

IMPROVEMENTS IN FUELS

The present invention relates to improvements in fuel compositions comprising renewable diesel and in particular to improving the properties of fuel compositions comprising renewable diesel at
5 low temperatures.

As fuels cool crystals begin to form within the fuels. These can cause problems during storage, transportation and combustion of the fuel.

10 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 standardised tests for
15 measuring PP and, especially, CP and CFPP are among the common working tools for persons skilled in the art.

A standard test used to measure the pour point of diesel fuels is ASTM D5949.

20 The cloud point (CP) of a fuel is the temperature at which a cloud of wax crystals first appears in a liquid when it is cooled under conditions prescribed in the test method as defined in ASTM D2500 or ASTM D5773.

At temperatures below the cloud point but above the pour point, the wax crystals can reach a
25 size and shape capable of plugging fuel lines, screens, and filters even though the fuel will physically flow. These problems are well recognized in the art and have a number of recognised test methods such as the CFPP value (cold filter plugging point, determined in accordance with DIN EN116 or ASTM D6371).

30 Tests such as these were introduced to give an indication of low temperature operability as the cloud point test was considered to be too pessimistic.

Cold flow improvers (CFIs) and wax anti-settling additives (WASAs) have been developed to ameliorate the problems of wax precipitation below the cloud point in fuels, and their effect can
35 be studied by the test methods described above, comparing the results between unadditised fuels and additised fuels.

Some such additives may assist in keeping the so-called "waxes" in solution in the fuel; others may alter their crystal morphology or size, so that filterability and pourability are maintained in spite of precipitation.

- 5 The present invention relates in particular to improving the low temperature properties of fuel compositions comprising renewable diesel.

10 In recent years environmental pressures have meant that greener alternatives to fossil fuels have been increasingly used. It is now common to replace some or all of diesel obtained from petroleum sources with diesel obtained from natural or renewable sources. However inclusion of a renewable diesel component can have a significant impact on the properties of a fuel at low temperatures.

15 The chemical nature of renewable diesel is quite different to that of mineral diesel. Mineral diesel is derived from petroleum and comprises a mixture of alkanes comprising a high degree of branching, along with aromatic and olefinic compounds.

20 Renewable diesel is prepared by the hydrodeoxygenation of fats and oils and comprises primarily straight chain alkanes. These have a different chemical composition to mineral diesel.

Because the chemical nature of renewable diesel differs to that of mineral diesel, different waxes and precipitates form as these fuels cool. For blended fuels the wax crystals which form in one component may be less soluble in other components of the fuel. This can lead to increased problems, for example with filterability of the fuel, at low temperatures.

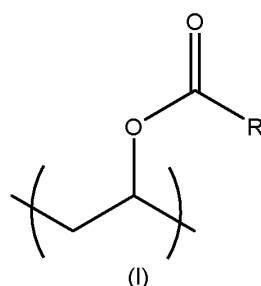
25 Due to the different compositions of these fuels, additives which improve the low temperature properties of mineral diesel fuels do not necessarily improve the low temperature properties of fuel compositions comprising renewable diesel.

30 The present inventors have found that certain additives are especially effective at improving the low temperature properties of fuel compositions comprising renewable diesel. In particular the inventors have found that certain additives depress the cloud point of said fuel compositions.

35 According to a first aspect of the present invention there is provided a fuel composition comprising renewable diesel and one or more low temperature enhancing additives selected from:

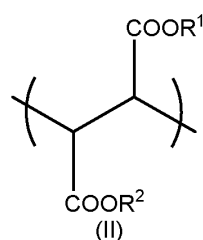
- (a) a copolymer comprising units of formula (I):

3



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;

10

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

15

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

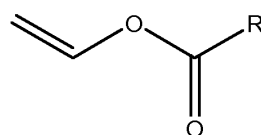
In some embodiments the fuel composition comprises additive (a).

20 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.

25

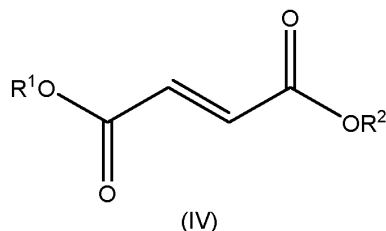
Additive (a) is preferably a copolymer prepared by reacting monomers of vinyl ester of formula (III):



4

(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.

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.

Each of R¹ and R² may be the same or different. Preferably R¹ is the same as R².

Each of R¹ and R² is an alkyl or alkenyl group. Preferably each is an alkyl group, preferably an unsubstituted alkyl group. R¹ and R² may be straight chained or branched. Preferably each of R¹ and R² is a straight chain alkyl group.

In some embodiments each of R¹ and R² is an alkyl group having 6 to 22 carbon atoms, preferably 8 to 18 carbon atoms.

Preferably each of R¹ and R² 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.

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%.

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%.

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).

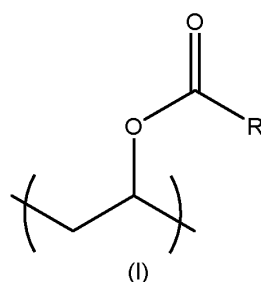
Preferably additive (a) is a random copolymer.

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.

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.

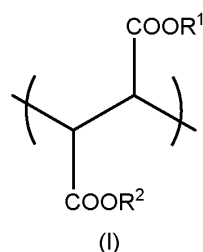
In especially preferred embodiments additive (a) is a copolymer comprising units of formula (I):

6



and units of formula (II):

5



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).

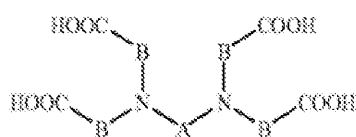
In some embodiments the fuel composition comprises (b) the reaction product of a polycarboxylic acid having at least one tertiary amino group and a primary or secondary amine.

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.

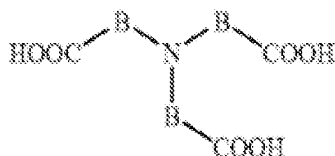
25

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

7



(V)



(VI)

5

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.

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.

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 HNR₂ in which each R is independently a straight chain or branched C₁₀ to C₃₀ alkyl or alkenyl group, preferably a C₁₄ to C₂₄ 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.

25

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.

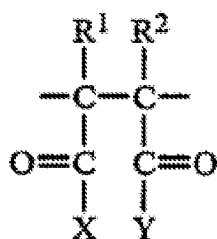
5 An especially preferred additive component (b) is the reaction product of 1 mole of ethylenediamine tetraacetic acid and 4 moles of hydrogenated tallow fatty amine.

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 10 2 moles of a dialkylamine, for example ditallow fatty amine (hydrogenated or un hydrogenated).

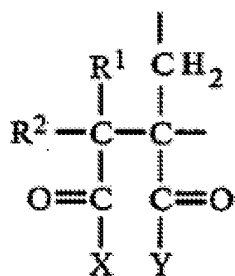
In some embodiments the fuel composition comprises (c) the reaction product of secondary amines and a copolymer of an α,β -unsaturated dicarboxylic anhydride and an α -olefin.

15 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)



20 (VII)



(VIII)

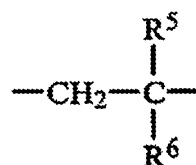
wherein R^1 and R^2 are, independently of one another, hydrogen or methyl,

X and Y are identical or different groups and selected from and N- HR^3 group wherein R^3 is C_6 -

25 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 $H_2N^+(R^3)_2$ or $H_3N^+R^3$, C_6-C_{40} -alkyl, C_5-C_{20} -cycloalkyl or C_6-C_{18} -aryl;

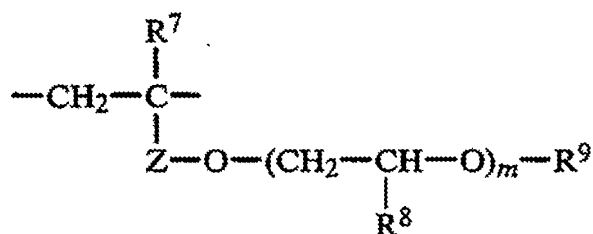
b) 19-80 mol % of bivalent structural units (IX)



5 (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):



(X)

- 10 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 $-C(O)-R^{10}$,
wherein R^{10} is C_1-C_{40} -alkyl, C_5-C_{10} -cycloalkyl or C_6-C_{18} -aryl.

- As will be appreciated by the skilled person, the copolymer may comprise small amounts of
15 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 C_6-C_{40} alkyl and Y is a group of the formula OR^4 , wherein R^4 is
20 a cation of formula $H_2N^+(R^3)_2$ wherein R^3 is C_6-C_{40} alkyl.

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.

- 25 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.

In some embodiments the fuel composition comprises component (a).

In some embodiments the fuel composition comprises component (b).

In some embodiments the fuel composition comprises component (c).

5

In some embodiments the fuel composition comprises component (a) and component (b).

In some embodiments the fuel composition comprises component (a) and component (c).

10 In some embodiments the fuel composition comprises component (b) and component (c).

In some especially preferred embodiments the fuel composition comprises component (a), component (b) and component (c).

15 In some embodiments the fuel composition comprises component (a) but does not comprise component (b) or component (c).

The fuel composition of the present invention comprises renewable diesel. It may comprise only renewable diesel and one or more additives or it may comprise a blend of renewable diesel and
20 a further diesel fuel.

Preferably the fuel composition has a low sulphur content fuel, preferably a sulphur content less than 200 ppm, preferably less than 100 ppm, preferably less than 50 ppm, preferably less than
25 20 ppm, preferably less than 15 ppm, preferably less than 10 ppm.

25

In some 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.

30 In some embodiments the diesel fuel comprises renewable diesel and biodiesel.

In some embodiments the diesel fuel comprises renewable diesel and mineral diesel.

In some embodiments the diesel fuel comprises mineral diesel, biodiesel and renewable diesel.

35

The fuel composition comprises renewable diesel. 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.

5 Preferably the renewable diesel present in the fuel compositions of the present invention 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.

10 The renewable diesel present in the fuel composition of the present invention may comprise greater than 4 wt%, preferably greater than 5 wt%, of C14 to C16 n-alkanes.

15 The renewable diesel present in the fuel composition of the present invention 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 present in the fuel composition of the present invention may comprise less than 8 wt%, preferably less than 6 wt%, of C14 to C16 n-alkanes.

20 The renewable diesel present in the fuel composition of the present invention may comprise less than 20 wt%, preferably less than 18 wt%, more preferably less than 16 wt%, of C14 to C18 n-alkanes.

25 The renewable diesel present in the fuel composition of the present invention 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.

30 The renewable diesel present in the fuel composition of the present invention 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 present in the fuel composition of the present invention may comprise from 4 to 8 wt%, preferably from 5 to 6 wt%, of C14 to C16 n-alkanes.

35 The renewable diesel present in the fuel composition of the present invention 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 present in the fuel composition of the present invention may comprise from 3 to 30 wt% of C6 to C24 n-alkanes (i.e. n-paraffin).

5 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 distillates.

10

By mineral fuels herein we mean fuels derived wholly from mineral (i.e. petroleum) sources.

15 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 oil, nasturtium seed oil, mustard seed oil, olive oil, sesame oil, soybean oil, com oil, peanut oil, 20 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.

25

The 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).

30 The diesel fuel composition may comprise one or more further components, for example the fuels referred to as 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.

35 In some embodiments the fuel composition may comprise a pyrolysis fuel oil, for example 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 fuels.

In some embodiments the diesel fuel composition may be a blended diesel fuel comprising mineral diesel and renewable diesel. In such blends the renewable diesel may be present in an amount of (by volume), 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%,
5 up to 90%, up to 95% or up to 99%.

In some embodiments the fuel composition may comprise neat renewable diesel.

A fuel which comprises 100% renewable diesel is denoted as R100, a fuel which comprises 90%
10 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
15 and mixtures thereof.

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

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

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

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

In some embodiments the diesel fuel comprises renewable diesel and from 1 to 30 vol%,
30 preferably from 1 to 20 vol%, more preferably from 1 to 10 vol% of a fuel selected from biodiesel, mineral diesel and mixtures thereof.

Suitably the one or more low temperature enhancing additives are present in the diesel fuel composition in an amount of at least 1 ppm, preferably at least 10 ppm, more preferably at least
35 30 ppm, suitably at least 50 ppm.

Suitably the one or more low temperature enhancing additives are present in the fuel composition in an amount of less than 30000 ppm, preferably less than 10000 ppm, preferably less than 5000 ppm, preferably less than 3000 ppm, for example less than 2500 ppm.

Suitably the one or more low temperature enhancing additives are present in the fuel composition in an amount of from 1 to 20000 ppm, preferably 10 to 10000 ppm, more preferably 30 to 5000 ppm, for example 50 to 2500 ppm, 70 to 1000 ppm or 100 to 750 ppm.

5

In this specification any reference to ppm is to parts per million by volume. The values given in parts per million (ppm) for treat rates denote the amount of active agent present in the composition and do not include any diluent, carriers or other materials that may be present.

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

15

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

20

In some embodiments the composition may comprise one or more further 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.

25

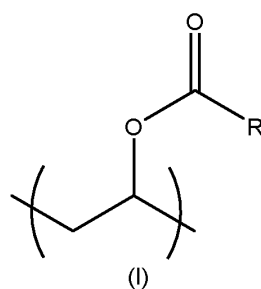
According to a second aspect of the present invention there is provided a method of improving the low temperature properties of a fuel composition comprising renewable diesel, the method comprising admixing into the composition one or more low temperature enhancing additives selected from:

30

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

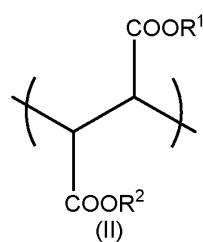
35

15



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;

10

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

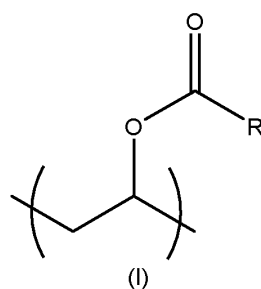
15

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

According to a third aspect of the present invention there is provided the use of one or more low temperature enhancing additives selected from:

20

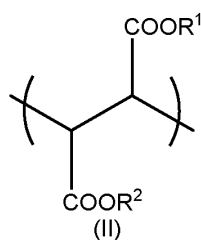
(a) a copolymer comprising units of formula (I):



25

and units of formula (II):

16



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

to improve the low temperature properties of a fuel composition comprising renewable diesel.

- Preferred aspects of the second and third aspects of the present invention are as described in relation to the first aspect.

The method and use of the present invention improve the low temperature properties of a fuel composition comprising renewable diesel. Preferably the method and use depress the cloud point of a fuel composition comprising renewable diesel.

Preferably the method and use depress the cloud point of a fuel composition comprising renewable diesel by at least 0.5 °C, preferably at least 1 °C.

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

Example 1

The following additives were dosed into a renewable diesel fuel at the treat rates specified and the cloud point and pour points of the resultant compositions were measured.

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.

- B - a copolymer of maleic anhydride and a C18 α -olefin reacted with 2 equivalents of ditallow fatty amine
- 5 C - the reaction product of 1 mole of ethylenediamine tetraacetic acid and 4 moles of hydrogenated tallow fatty amine
- D – a copolymer of vinyl acetate and dialkyl fumarate with alkyl groups having 12 to 14 carbon atoms wherein the copolymer has a number average molecular weight of approximately 8200.
- 10 E - a copolymer of vinyl acetate and dialkyl fumarate with alkyl groups having 16 carbon atoms wherein the copolymer has a number average molecular weight of approximately 7000
- F - a copolymer of vinyl acetate and dialkyl fumarate with alkyl groups having 16 to 18 carbon atoms wherein the copolymer has a number average molecular weight of approximately 14000.
- 15

The results are shown in table 1:

Table 1

Additive	Treat rate (ppm active)	Cloud Point, °C ASTM D5773	Pour Point, °C ASTM D5949
None	0	-5.3	-4.5
A	500	-6.5	-6
B	200	-7.1	-6
C	250	-7.2	-6
D	125	-7.0	-6
E	125	-6.1	-6
F	125	-5.7	-6

20

Example 2

Additive D was dosed into a range of different renewable diesel fuels in the amounts detailed in table 2 and the cloud point and pour points of the resultant compositions were measured.

25

Table 2

Fuel	Treat rate (ppm active)	Cloud Point, °C ASTM D5773	Pour Point, °C ASTM D5949	Δ CP, °C
1	0	-10.9	-12	

1	250	-12.1	-12	1.2
2	0	-11.4	-15	
2	500	-14.0	-15	2.6
3	0	-19.9	-24	
3	500	-22.0	-24	2.1
4	0	-9.3	-12	
4	250	-10.8	-12	1.5

Example 3

- 5 Additive D was dosed into a range of renewable diesel fuels comprising conventional mineral diesel and renewable diesel in the amounts detailed in table 3 and the cloud point and pour points of the resultant compositions were measured.

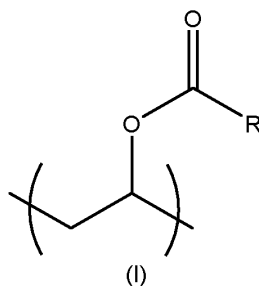
Table 3

% renewable diesel (% by volume)	Treat Rate (ppm active)	Average Cloud Point (°C)
0	0	-15.5
20	0	-15.6
	125	-17.2
	250	-17.4
50	0	-14.9
	125	-16.5
	250	-15.8
80	0	-12.8
	125	-14.2
	250	-14.3
100	0	-8.3
	125	-10.2
	250	-10.6

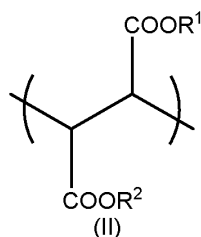
Claims

1. A fuel composition comprising renewable diesel and one or more low temperature enhancing additives selected from:

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



10 and units of formula (II):



15 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

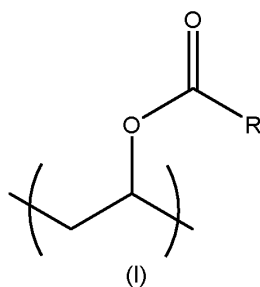
20

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

2. A method of improving the low temperature properties of a fuel composition comprising renewable diesel, the method comprising admixing into the composition one or more low temperature enhancing additives selected from:

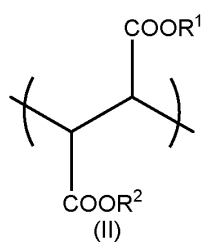
- 25 (a) a copolymer comprising units of formula (I):

20



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;

10

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

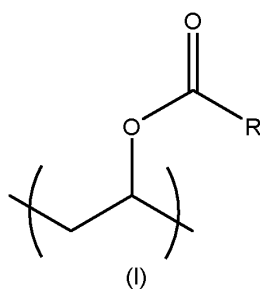
15

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

3. The use of one or more low temperature enhancing additives selected from:

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

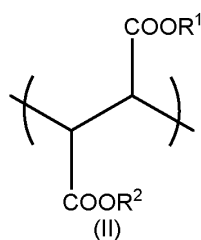
20



and units of formula (II):

25

21

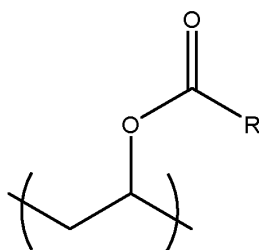


wherein R is an alkyl group and each of R^1 and R^2 is an alkyl or alkenyl group having 6 to 22 carbon atoms;

- (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

to improve the low temperature properties of a fuel composition comprising renewable diesel.

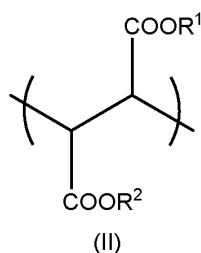
4. A composition, method or use according to any preceding claim wherein each of R^1 and R^2 is an alkyl or alkenyl group having 8 to 14 carbon atoms.
5. A composition, method or use according to any preceding claim wherein the one or more low temperature enhancing additives comprises component (a).
6. A composition, method or use according to any preceding claim wherein the one or more low temperature enhancing additives comprises component (b).
7. A composition, method or use according to any preceding claim wherein the one or more low temperature enhancing additives comprises component (c).
8. A composition, method or use according to any preceding claim wherein the one or more low temperature enhancing additives comprises a copolymer comprising units of formula (I):



22

(I)

and units of formula (II):



10 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.

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).

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

25 12. A composition, method or use according to any preceding claim wherein the fuel comprises a blend of renewable diesel and a further diesel fuel.

13. A composition, method or use according to claim 12 wherein the further diesel fuel is selected from biodiesel, mineral diesel and mixtures thereof.

30 14. A method or use according to any of claims 2 to 13 which depress the cloud point of the fuel composition by at least 1 °C.