture of two or more such additives. References herein to the additive or an additive include embodiments in which two or more additives are present.

20 The present invention relates to reducing the filter blocking tendency of fuel compositions comprising a biodiesel component and a renewable diesel component.

The fuel compositions may optionally further comprise a mineral diesel component.

25 In some embodiments the fuel composition used in the present invention may comprise a petroleum-based fuel oil, especially a middle distillate fuel oil. Such distillate fuel oils generally boil within the range of from 110°C to 500°C, e.g. 150°C to 400°C. The diesel fuel may comprise atmospheric distillate or vacuum 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
30 distillates.

In preferred embodiments the fuel compositions do not comprise a mineral diesel component.

35 In this specification by biodiesel we mean to refer to esters of fatty acids. Such fuels are commonly referred to as first generation biodiesel. Biodiesel as defined herein contains esters of, for example, vegetable oils, animal fats and used cooking fats. This form of biodiesel may be obtained by transesterification of oils, with an alcohol, usually a monoalcohol, usually in the presence of a catalyst. The fatty acids used to produce the fuel may originate from a wide variety of natural sources including, but not limited to, vegetable oil, canola oil, safflower oil, sunflower
40 oil, nasturtium seed oil, mustard seed oil, olive oil, sesame oil, soybean oil, corn oil, peanut oil,

- cottonseed oil, rice bran oil, babassu nut oil, castor oil, palm oil, rapeseed oil, low erucic acid rapeseed oil, palm kernel oil, lupin oil, jatropha oil, coconut oil, flaxseed oil, evening primrose oil, jojoba oil, camelina oil, tallow, beef tallow, butter, chicken fat, lard, dairy butterfat, shea butter, used frying oil, oil miscella, used cooking oil, yellow trap grease, hydrogenated oils, derivatives of the oils, fractions of the oils, conjugated derivatives of the oils, and mixtures of any thereof.

In this specification by renewable diesel we mean to refer to diesel fuel obtained by the hydrodeoxygenation of fats and oils. Such fuels are often referred to as second generation biodiesel and are 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 is marketed by ConocoPhillips as Renewable Diesel and by Neste as NExBTL. Renewable diesel fuels are sometimes known as hydrogenated vegetable oils (or HVOs).

- Preferably the renewable diesel component comprises less than 5 wt% aromatic compounds, preferably less than 1 wt%, suitably less than 0.1 wt%. Most preferably the renewable diesel used in the present invention is substantially free of aromatic compounds.

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

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

The renewable diesel component 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 component may comprise greater than 4 wt%, preferably greater than 5 wt%, of C14 to C16 n-alkanes and less than 8 wt%, preferably less than 6 wt%, of C14 to C16 n-alkanes.

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

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

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

- 10 The fuel composition comprises a renewable diesel component and a biodiesel component. Preferably the renewable diesel component makes up at least 10 vol% of all fuel components present in the composition, preferably at least 30 vol%, more preferably at least 40 vol%, preferably at least 50 vol%.

- 15 Suitably the renewable diesel component makes up at least 60 vol%, suitably at least 70 vol%, for example, at least 75 vol% of all fuel components in the fuel composition.

- 20 The renewable diesel component may provide up to 99 vol% of all fuel components present in the fuel composition, preferably up to 95 vol%, suitably up to 90 vol%, for example up to 85 vol%.

- 25 The biodiesel component may make up at least 1 vol% of all fuel components present in the fuel composition, preferably at least 3 vol%, suitably at least 5 vol%, preferably at least 8 vol%, for example at least 10 vol%. The biodiesel component may make up at least 12 vol% of all fuel components present in the fuel composition, for example at least 15 vol%.

- 30 The biodiesel component may provide up to 90 vol% of all fuel components present in the fuel composition, for example up to 70 vol%, suitably up to 50 vol%, for example up to 40 vol% or up to 30 vol%. The biodiesel component may provide up to 25 vol% of all fuel components present in the fuel composition.

- 35 In some preferred embodiments, the fuel composition comprises from 1 to 40 vol%, preferably 5 to 35 vol% of a biodiesel component and from 60 to 99 vol%, preferably 65 to 95 vol% of a renewable diesel component.

In some further preferred embodiments, the fuel composition comprises from 10 to 30 vol%, preferably 15 to 25 vol% of a biodiesel component and from 70 to 90 vol%, preferably from 75 to 85 vol% of a renewable diesel component.

In some especially preferred embodiments, the fuel composition comprises approximately 80 vol% of a renewable diesel component and approximately 20 vol% of a biodiesel component.

5 Preferably the fuel composition comprises less than 10 vol% mineral diesel, preferably less than 5 vol%, more preferably less than 3 vol%, preferably less than 1 vol%, for example less than 0.5 vol% or less than 0.1 vol% mineral diesel.

10 In some embodiments the fuel composition may comprise trace amounts of mineral diesel. Such trace amounts may be present due to contamination of the fuel composition during transport and/or storage using pipelines and/or tanks that previously contained mineral diesel.

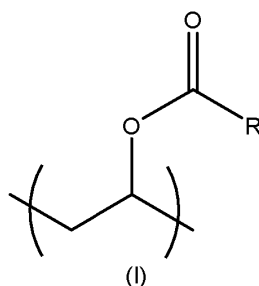
In especially preferred embodiments, the fuel composition does not comprise a mineral diesel component.

15 In the present invention the filter blocking tendency of the fuel compositions comprising a biodiesel component and a renewable diesel component is reduced by the addition of one or more additives selected from components (a), (b) and (c) which are further defined herein.

20 The present invention may involve the use of a single additive or it may involve the use of a mixture of additives

The invention may involve the use of one or more additives of component (a) and/or one or more additives of component (b) and/or one or more additives of component (c).

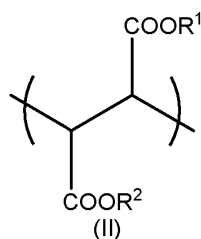
25 In some embodiments the one or more additives used in the present invention comprise (a) a copolymer comprising units of formula (I):



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and units of formula (II):

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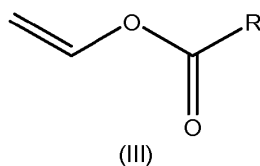


wherein R is an alkyl group and each of R¹ and R² is an alkyl or alkenyl group having 6 to 22 carbon atoms.

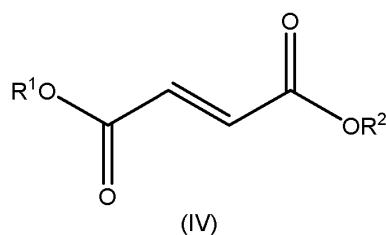
Additive (a) may be prepared by copolymerising vinyl ester monomers and fumaric acid monomers and then esterifying the acid residues.

Preferably additive (a) is prepared by copolymerising vinyl ester monomers and dialkyl fumarate monomers.

Additive (a) is preferably a copolymer prepared by reacting monomers of vinyl ester of formula (III):



and dialkyl fumarate monomers of formula (IV):



Each monomer of formula (III) used to prepare copolymer additive (a) may be the same or the copolymer may be prepared from a mixture of two or more different monomers of formula (III).

R is an alkyl group, preferably an unsubstituted alkyl group.

Preferably R is an alkyl group having 1 to 30 carbon atoms, preferably 1 to 20 carbon atoms, more preferably 1 to 10 carbon atoms, more preferably 1 to 6 carbon atoms.

Preferably R is an unsubstituted alkyl group having 1 to 4 carbon atoms.

Most preferably R is methyl and the monomer of formula (III) is vinyl acetate.

- 5 Each monomer of formula (IV) used to prepare copolymer additive (a) may be the same or the copolymer may be prepared from a mixture of two or more different monomers of formula (IV).

Preferably all of the monomers of formula (IV) used to prepare additive (a) are the same.

- 10 Each of R^1 and R^2 may be the same or different. Preferably R^1 is the same as R^2 .

Each of R^1 and R^2 is an alkyl or alkenyl group. Preferably each is an alkyl group, preferably an unsubstituted alkyl group. R^1 and R^2 may be straight chained or branched. Preferably each of R^1 and R^2 is a straight chain alkyl group.

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In some embodiments each of R^1 and R^2 is an alkyl group having 6 to 22 carbon atoms, preferably 8 to 18 carbon atoms.

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Preferably each of R^1 and R^2 is an alkyl group having 6 to 14 carbon atoms, preferably 8 to 14 carbon atoms, more preferably 10 to 14 carbon atoms, and most preferably 12 to 14 carbon atoms.

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Additive (a) is a copolymer comprising units of formula (I) and units of formula (II). In some embodiments additive (a) may comprise further additional units which are not of formula (I) or formula (II). In such embodiments the copolymer is suitably prepared from vinyl ester monomers, fumaric acid derived monomers (preferably dialkyl fumarate) and one or more further monomer units. In preferred embodiments the one or more further monomers units comprise less than 20 mol% of all monomer units used to prepare additive (a), preferably less than 10 mol%, more preferably less than 5 mol%, more preferably less than 1 mol%.

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In preferred embodiments additive (a) consists essentially of units of formula (I) and units of formula (II). By this we mean that units of formula (I) and units of formula (II) together provide at least 80 mol% of all monomer derived units present in the copolymer, preferably at least 90 mol%, more preferably at least 95 mol%, more preferably at least 99 mol%, for example at least 99.5 mol% or at least 99.9 mol%.

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Suitably additive (a) comprises from 10 to 90 mol% of units of formula (I) and from 90 to 10 mol% of units of formula (II); preferably from 25 to 75 mol% of units of formula (I) and from 25 to 75

mol% of units of formula (II); more preferably from 40 to 60 mol% of units of formula (I) and from 60 to 40 mol% of units of formula (II).

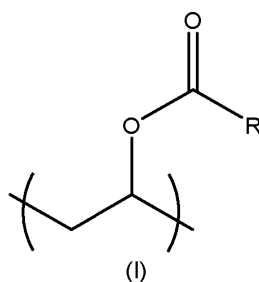
Preferably additive (a) is a random copolymer.

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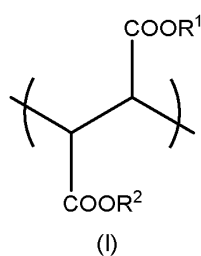
Suitably the copolymer additive (a) has a number average molecular weight of from 1000 to 100000, preferably from 2000 to 50000, more preferably from 5000 to 25000, for example from 6000 to 20000.

10 In some especially preferred embodiments copolymer additive (a) has a number average molecular weight of from 4000 to 25000, preferably 5000 to 20000, more preferably 6000 to 15000. In some embodiments copolymer additive (a) has a number average molecular weight of 8000 to 10000.

15 In especially preferred embodiments additive (a) is a copolymer comprising units of formula (I):



20 and units of formula (II):



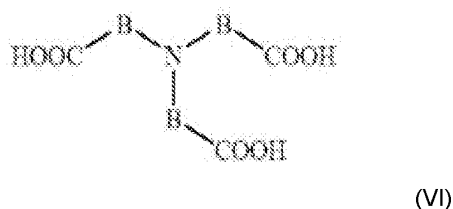
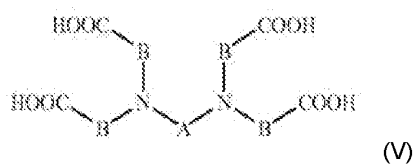
25 wherein R is an alkyl group and each of R¹ and R² is an alkyl group having 10 to 14 carbon atoms, and preferably 12 to 14 carbon atoms and which copolymer has a number average molecular weight of from 4000 to 25000, preferably 5000 to 20000, more preferably 6000 to 15000. Most preferably the copolymer comprises from 40 to 60 mol % of units of formula (I) and from 60 to 40 mol % of units of formula (II).

In some embodiments the one or more additives used in the present invention comprise (b) the reaction product of a polycarboxylic acid having at least one tertiary amino group and a primary or secondary amine.

- 5 The polycarboxylic acid having at least one tertiary amino group preferably has 2 to 20 carbon atoms, at least one tertiary amino group and 2 to 12 carboxylic acid groups. Each carboxylic acid group in the polycarboxylic acid preferably has from 2 to 10 carbon atoms. The polycarboxylic acid groups may be the same or different. Preferably each carboxylic acid group is an acetic acid group. The polycarboxylic acid preferably has from 1 to 3 tertiary amino groups and from 2 to 8 carboxylic acid groups. In preferred embodiments the polycarboxylic acid has 3 to 5, preferably 3 or 4 carboxylic acid groups and 1 to 3, preferably 1 or 2 tertiary amino groups.

In some preferred embodiments the polycarboxylic acid has the formula (V) or (VI):

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wherein A is a straight chain or branched C₂-C₆ alkylene group or HOOC-B-N(CH₂CH₂)₂ and B is a C₁ to C₁₉ alkylene group.

25 Preferably A has 2 to 4 carbon atoms, more preferably 2 or 3 carbon atoms, most preferably 2 carbon atoms.

Preferably B has 1 to 10, more preferably 1 to 4 carbon atoms.

30 Preferred carboxylic acids used to prepare additive (b) include nitrilotriacetic acid, ethylenediamine tetraacetic acid and propylene-1,2-diamine tetraacetic acid.

- To form additive (b) the polycarboxylic acid is reacted with a primary or secondary amine. Most preferably the polycarboxylic acid is reacted with a secondary amine, preferably a secondary amine of formula HNR_2 in which each R is independently a straight chain or branched C_{10} to C_{30} alkyl or alkenyl group, preferably a C_{14} to C_{24} alkyl or alkenyl group. Preferably each R is an alkyl group. Preferably each R is the same.

The secondary amines may react with the polycarboxylic acid to form an amide and/or an ammonium salt. In preferred embodiments all of the amines react to form amides.

- Preferred amines for reaction with the polycarboxylic acid include dioleylamine, dipalmitamine, dicoconut fatty amine, distearylamine, dibehenyl amine and hydrogenated and/or unhydrogenated ditallow fatty amine. Ditallow fatty amine is especially preferred.

- Preferably the amines are reacted with the carboxylic acid in a ratio of from 0.5 to 1.5, preferably from 0.8 to 1.2 moles of amine per carboxylic group present in the carboxylic acid.

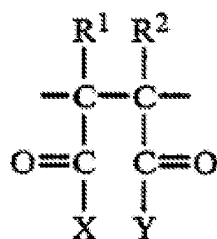
An especially preferred additive component (b) is the reaction product of 1 mole of ethylenediamine tetraacetic acid and 4 moles of hydrogenated tallow fatty amine.

- Other preferred compounds of this type include the N, N dialkyl ammonium salts of 2-N,N' dialkylamidobenzoates, for example the reaction product of 1 mole of phthalic anhydride with 2 moles of ditallow fatty amine and the reaction product of 1 mole of alkenyl-spiro-bis lactone with 2 moles of a dialkylamine, for example ditallow fatty amine (hydrogenated or un hydrogenated).

- In some embodiments the one or more additives used in the present invention comprise (c) the reaction product of secondary amines and a copolymer of an α,β -unsaturated dicarboxylic anhydride and an α -olefin.

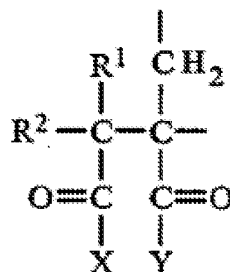
- Preferred compounds of this type are copolymers based on α,β -unsaturated dicarboxylic anhydrides, α,β -unsaturated compounds and optionally polyoxyalkylene ethers of lower unsaturated alcohols, which comprise:

a) 20-80 mol % of bivalent structural units (VII) and/or (VIII)



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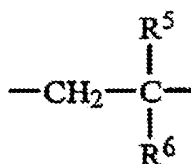
(VII)



(VIII)

wherein R^1 and R^2 are, independently of one another, hydrogen or methyl,

- 5 X and Y are identical or different groups and selected from and N- HR^3 group wherein R^3 is C_6 - C_{40} -alkyl, C_5 - C_{20} -cycloalkyl or C_6 - C_{18} -aryl; an N- $(\text{R}^3)_2$ group wherein each R^3 is identical or different and is as defined above; and an OR^4 group wherein R^4 is hydrogen, a cation of the formula $\text{H}_2\text{N}^+(\text{R}^3)_2$ or $\text{H}_3\text{N}^+\text{R}^3$, C_6 - C_{40} -alkyl, C_5 - C_{20} -cycloalkyl or C_6 - C_{18} -aryl;
- b) 19-80 mol % of bivalent structural units (IX)

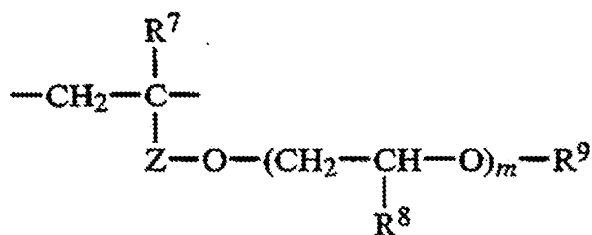


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(IX)

in which R^5 is hydrogen or C_1 - C_4 -alkyl and R^6 is C_6 - C_{60} -alkyl or C_6 - C_{18} -aryl; and

c) 0-30 mol % of bivalent structural units (X):



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(X)

in which R^7 is hydrogen or methyl, R^8 is hydrogen or C_1 - C_4 -alkyl, Z is C_1 - C_4 -alkylene

m is a number from 1 to 100, R^9 is C_1 - C_{24} -alkyl, C_5 - C_{20} -cycloalkyl, C_6 - C_{18} -aryl or $-\text{C}(\text{O})-\text{R}^{10}$, wherein R^{10} is C_1 - C_{40} -alkyl, C_5 - C_{10} -cycloalkyl or C_6 - C_{18} -aryl.

- 20 As will be appreciated by the skilled person, the copolymer may comprise small amounts of unopened anhydride or imide structural units derived from the α,β -unsaturated dicarboxylic anhydride structural units (VII) and/or (VIII).

Preferred copolymers do not contain structural units X. In preferred embodiments X is a group of formula $N-(R^3)_2$ wherein R^3 is C₆-C₄₀ alkyl and Y is a group of the formula OR^4 , wherein R^4 is a cation of formula $H_2N^+(R^3)_2$ wherein R^3 is C₆-C₄₀ alkyl.

- 5 Preferred additives (c) are derived from copolymers of maleic anhydride and an α -olefin having 6 to 30 carbon atoms reacted with 2 equivalents of a fatty amine.

An especially preferred additive (c) is prepared from a copolymer of maleic anhydride and a C18 α -olefin reacted with 2 equivalents of ditallow fatty amine.

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In some embodiments the one or more additives used in the present invention comprise component (a).

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In some embodiments the one or more additives used in the present invention comprise component (b).

In some embodiments the one or more additives used in the present invention comprise component (c).

- 20 In some embodiments the one or more additives used in the present invention comprise component (a) and component (b).

In some embodiments the one or more additives used in the present invention comprise component (a) and component (c).

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In some embodiments the one or more additives used in the present invention comprise component (b) and component (c).

- 30 In some embodiments the one or more additives used in the present invention comprise component (a), component (b) and component (c).

In some embodiments the one or more additives used in the present invention comprise component (a), but do not comprise component (b) or component (c).

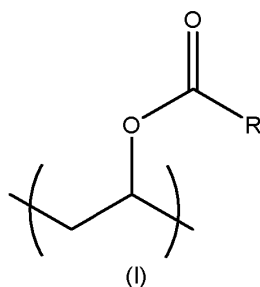
- 35 For the avoidance of doubt each additive used in the present invention may comprise a mixture of compounds and references to an additive (or to the additive) include mixtures, unless otherwise stated. In particular mixtures of isomers and mixtures of homologues are within the scope of the invention.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

the additives described herein may comprise mixtures of isomers and/or mixtures of homologues.

The invention relates to the use of one or more additives selected from:

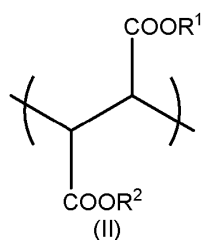
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(a) a copolymer comprising units of formula (I):



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and units of formula (II):



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wherein R is an alkyl group and each of R¹ and R² is an alkyl or alkenyl group having 6 to 22 carbon atoms;

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(b) the reaction product of a polycarboxylic acid having at least one tertiary amino group and a primary or secondary amine; and

(c) the reaction product of secondary amines and a copolymer of maleic anhydride and an α -olefin.

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Suitable treat rates of the one or more additives used in the present invention may depend on the type of fuel used and different levels of additive may be needed to achieve different levels of performance.

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The one or more additives may be added to fuel at any convenient place in the supply chain. For example, one or more additives may be added to fuel at the refinery, at a distribution terminal or after the fuel has left the distribution terminal. The one or more additives may be added to the renewable diesel component and/or the biodiesel component before the components are

blended; and/or the one or more additives may be added to the blended fuel after the components have been mixed. If the one or more additives 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 one or more additives 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 one or more additives in small bottles suitable for direct addition to fuel storage tanks or vehicle tanks.

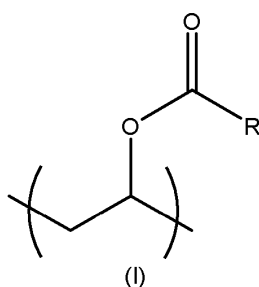
The one or more additives are suitably present in the fuel composition in total in an amount of at least 1 ppm, preferably at least 2 ppm, suitably at least 5 ppm.

The one or more additives may be present in the fuel composition in total in an amount of up to 1000 ppm, suitably up to 750 ppm, for example up to 600 ppm.

The one or more additives is preferably present in the fuel composition in total in an amount of from the 1 to 1000 ppm, preferably 2 to 500 ppm, for example 5 to 350 ppm.

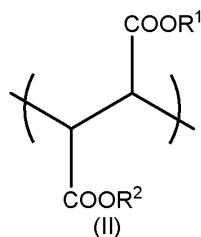
For the avoidance of doubt when the fuel composition comprises a mixture of two or more additives, the above amounts refer to the total amount of all additives (a), (b) and (c) present in the composition. Unless otherwise stated, all references to ppm in this specification are to parts per million by weight.

In some embodiments the fuel composition comprises from 0.1 to 10000 ppm, preferably from 1 to 1000 ppm, preferably from 5 to 500 ppm, for example 10 to 250 ppm of (a) a copolymer comprising units of formula (I):



and units of formula (II):

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wherein R is an alkyl group and each of R¹ and R² is an alkyl or alkenyl group having 6 to 22 carbon atoms.

In some embodiments the fuel composition comprises from 0.1 to 10000 ppm, preferably from 1 to 1000 ppm, preferably from 5 to 500 ppm, for example 10 to 250 ppm of (b) the reaction product of a polycarboxylic acid having at least one tertiary amino group and a primary or secondary amine.

In some embodiments the fuel composition comprises from 0.1 to 10000 ppm, preferably from 1 to 1000 ppm, preferably from 5 to 500 ppm, for example 10 to 250 ppm of (c) the reaction product of secondary amines and a copolymer of maleic anhydride and an α -olefin.

Each of additives (a), (b) and (c) may be provided as a mixture of compounds. Each of the additives (a), (b) and (c) may be provided as a crude reaction product, i.e. without purification after preparation. The above amounts refer to the total of all such compounds present in the composition.

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

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

In some preferred embodiments the diesel fuel composition of the present invention comprises one or more detergents. Nitrogen-containing detergents are preferred. Suitable detergents will be known to the person skilled in the art.

In some embodiments the composition may comprise one or more low temperature enhancing additives. Such compounds are commonly known to those skilled in the art as cold flow improvers. Suitable further cold flow improver additives for use herein include ethylene vinyl acetate co-polymers; terpolymers of ethylene, vinyl acetate and a third monomer; polyalkyl methacrylates; alphaolefin maleic anhydride copolymers; ester or imide derivatives of alphaolefin maleic anhydride copolymers; and combinations thereof.

The present invention relates to reducing the filter blocking tendency of a fuel composition having a tendency to block filters.

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By a fuel composition having a tendency to block filters we mean to refer to a fuel composition which, if untreated with one or more additives as described herein, would cause blocking of filters. The tendency of a fuel composition to block filters may be measured by a number of standard industry tests. The fuel compositions suitable for treatment according to the present invention are fuel compositions which do not satisfy the requirements of such standard tests without the addition of the claimed one or more additives. Reduction of the filter blocking tendency of the fuel compositions may be demonstrated by achieving an improved performance in one of these tests.

Standard test methods for determining filter blocking tendency (FBT) are described in ASTM D2068 and IP387. This general procedure is commonly used for middle distillate fuels containing biodiesel and biodiesel blends. Another test suitable for measuring filter blocking tendency is set out in IP618. The present invention may be assessed using one of these tests.

A preferred method by which the filter blocking tendency of the present invention can be determined is the Canadian Cold Soak Filter Blocking Tendency test (CSFBT). In this test fuel is stored at 1 °C for 16 hours before the filterability is assessed. The procedure for this test is set out in CAN/CGSB 3.0 No. 142.0-2019 and a modified version in which renewable fuel is used in place of a specified isoparaffinic solvent is described in example 2. A similar test is the European Cold Soak test CS IP387 in which fuel is stored at 5°C for 16 hours.

References herein to a result achieved in or measured by a CSFBT test refer to the method set out in example 2.

In preferred embodiments the present invention reduces the filter blocking tendency of the fuel composition as measured by the method of the CSFBT test. According to the method the CSFBT test fuel compositions are cooled to 1 °C for 16 hours and then tested by filtration to

provide a unitless value. The value is an indicator of how likely the fuel is to block filters and a value of less than 2 is generally considered acceptable.

5 Preferably the present invention reduces the filter blocking tendency of a fuel composition which achieves a CSFBT test result of greater than 2 prior to being treated with one or more additives according to the invention. Suitably a fuel composition provided by the present invention achieves a CSFBT test result of less than 2.

10 Thus the use of the first aspect and the method of the second aspect of the invention preferably provide a fuel composition having a filter blocking tendency of less than 2 as measured by the method of the CSFBT test.

Suitably the fuel composition of the third aspect has a filter blocking tendency of less than 2 as measured by the method of the CSFBT test.

15 Preferably the present invention reduces the score of a fuel composition in a CSFBT test by at least 10%, suitably at least 20%, more preferably at least 30%, for example at least 40% or at least 50%.

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

Example 1

25 Blended fuel compositions were prepared by blending renewable diesel fuel component R1 with biodiesel fuels components B1 or B2, having the following properties:

Component fuel	Cloud Point, ASTM D7689 (°C)	Pour Point, ASTM D7346 (°C)
R1	-11.5	-12
B1	14.9	15
B2	15.1	15

30 Additive A - a copolymer of vinyl acetate and dialkyl fumarate with alkyl groups having 14 carbon atoms wherein the number average molecular weight of the copolymer is approximately 9000 - was dosed into the blended fuels to provide the following compositions:

Fuel composition	R1 (%vol)	B1 (%vol)	B2 (%vol)	Additive A (ppm active)
1	80	20		0

2	80	20		104
3	80	20		208
4	80		20	0
5	80		20	104
6	80		20	208

Example 2

Fuel compositions 1 to 6 were tested according to a modification of the procedure of the standard CSFBT test method set out in CAN/CGSB 3.0, No. 142-2019.

The summary of the modified test method is as follows:

1. A sample of the fuel composition is first conditioned to erase its thermal history.
2. The fuel composition is then held at 1 °C for 16 h.
3. The fuel composition is then warmed to 25 °C for 2-4 h.
4. After warming, the fuel composition is then passed at a constant rate of flow (20 mL/min) through a glass fibre filter medium (1.6 µm pore size).
- 4.1. The pressure drop across the filter is monitored until 300 mL of the fuel composition has passed through the filter, and the maximum pressure drop is used to calculate the CSFBT result, or
- 4.2. If a pressure drop of 105 kPa is reached before 300 mL of the fuel composition is filtered, the volume filtered when 105 kPa is reached is used to calculate the CSFBT result.
5. Results of the CSFBT test can range from 1.0 for a fuel composition with very good filterability (essentially no separated materials under the test conditions), to more than 10 for a fuel composition with poor filterability (a relatively high level of separated materials under test conditions).

The results are shown in Table 1:

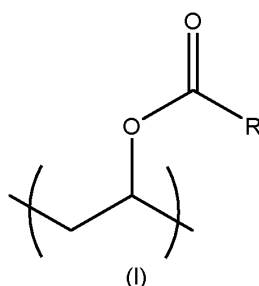
Table 1

Fuel composition	CSFBT result
1	3.88
2	1.56
3	1.47
4	2.90
5	1.49
6	1.69

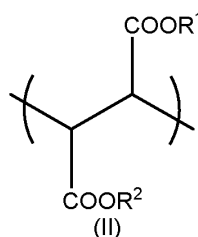
Claims

1. The use of at one or more additives to reduce the filter blocking tendency of a fuel composition having a tendency to block filters, wherein the fuel composition comprises a renewable diesel component and a biodiesel component; and wherein the one or more additives are selected from

(a) a copolymer comprising units of formula (I):



and units of formula (II):



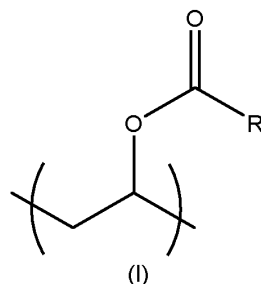
wherein R is an alkyl group and each of R¹ and R² is an alkyl or alkenyl group having 6 to 22 carbon atoms;

- (b) the reaction product of a polycarboxylic acid having at least one tertiary amino group and a primary or secondary amine; and
- (c) the reaction product of secondary amines and a copolymer of maleic anhydride and an α -olefin.

2. A method of reducing the filter blocking tendency of a fuel composition having a tendency to block filters and which comprises a biodiesel component and a renewable diesel component, the method comprising dosing into the fuel one or more additives selected from

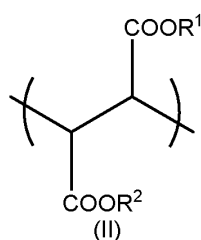
(a) a copolymer comprising units of formula (I):

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and units of formula (II):

5



wherein R is an alkyl group and each of R¹ and R² is an alkyl or alkenyl group having 6 to 22 carbon atoms;

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(b) the reaction product of a polycarboxylic acid having at least one tertiary amino group and a primary or secondary amine; and

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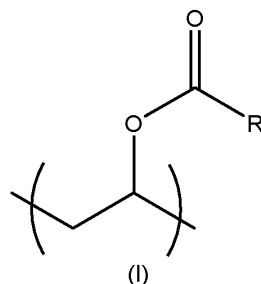
(c) the reaction product of secondary amines and a copolymer of maleic anhydride and an α -olefin.

3. A fuel composition comprising a renewable diesel component, a biodiesel component and one or more additives; wherein the fuel composition has a reduced filter blocking tendency compared with an otherwise identical fuel composition which does not comprise the one or more additives and has a tendency to block filters; and wherein the one or more additives are selected from

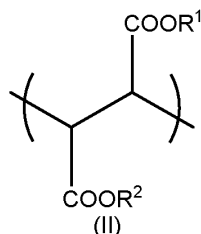
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(a) a copolymer comprising units of formula (I):

25



and units of formula (II):



wherein R is an alkyl group and each of R¹ and R² is an alkyl or alkenyl group having 6 to 22 carbon atoms;

(b) the reaction product of a polycarboxylic acid having at least one tertiary amino group and a primary or secondary amine; and

(c) the reaction product of secondary amines and a copolymer of maleic anhydride and an α -olefin.

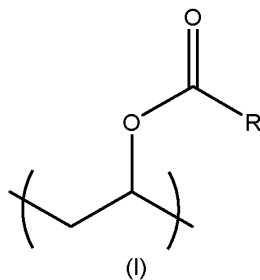
4. A composition, method or use according to any preceding claim wherein each of R¹ and R² is an alkyl or alkenyl group having 8 to 14 carbon atoms.

5. A composition, method or use according to any preceding claim wherein the one or more additives comprise component (a).

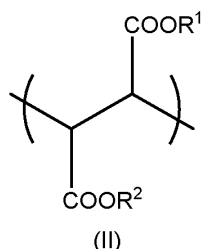
6. A composition, method or use according to any preceding claim wherein the one or more additives comprise component (b).

7. A composition, method or use according to any preceding claim wherein the one or more additives comprise component (c).

8. A composition, method or use according to any preceding claim wherein the one or additives comprise a copolymer comprising units of formula (I):



and units of formula (II):



5

wherein R is an alkyl group each of R¹ and R² is an alkyl group having 10 to 14 carbon atoms, preferably 12 to 14 carbon atoms and which copolymer has a number average molecular weight of 4000 to 25000, preferably 5000 to 20000, more preferably 6000 to 15000.

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9. A composition, method or use according to claim 8 wherein the copolymer comprises from 40 to 60 mol % of units of formula (I) and from 60 to 40 mol % of units of formula (II).

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10. A composition, method or use according to any preceding claim wherein the one or more additives comprise the reaction product of 1 mole of ethylenediamine tetraacetic acid and 4 moles of hydrogenated tallow fatty amine.

20

11. A composition, method or use according to any preceding claim wherein the one or more additives comprise the reaction product of a copolymer of maleic anhydride and a C18 α -olefin and 2 equivalents of ditallow fatty amine.

25

12. A use, method or composition according to any preceding claim wherein the fuel composition comprises from 1 to 40 vol% (preferably from 5 to 35 vol%) of a biodiesel component and from 60 to 99 vol% (preferably from 65 to 95 vol%) of a renewable diesel component.

13. A use or method according to any of claims 1, 2 or 4 to 12 which provides a reduced filter blocking tendency as measured by the Canadian Cold Soak Filter Blocking Tendency test CAN/CGSB-3.0 No. 142.0-2019, modified as set out in example 2.

30

14. A composition according to any of claims 3 to 12 which has a filter blocking tendency of less than 2 as measured by the Canadian Cold Soak Filter Blocking Tendency test CAN/CGSB-3.0 No. 142.0-2019, modified as set out in example 2.