

Compositions, Methods and Uses

The present invention relates to fuel compositions derived from plastic pyrolysis oils and to methods and uses relating thereto. In particular the invention relates to additives for improving the stability of fuel compositions derived from plastic pyrolysis oils.

Pyrolysis oils are the fluids generated directly from the pyrolysis of waste, for example plastic waste, biomass for example agricultural waste, forestry waste, waste cooking oils, algae waste, used tyres or waste rubber. Examples of waste plastic which may be pyrolysed to produce plastic pyrolysis oils include low density polyethylene, high density polyethylene, ultra high density polyethylene, polypropylene, polystyrene, polyethylene terephthalates (PET), rubber (e.g. from tyres), polyacrylate and polynitrile.

The treatment of waste plastic to provide a pyrolysis oil typically involves first grinding the plastic and then optionally melting it, for example at about 200°C. The molten plastic may be optionally further processed, for example by passing through a heated screw heater before heating in the absence of oxygen at temperatures of 400 to 600°C which leads to thermal decomposition of the plastic. The mixture obtained may then be contacted with a suitable catalyst. The mixture is then condensed to produce a crude plastic pyrolysis oil, which may be otherwise known as synthetic crude oil. The crude plastic pyrolysis oil can either be sold in crude form or be treated at a refinery to provide finished fuels. At the refinery the pyrolysis oil may be optionally washed to remove char and to reduce its metal content. The various processing steps and the temperatures used depends on the nature of the plastic feedstock.

Refining the optionally washed crude plastic pyrolysis oil involves heating the oil in a distillation column and collecting the desired fractions. This may be done on-site where the crude plastic pyrolysis oil is produced or may be carried out in a separate refinery. Diesel fuel fractions typically make up around a quarter of the distillation products obtained from such refining of crude plastic pyrolysis oils.

Although the fuels obtained from the distillation of crude pyrolysis oils have the same boiling point ranges as middle distillate fuels obtained from mineral sources, the chemical composition of the distillate fuel oil obtained is quite different.

Fuels obtained from the fractional distillation of crude oil typically contain high levels sulfur and aromatic compounds. These fuels usually need to be hydrotreated before use.

Fuels obtained from the fractional distillation of plastic pyrolysis oils typically have a much lower proportion of sulfur containing compounds than those obtained from the fractional

distillation of crude oil. This means that hydrotreatment is not always necessary and straight run distillate fractions can be used directly in internal combustion engines, such as in diesel engines, especially diesel engines having a high-pressure fuel system. Suitably such diesel engines have a fuel pressure in excess of 1350 bar (1.35×10^8 Pa). The diesel engine may
5 have a fuel pressure of up to 2000 bar (2×10^8 Pa) or more. However, because the chemical composition of fuels obtained from plastic pyrolysis oils is quite different to that of mineral derived fuels, the stability of these fuels is different.

Additives are often added to fuel to reduce or prevent sedimentation and/or oxidation during
10 storage. Different fuels degrade in different ways, for example by thermal, oxidative, polymerisation or condensation pathways. Sediments or precipitates which may form on storage or at low temperatures in fuels derived from pyrolysis oils are different to those which form in mineral oil derived fuels. Also, the amounts and types of straight chain alkane compounds (paraffins) contained in fuels obtained from pyrolysis oils may differ significantly
15 from the fuels obtained from mineral oil. This means that additives which are used, for example, to provide stability in mineral distillate fuels are not necessarily effective in fuels obtained from the distillation of pyrolysis oils. To enable such fuels to be fully utilised there is a need to provide stabilising additives to ensure such fuels meet the required standards, especially ASTM D975.

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The present inventors have found that certain compounds are effective at reducing sedimentation from and/or improving the stability of fuel compositions obtained from the distillation pyrolysis oils.

25 According to a first aspect of the present invention there is provided a fuel composition comprising a middle distillate fuel oil obtained from the distillation of a pyrolysis oil and, as an additive, one or more of:

- (a) an antioxidant; and
- (b) a stabilising additive selected from (x) alkoxyated amine compounds; (y) aldehyde-
30 alkylphenol copolymers; (z) acylated nitrogen compounds; and mixtures thereof.

The first aspect of the present invention relates to a fuel composition comprising a middle distillate fraction obtained from distillation of a pyrolysis oil.

35 The pyrolysis oil may be obtained from the pyrolysis of any type of waste. The components of the pyrolysis oil and the properties thereof and the distillate fraction obtained therefrom will depend on the types of waste that was pyrolysed and the pyrolysis conditions. For example the pyrolysis oil may be obtained from the pyrolysis of plastic waste, agricultural waste, forestry waste, waste cooking oils, algae waste, used tyres and rubber waste.

Preferably the pyrolysis oil comprises a plastic pyrolysis oil. The plastic pyrolysis oil may be obtained from the pyrolysis of any type of plastic.

- 5 Preferred plastic pyrolysis oils are obtained from the pyrolysis of one or polymers selected from low density polyethylene, high density polyethylene, ultra high density polyethylene, polypropylene, PET, polyacrylate, polynitrile and mixtures thereof.

- 10 The fuel composition of the present invention comprises a middle distillate fuel oil obtained from the distillation of a pyrolysis oil, preferably a plastic pyrolysis oil. Suitably the middle distillate oil boils in the range 110°C to 500°, preferably 150°C to 400°C.

- 15 The fuel composition of the present invention is suitable for use as diesel fuel oil. Preferably the fuel composition complies with ASTM D975. The fuel component of the fuel composition may consist essentially of a middle distillate fuel oil obtained from a pyrolysis oil or it may comprise a blended fuel comprising a distillate obtained from a pyrolysis oil, preferably a plastic pyrolysis oil and one or more further middle distillate components, for example one or more further middle distillate components obtained from mineral and/or renewable sources. Fuel components obtained from other synthetic sources may also be included.

- 20 The middle distillate fuel oil obtained from the pyrolysis oil may optionally be hydrotreated and/or treated using a cracking process. However, due to the typically low aromatic and sulfur content of middle distillate fuel oils obtained from pyrolysis oils it is possible to use straight run distillates.

- 25 In some embodiments the fuel composition of the first aspect comprises a straight run middle distillate fraction oil directly obtained from the distillation of a pyrolysis oil without further treatment.

- 30 In some embodiments the fuel composition of the first aspect may comprise a blended fuel oil comprising a middle distillate fuel oil obtained from the fractional distillation of a plastic pyrolysis oil and one or more fuel oils obtained from hydrocarbon and/or renewable sources.

- 35 The fuel composition 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 middle distillate fuel oil 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 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).

5 The fuel composition may comprise a renewable fuel such as a biofuel composition or biodiesel composition.

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

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

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

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

30 In some embodiments the fuel composition comprises a blended fuel comprising from 5 to 10 vol% of a middle distillate fuel oil obtained from the distillation of a pyrolysis oil and from 90 to 95 vol% of one or fuel oils obtained from hydrocarbon and/or renewable sources.

35 The fuel composition of the present invention comprises a middle distillate fuel oil obtained from the distillation of a pyrolysis oil. This component of the fuel composition comprises paraffins. Preferably at least 50 wt% of the paraffin compounds present in this component of the fuel composition (i.e.. the middle distillate fuel oil obtained from the distillation of a pyrolysis oil) have at least 18 carbons, preferably at least 60 wt%, suitably at least 70 wt%, for example at least 80 wt%.

In preferred embodiments the 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.

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The fuel composition of the first aspect comprises one or more of (a) an antioxidant and (b) a stabilising additive.

In some embodiments the composition of the first aspect comprises (a) an antioxidant.

10 Mixtures of two or more antioxidants may be present.

In some embodiments the composition of the first aspect comprises (b) a stabilising additive.

In some embodiments the composition of the first aspect comprises (a) an antioxidant and (b) a stabilising additive.

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The stabilising additive may comprise (x) alkoxyated amine compounds, (y) aldehyde-alkylphenol copolymers, (z) acylated nitrogen compounds, or mixtures thereof.

20 In some embodiments the composition of the first aspect comprises (b) a stabilising additive comprising (x) alkoxyated amine compounds.

In some embodiments the composition of the first aspect comprises (b) a stabilising additive comprising (y) aldehyde-alkylphenol copolymers.

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In some embodiments the composition of the first aspect comprises (b) a stabilising additive comprising (z) acylated nitrogen compounds.

30 In some preferred embodiments the composition of the first aspect comprises (b) a stabilising additive comprising (x) alkoxyated amine compounds and (y) aldehyde-alkylphenol copolymers.

In some embodiments the composition of the first aspect comprises (b) a stabilising additive comprising (x) alkoxyated amine compounds and (z) acylated nitrogen compounds.

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In some embodiments the composition of the first aspect comprises (b) a stabilising additive comprising (y) aldehyde-alkyl phenol copolymers and (z) acylated nitrogen compounds.

In some embodiments the composition of the first aspect comprises (b) a stabilising additive comprising (x) alkoxylated amine compounds, (y) aldehyde-alkylphenol copolymers and (z) acylated nitrogen compounds.

- 5 In some embodiments the composition of the first aspect comprises (a) an antioxidant and (b) a stabilising additive comprising (x) alkoxylated amine compounds.

In some embodiments the composition of the first aspect comprises (a) an antioxidant and (b) a stabilising additive comprising (y) aldehyde-alkylphenol copolymers.

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In some embodiments the composition of the first aspect comprises (a) an antioxidant and (b) a stabilising additive comprising (z) acylated nitrogen compounds.

- 15 In some preferred embodiments the composition of the first aspect comprises (a) an antioxidant and (b) a stabilising additive comprising (x) alkoxylated amine compounds and (y) aldehyde-alkylphenol copolymers.

- 20 In some preferred embodiments the composition of the first aspect comprises (a) an antioxidant and (b) a stabilising additive comprising (x) alkoxylated amine compounds and (z) acylated nitrogen compounds.

- 25 In some embodiments the composition of the first aspect comprises (a) an antioxidant and (b) a stabilising additive comprising (y) aldehyde-alkylphenol copolymers and (z) acylated nitrogen compounds.

- In some preferred embodiments the composition of the first aspect comprises (a) an antioxidant and (b) a stabilising additive comprising (x) alkoxylated amine compounds (y) aldehyde-alkylphenol copolymers and (z) acylated nitrogen compounds.

- 30 Suitable antioxidants for use herein include phenolic antioxidants and nitrogen containing antioxidants.

- In some preferred embodiments the fuel composition of the first aspect comprises a phenolic antioxidant.

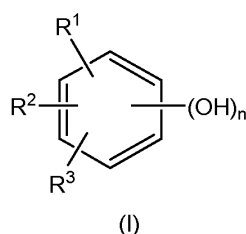
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In some embodiments the fuel composition of the first aspect comprises a nitrogen containing antioxidant and a phenolic antioxidant.

Any suitable phenolic antioxidant may be used. Suitable antioxidants will be known to the person skilled in the art.

By phenolic antioxidant compound we mean to include any compound which contains a phenol moiety i.e., a benzene ring which is substituted with a hydroxyl group. This may be a very simple compound, for example a benzene diol, an alkyl substituted phenol or a benzene triol. Alternatively the phenolic antioxidant may be part of a more complex molecule. It may include two phenol moieties, for example, see the compounds disclosed in US 2006/0219979.

Suitable phenolic antioxidant compounds for use in the present invention include those of formula (I):



wherein R¹ is selected from an optionally substituted alkyl or alkenyl group, an aryl group, an aralkyl group; an ester, a carboxylic acid, an aldehyde, a ketone, an ether, an alcohol, an amine or an amide; R² and R³ are independently selected from hydrogen, an optionally substituted alkyl or alkenyl group, an aryl group, an ester group, a ketone, an aldehyde, a carboxylic acid, an ether, an alcohol, an amine or an amide; and n is an integer from 1 to 5.

Preferably R¹ is an alkyl group, preferably having 1 to 9 carbon atoms, and may be straight chained or branched. Preferably R¹ is selected from methyl, ethyl, isopropyl, and tertiary butyl. R¹ and R² may together form a cyclic substituent, either alkyl or aryl. R² and R³ are preferably hydrogen or an alkyl group having 1 to 9 carbon atoms. Preferably R² and R³ are independently selected from hydrogen, methyl, ethyl, tertiary butyl and isopropyl. Preferably n is 1, 2 or 3.

Preferred phenolic antioxidant compounds for use in the present invention are substituted benzene compounds having 1 or more hydroxy substituents. Examples include tertiarybutylhydroquinone (TBHQ or MTBHQ), 2,5-di-tertiarybutylhydroquinone (DTBHQ), pyrogallol, pyrocatechol 2,6-di-*tert*-butyl-4-methylphenol (BHT), 2,6-ditertiary-butyl-phenol, propylgallate and tertiarybutylcatechol.

One especially preferred phenolic antioxidant for use herein is 2,6-ditertiary-butyl-phenol. However as the skilled person will appreciate commercial sources of this compound often comprise mixtures including tertiary and tritertiary-butyl-phenols.

- 5 Suitable nitrogen containing antioxidants include aromatic amines, hindered amines, N-oxides, polyalkylene polyamines, phenylene diamines, substituted hydroxylamines and mixtures thereof.

10 Suitable aromatic amines include diaminobenzene and alkylated diamino benzenes, especially dialkylated and trialkylated diaminobenzenes, for example *p*-phenylenediamine, 3,5-diethyltoluene-2,4-diamine; 3,5-diethyltoluene-2,2-diamine; 2,4,6-triethylbenzene-2,6-diamine alkylated diphenyl amines; diphenylamines and alkylated diphenylamines, for example N,N-diphenyl-1,4-phenylenediamines; and naphthylamines, for example N-phenyl-1-naphthylamine and N-phenyl-2-naphthylamine.

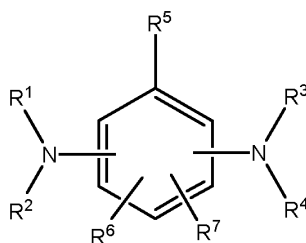
15 Suitable hindered amines include secondary and tertiary aliphatic amines, for example dimethyl cyclohexylamine and diethylhydroxylamine.

20 Suitable N-oxides include (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) and derivatives thereof.

Preferably the one or more nitrogen containing antioxidants (a) are selected from:

- 25 (i) phenylenediamines;
(ii) substituted hydroxylamines; and
(iii) mixtures thereof.

Some preferred phenylenediamine antioxidants (i) suitable for use in the present invention include those of formula:



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wherein R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ are independently selected from hydrogen, an optionally substituted alkyl, alkenyl, aryl, alkaryl or aralkyl group, an ester, a carboxylic acid, an aldehyde, a ketone, an ether, an alcohol, an amine or an amide. Preferably R¹ is hydrogen. Preferably

- R^3 is hydrogen. Preferably R^2 is an alkyl group, preferably having 1-10 carbon atoms. More preferably R^2 is an alkyl group having 1-5 carbon atoms. Preferably R^2 is selected from methyl, ethyl, propyl, isopropyl, butyl, isobutyl, secbutyl and tertiarybutyl. Most preferably R^2 is isopropyl or secbutyl. Preferably R^4 is an alkyl group, preferably having 1-10 carbon atoms.
- 5 More preferably R^4 is an alkyl group having 1-5 carbon atoms. R^4 is preferably selected from methyl, ethyl, propyl, isopropyl, secbutyl, butyl, tertiarybutyl and isobutyl. Most preferably R^4 is isopropyl or sec butyl.

- R^5 , R^6 and R^7 are preferably selected from hydrogen or alkyl groups, more preferably from hydrogen and alkyl groups having 1-10 carbon atoms, more preferably from hydrogen and alkyl groups having 1-5 carbon atoms. Preferably R^5 , R^6 and R^7 are independently selected from hydrogen, methyl, ethyl, propyl, isopropyl, butyl, tertiarybutyl and isobutyl. Most preferably R^5 is hydrogen. Most preferably R^6 is hydrogen. Most preferably R^7 is hydrogen.
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- 15 In especially preferred embodiments each of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 is hydrogen and component (i) comprises p-phenylene diamine.

Component (i) may comprise a mixture of compounds and/or a mixture of isomers.

- 20 Preferred substituted hydroxylamine compounds (ii) for use herein are compounds of formula R_2NOH in which at least one R group is an optionally substituted hydrocarbyl group. The other R group may be hydrogen. Preferably each R is an optionally substituted hydrocarbyl group. Each R may be the same or different. Preferably each R is the same.
- 25 Preferably each R is an optionally substituted alkyl or alkenyl group, preferably having from 1 to 12 carbon atoms, suitably 1 to 10 or 1 to 8 carbon atoms, for example 1 to 6, preferably from 1 to 4 carbon atoms. Preferably each R is an alkyl group. Each R may be a substituted alkyl group, for example a hydroxy substituted alkyl group. Preferably each R is an unsubstituted alkyl group or a hydroxy alkyl group. More preferably each R is an
- 30 unsubstituted alkyl group. The alkyl chain may be straight-chained or branched. Preferably each R is selected from methyl, ethyl, propyl and butyl, including isomers thereof. Most preferably each R is ethyl.

Preferably component (ii) comprises diethylhydroxylamine.

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Component (ii) may comprise a mixture of compounds and/or a mixture of isomers.

In some embodiments the fuel composition of the first aspect includes (i) phenylenediamines.

In some embodiments the fuel composition of the first aspect includes (ii) substituted hydroxylamines.

5 In some embodiments the fuel composition of the first aspect includes (i) phenylenediamines and (ii) substituted hydroxylamines.

The fuel composition of the first aspect may comprise (b) a stabilising additive selected from (x) alkoxyated amine compounds, (y) aldehyde-alkylphenol copolymers, (z) acylated nitrogen compounds or mixtures thereof.

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By stabilising additive we mean to refer to a component which improves the stability of the fuel composition, for example the storage or oxidation stability thereof, or which aids the dispersion of solids, waxes or high molecular weight gums within the fuel composition. Suitable stabilising additives may be known in the art as dispersants.

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In some embodiments the composition of the first aspect may comprise (x) alkoxyated amine compounds.

20 The fuel composition may include any alkoxyated amine compound. By this we mean to include any compound including an amine functional group which has been reacted with at least one alkylene oxide moiety.

In preferred embodiments the alkoxyated amine compounds include more than one alkylene oxide residue.

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Suitably alkylene oxide residues include ethylene oxide residues, propylene oxide residues, butylene oxide residues and mixtures thereof.

30 Preferably the alkoxyated amine compounds include ethylene oxide residues, propylene oxide residues, or mixtures thereof.

Preferably the alkoxyated amine compounds are alkoxyated amines, alkoxyated diamines or alkoxyated polyamines.

35 Some preferred alkoxyated amine compounds for use herein have the formula $A-(RO)_n-H$ wherein A is the residue of an amine and RO is an alkylene oxide residue and n is at least one.

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 $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}(\text{CH}_3)-$, $-\text{CH}_2\text{C}(\text{CH}_3)_2-$, $-\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)-$ or $-\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)-$.

- 5 R may comprise a mixture of isomers. For example when R is propylene, the polyhydric alcohol may include moieties $-\text{CH}_2\text{CH}(\text{CH}_3)-$ and $-\text{CH}(\text{CH}_3)\text{CH}_2-$ in any order within the chain.

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

Preferably R is ethylene and/or propylene. More preferably R is $-\text{CH}_2\text{CH}_2-$ or $-\text{CH}(\text{CH}_3)\text{CH}_2-$.

In some preferred embodiments the alkoxyated amine compounds (i) comprise a mixture of
15 ethylene oxide residues and propylene oxide residues.

n is at least 1. Preferably n is from 5 to 1000, preferably from 5 to 500, more preferably from 10 to 400, more preferably from 15 to 300, preferably from 20 to 250, suitably from 30 to 200, preferably from 50 to 150.

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A is the residue of an amine. Suitably A is the residue of an amino or polyamino compound having at least one NH group. Suitable amino compounds include primary or secondary monoamines having hydrocarbon substituents of 1 to 30 carbon atoms or hydroxyl-substituted hydrocarbon substituents of 1 to about 30 carbon atoms.

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Preferably A is the residue of a polyamine.

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

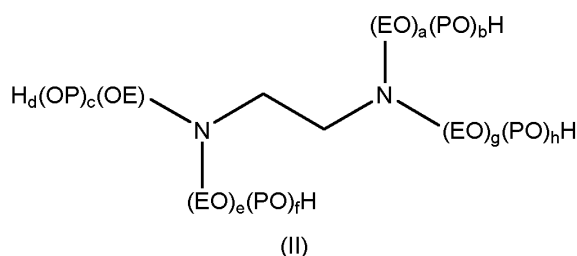
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Preferably the polyamine has 2 to 15 nitrogen atoms, preferably 2 to 10 nitrogen atoms, more preferably 2 to 8 nitrogen atoms.

The polyamine may, for example, be selected from ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylene-hexamine, hexaethyleneheptamine, heptaethyleneoctamine, propane-1,2-diamine, 2(2-aminoethylamino)ethanol, N,N'-bis (2-aminoethyl) ethylenediamine ($N(CH_2CH_2NH_2)_3$), diphenyl 4, 4'-diamine, diamino naphthalene, phenylene diamine, xylene diamine, 1,2-diaminopropane and 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diamino pentane and 1,6-diamino hexane.

Most preferably A is the residue of ethylenediamine.

10 In some preferred embodiments the alkoxyated amine compounds (x) comprise compounds of formula (II):



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wherein EO represents an ethylene oxide residue, PO represents a propylene oxide residue and at least one of a, b, c, d, e, f, g and h is not 0. The compounds of formula (II) may be prepared by reaction of the ethylene diamine with the ethylene oxide and propylene oxide (when both present) in any combination thereof and in any order, i.e. so as to provide compounds of formula (II) in which the ethylene oxide and propylene oxide residues may be present in any combination and in any order as bonded to the nitrogen of the amine group.

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Preferably each of a, b, c, d, e, f, g and h is at least one. Preferably the sum of a, b, c, d, e, f, g and h is from 10 to 500, preferably from 20 to 250, more preferably from 40 to 200.

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The skilled person will appreciate that polymeric compounds of formula (II) are usually in the form of mixtures.

Some suitable alkoxyated amine compounds for use herein are described in US6838422.

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In some embodiments the composition of the first aspect may comprise (y) aldehyde-alkylphenol copolymers.

Any suitable aldehyde-alkylphenol copolymer may be used and such compounds will be known to those skilled in the art.

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Preferably the aldehyde used to prepare the aldehyde-alkylphenol copolymers is selected from formaldehyde or a reactive equivalent thereof, for example paraformaldehyde, C₂ to C₁₀ aldehydes and aromatic aldehydes, for example benzaldehyde.

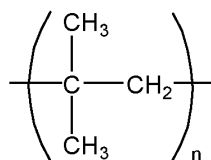
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Preferred aldehyde-alkylphenol copolymers are copolymers of formaldehyde and an alkyl phenol. Preferably the phenol is mono-substituted with an alkyl group, preferably at the para position. Preferred alkyl groups have 1 to 40 carbon atoms, preferably 2 to 36 carbon atoms, more preferably 4 to 30 carbon atoms, for example 6 to 24 carbon atoms.

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In some embodiments the alkyl phenol is a polyisobutenyl (PIB) substituted phenol.

Polyisobutenyl (PIB) substituted phenols include a hydrocarbyl chain having the repeating unit:



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Poly(isobutenes) are prepared by the addition polymerisation of isobutene, (CH₃)₂C=CH₂. Each molecule of the resulting polymer will include a single alkene moiety.

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

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

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

In some embodiments the phenol may include a PIB substituent having an average molecular weight of up to 2800, preferably up to 2600, for example up to 2500 or up to 2400.

5 In some embodiments the phenol may include a PIB substituent having an average molecular weight of from 400 to 2500, for example from 450 to 2400, preferably from 500 to 1500, suitably from 550 to 1300.

10 In some embodiments the phenol may include a PIB substituent having an average molecular weight of from 200 to 600.

In some embodiments the phenol may include a PIB substituent having an average molecular weight of from 500 to 1000.

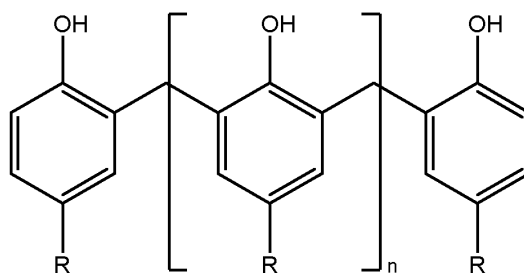
15 In some embodiments the phenol may include a PIB substituent having an average molecular weight of from 700 to 1300.

In some embodiments the phenol may include a PIB substituent having an average molecular weight of from 1000 to 2000.

20 In some embodiments the phenol may include a PIB substituent having an average molecular weight of from 1700 to 2600, for example 2000 to 2500.

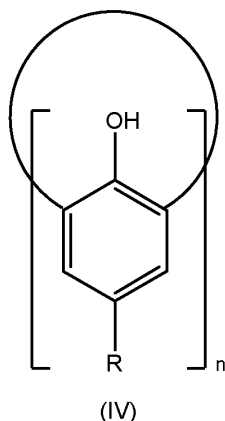
In some preferred embodiment the aldehyde-alkylphenol copolymers (y) have the structures (III) or (IV):

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(III)

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wherein R is hydrogen or an alkyl group and n is at least 1.

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Preferably n is from 2 to 12, preferably from 5 to 9; and R is C3 -C24 -alkyl, preferably C4 -C12 -alkyl, in particular isononyl, isobutyl or amyl, C6 -C12 -aryl or -hydroxyaryl or C7 -C12 -aralkyl.

As the skilled person will appreciate the aldehyde-alkyl phenol copolymers may be prepared from mixtures of monomers, in particular compounds in which R comprises a mixture of alkyl groups. Further suitable aldehyde-alkyl phenol copolymers for use herein include compounds of formula (III) in which the terminal phenol groups are further functionalised, for example by reaction with a fatty acid or an amine and an aldehyde via a Mannich reaction. Compounds of this type are described, for example, in US2007/221539.

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Preferably the aldehyde-alkylphenol copolymer has a number average molecular weight of from 500 to 20000, preferably from 1000 to 10000, more preferably from 1500 to 5000, for example from 2000 to 3500.

20 In some embodiments the composition of the first aspect may comprise (z) acylated nitrogen compounds.

Suitable acylated nitrogen compounds (z) may be made by reacting a carboxylic acid acylating agent with an amine and are known to those skilled in the art. In such compounds the acylating agent is linked to the amino compound through an imido, amido, amidine or acyloxy ammonium linkage.

Preferred acylated nitrogen-containing compounds are hydrocarbonyl substituted. The hydrocarbonyl substituent may be in either the carboxylic acid acylating agent derived portion of the molecule or in the amine derived portion of the molecule, or both. Preferably, however, it

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is in the acylating agent portion. A preferred class of acylated nitrogen-containing compounds suitable for use in the present invention are those formed by the reaction of an acylating agent having a hydrocarbyl substituent of at least 8 carbon atoms and a compound comprising at least one primary or secondary amine group.

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The acylating agent may be a mono- or polycarboxylic acid (or reactive equivalent thereof) for example a substituted succinic, phthalic or propionic acid or anhydride.

10 Suitable hydrocarbyl substituted acylating agents and means of preparing them are well known in the art.

Illustrative of hydrocarbyl substituent based groups containing at least eight carbon atoms are n-octyl, n-decyl, n-dodecyl, tetrapropenyl, n-octadecyl, oleyl, chlorooctadecyl, tricontanyl, etc. The hydrocarbyl based substituents may be made from homo- or interpolymers (e.g. 15 copolymers, terpolymers) of mono- and di-olefins having 2 to 10 carbon atoms, for example ethylene, propylene, butane-1, isobutene, butadiene, isoprene, 1-hexene, 1-octene, etc. Preferably these olefins are 1-monoolefins.

20 The term "hydrocarbyl" as used herein denotes a group having a carbon atom directly attached to the remainder of the molecule and having a predominantly aliphatic hydrocarbon character.

The hydrocarbyl-based substituents are preferably predominantly saturated, that is, they contain no more than one carbon-to-carbon unsaturated bond for every ten carbon-to-carbon single bonds present. Most preferably they contain no more than one carbon-to-carbon non- 25 aromatic unsaturated bond for every 50 carbon-to-carbon bonds present.

The hydrocarbyl substituent in such acylating agents preferably comprises at least 10, more preferably at least 12, for example at least 30 or at least 40 carbon atoms. It may comprise up to about 200 carbon atoms. Preferably the hydrocarbyl substituent of the acylating agent has 30 a number average molecular weight (Mn) of between 170 to 2800, for example from 250 to 1500, preferably from 500 to 1500 and more preferably 500 to 1100. An Mn of 700 to 1300 is especially preferred. In a particularly preferred embodiment, the hydrocarbyl substituent has a number average molecular weight of 700 – 1000, preferably 700 – 850 for example 750.

35 The carboxylic acid-derived acylating agent may comprise a mixture of compounds. For example a mixture of compounds having different hydrocarbyl substituents may be used. In some embodiments the acylating agent may have more than one hydrocarbyl substituent. In such embodiments each hydrocarbyl substituent may be the same or different.

Preferred hydrocarbyl-based substituents are polyisobutenes. Such compounds are known to the person skilled in the art.

Preferred hydrocarbyl substituted acylating agents are polyisobutenyl succinic anhydrides.

- 5 These compounds are commonly referred to as "PIBSAs" and are known to the person skilled in the art.

Conventional polyisobutenes and so-called "highly-reactive" polyisobutenes are suitable for use in the invention. Highly reactive polyisobutenes in this context are defined as
10 polyisobutenes wherein at least 50%, preferably 70% or more, of the terminal olefinic double bonds are of the vinylidene type as described in EP0565285. Particularly preferred polyisobutenes are those having more than 80 mol% and up to 100 mol% of terminal vinylidene groups such as those described in US7291758. Preferred polyisobutenes have preferred molecular weight ranges as described above for hydrocarbyl substituents generally.

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

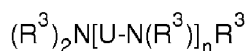
20 An internal olefin as used herein means any olefin containing predominantly a non-alpha double bond, that is a beta or higher olefin. Preferably such materials are substantially completely beta or higher olefins, for example containing less than 10% by weight alpha olefin, more preferably less than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

- 25 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.

30 Preferred carboxylic acid-derived acylating agents are polyisobutenyl substituted succinic anhydrides or PIBSAs. Especially preferred PIBSAs are those having a PIB molecular weight (Mn) of from 300 to 2800, preferably from 400 to 2300, more preferably from 500 to 1300.

- 35 The carboxylic acid-derived acylating agent is reacted with an amine. Suitably it is reacted with a primary or secondary amine. Examples of some suitable amines will now be described.

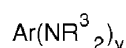
Amine compounds useful for reaction with the acylating agents include polyalkylene polyamines of the general formula:



wherein each R^3 is independently selected from a hydrogen atom, a hydrocarbyl group or a hydroxy-substituted hydrocarbyl group containing up to about 30 carbon atoms, with proviso that at least one R^3 is a hydrogen atom, n is a whole number from 1 to 10 and U is a C1-18 alkylene group. Preferably each R^3 is independently selected from hydrogen, methyl, ethyl, propyl, isopropyl, butyl and isomers thereof. Most preferably each R^3 is ethyl or hydrogen. U is preferably a C1-4 alkylene group, most preferably ethylene.

Other useful amines include heterocyclic-substituted polyamines including hydroxyalkyl-substituted polyamines wherein the polyamines are as described above and the heterocyclic substituent is selected from nitrogen-containing aliphatic and aromatic heterocycles, for example piperazines, imidazolines, pyrimidines, morpholines and derivatives thereof.

Other useful amines for reaction with acylating agents include aromatic polyamines of the general formula:



wherein Ar is an aromatic nucleus of 6 to 20 carbon atoms, each R^3 is as defined above and y is from 2 to 8.

Specific examples of polyalkylene polyamines include ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, tri(tri-methylene)tetramine, pentaethylenhexamine, hexaethylene-heptamine, 1,2-propylenediamine, and mixtures thereof. Other commercially available materials which comprise complex mixtures of polyamines may also be used. For example, higher ethylene polyamines optionally containing all or some of the above in addition to higher boiling fractions containing 8 or more nitrogen atoms etc. Specific examples of hydroxyalkyl-substituted polyamines include N-(2-hydroxyethyl) ethylene diamine, N,N'-bis(2-hydroxyethyl) ethylene diamine, N-(3-hydroxybutyl) tetramethylene diamine, etc. Specific examples of the heterocyclic-substituted polyamines (2) are N-2-aminoethyl piperazine, N-2 and N-3 amino propyl morpholine, N-3(dimethyl amino) propyl piperazine, 2-heptyl-3-(2-aminopropyl) imidazoline, 1,4-bis (2-aminoethyl) piperazine, 1-(2-hydroxy ethyl) piperazine, and 2-heptadecyl-1-(2-hydroxyethyl)-imidazoline, etc. Specific examples of the aromatic polyamines (3) are the various isomeric phenylene diamines, the various isomeric naphthalene diamines, etc.

Preferred amines are polyethylene polyamines including ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, hexaethyleneheptamine, and mixtures and isomers thereof.

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

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

In especially preferred embodiments the acylated nitrogen-containing additive (i) comprises the reaction product of a polyisobutene-substituted succinic acid or succinic anhydride and a polyethylene polyamine to form a succinimide detergent. Preferred polyethylene polyamines include ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, hexaethylene-heptamine and mixtures and isomers thereof. Suitably the polyisobutene substituent of the polyisobutene-substituted succinic acid or succinic anhydride has a number average molecular weight of between 500 and 2000, preferably between 500 and 1500, more preferably between 500 and 1100, suitably between 600 and 1000, preferably between 700 and 800, for example about 750.

Component (z) may comprise a mixture of two or more acylated nitrogen compounds.

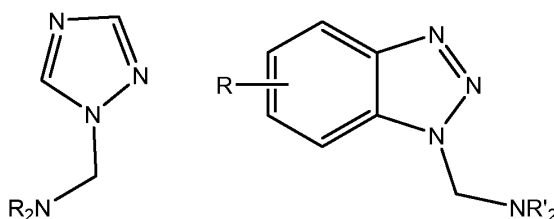
In the additive used in the present invention preferably at least 50 wt % of the additive has a number average molecular weight of more than 400, preferably at least 70% of the molecules, more preferably at least 90%, preferably at least 95%, suitably at least 97%.

A suitable method of measuring the molecular weight distribution of the additive is GPC using polystyrene standards.

The skilled person will appreciate that polyisobutene-substituted succinimide detergent additives typically contain a complex mixture of compounds. Such compounds are usually prepared by reacting polyisobutene (PIB) with maleic anhydride (MA) to form a polyisobutene-substituted succinic anhydride (PIBSA), which is then reacted with the polyamine (PAM) to form a polyisobutene-substituted succinimide (PIBSI). In the reaction of the PIB and MA more than one MA can react with each PIB and some unreacted PIB may remain. Each PIBSA molecule can react with one or more PAM molecule as described above. Varying the ratios of the different starting materials and including intermediate purification steps can affect the ratio of the various component of the final additive material.

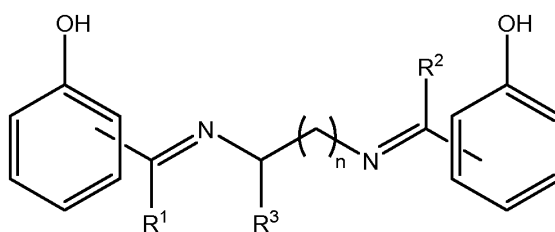
In some preferred embodiments the fuel compositions of the present invention further comprises a metal deactivating compound.

Any metal deactivating compound known to those skilled in the art may be used and include, for example, the substituted triazole compounds of formula (V) wherein R and R' are independently selected from an optionally substituted alkyl group or hydrogen.



(V)

Preferred metal deactivating compounds are those of formula (VI):

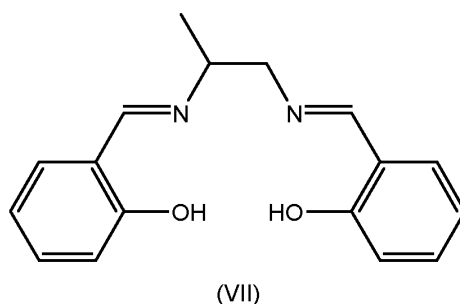


(VI)

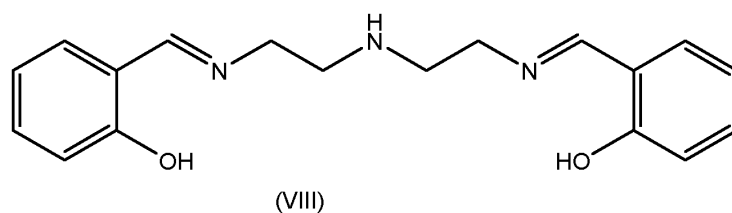
wherein R¹, R² and R³ are independently selected from an optionally substituted alkyl group or hydrogen, preferably an alkyl group from 1 to 4 carbon atoms or hydrogen. R¹ is preferably

hydrogen, R^2 is preferably hydrogen and R^3 is preferably methyl. n is an integer from 0 to 5, most preferably 1.

A particularly preferred metal deactivator is N,N' -disalicyclidene-1,2-diaminopropane, and has
5 the formula (VII):



10 Another preferred metal deactivating compound (VIII):



15 The composition of the first application of the present invention comprises a middle distillate fuel oil obtained from the distillation of a pyrolysis oil and one or more additives.

The composition may further comprises one or more fuel oils obtained from hydrocarbon and/or renewable sources.

20

In embodiments in which the fuel composition comprises a blended fuel comprising a fuel oil obtained from the distillation of a pyrolysis oil and one or more further fuel oils obtained from hydrocarbon and/or renewable sources, such fuels are often blended shortly before distribution. The component fuels are typically stored separately prior to blending and thus the
25 the present invention may suitably stabilise the fuel oil obtained from the distillation of a pyrolysis oil during storage.

The antioxidant, when present, is preferably included in the composition of the first aspect in an amount of at least 1 ppm, preferably at least 2 ppm, more preferably at least 5 ppm or at
30 least 10 ppm, as proportion of the middle distillate fuel oil obtained from the distillation of a

pyrolysis oil. In some embodiments, the antioxidant may be present in an amount of at least 50 ppm, as proportion of the middle distillate fuel oil obtained from the distillation of a pyrolysis oil.

- 5 The antioxidant, when present, may be included in the composition of the first aspect in an amount of up to 10000 ppm, preferably up to 5000 ppm, more preferably up to 2000 ppm, for example up to 1000 ppm, as proportion of the middle distillate fuel oil obtained from the distillation of a pyrolysis oil.
- 10 The antioxidant, when present, is preferably included in the composition of the first aspect in an amount of from 1 to 1000, preferably 2 to 500 ppm, as proportion of the middle distillate fuel oil obtained from the distillation of a pyrolysis oil.

- 15 The stabilising additive, when present, is preferably included in the composition of the first aspect in an amount of at least 1 ppm, preferably at least 2 ppm, more preferably at least 5 ppm, for example at least 10 ppm, as proportion of the middle distillate fuel oil obtained from the distillation of a pyrolysis oil. In some embodiments, the stabilising additive may be present in an amount of at least 50 ppm, as proportion of the middle distillate fuel oil obtained from the distillation of a pyrolysis oil.

- 20 The stabilising additive, when present, may be included in the composition of the first aspect in an amount of up to 10000 ppm, preferably up to 5000 ppm, more preferably up to 1000 ppm, for example up to 700 ppm, as proportion of the middle distillate fuel oil obtained from the distillation of a pyrolysis oil.

- 25 The stabilising additive, when present, is preferably included in the composition of the first aspect in an amount of from 1 to 1000, preferably 2 to 500 ppm, as proportion of the middle distillate fuel oil obtained from the distillation of a pyrolysis oil.

- 30 Alkoxylated amine compounds, when present, are preferably included in the composition of the first aspect in an amount of at least 1 ppm, preferably at least 2 ppm, more preferably at least 5 ppm, for example at least 10 ppm, as proportion of the middle distillate fuel oil obtained from the distillation of a pyrolysis oil. In some embodiments, the alkoxylated amine compounds may be present in an amount of at least 50 ppm, as proportion of the middle
- 35 distillate fuel oil obtained from the distillation of a pyrolysis oil.

Alkoxylated amine compounds, when present, may be included in the composition of the first aspect in an amount of up to 7000 ppm, preferably up to 3000 ppm, more preferably up to

1000 ppm, for example up to 500 ppm, as proportion of the middle distillate fuel oil obtained from the distillation of a pyrolysis oil.

- 5 The alkoxyated amine compounds, when present, are preferably included in the composition of the first aspect in an amount of from 1 to 1000, preferably 2 to 500 ppm, as proportion of the middle distillate fuel oil obtained from the distillation of a pyrolysis oil.

- 10 Aldehyde-alkylphenol copolymers, when present, when present, are preferably included in the composition of the first aspect in an amount of at least 1 ppm, preferably at least 2 ppm, more preferably at least 5 ppm, for example at least 10 ppm, as proportion of the middle distillate fuel oil obtained from the distillation of a pyrolysis oil. In some embodiments, the aldehyde-alkylphenol copolymers may be present in an amount of at least 50 ppm, as proportion of the middle distillate fuel oil obtained from the distillation of a pyrolysis oil.

- 15 Aldehyde-alkylphenol copolymers, when present, may be included in the composition of the first aspect in an amount of up to 5000 ppm, preferably up to 3000 ppm, more preferably up to 1000 ppm, for example up to 700 ppm, as proportion of the middle distillate fuel oil obtained from the distillation of a pyrolysis oil.

- 20 The aldehyde-alkylphenol copolymers, when present, are preferably included in the composition of the first aspect in an amount of from 1 to 1000, preferably 2 to 500 ppm, as proportion of the middle distillate fuel oil obtained from the distillation of a pyrolysis oil.

- 25 Acylated nitrogen compounds, when present, are preferably included in the composition of the first aspect in an amount of at least 1 ppm, preferably at least 2 ppm, more preferably at least 5 ppm, for example at least 10 ppm, as proportion of the middle distillate fuel oil obtained from the distillation of a pyrolysis oil. In some embodiments, the acylated nitrogen compounds may be present in an amount of at least 50 ppm, as proportion of the middle distillate fuel oil obtained from the distillation of a pyrolysis oil.

- 30 Acylated nitrogen compounds, when present, may be included in the composition of the first aspect in an amount of up to 5000 ppm, preferably up to 3000 ppm, more preferably up to 1000 ppm, for example up to 700 ppm, as proportion of the middle distillate fuel oil obtained from the distillation of a pyrolysis oil.

- 35 The acylated nitrogen compounds, when present, are preferably included in the composition of the first aspect in an amount of from 1 to 1000, preferably 2 to 500 ppm, as proportion of the middle distillate fuel oil obtained from the distillation of a pyrolysis oil.

Metal deactivating compounds, when present, are preferably included in the composition of the first aspect in an amount of at least 0.1 ppm, preferably at least 0.25 ppm, more preferably at least 0.5 ppm, for example at least 1 ppm, as proportion of the middle distillate fuel oil obtained from the distillation of a pyrolysis oil.

5

Metal deactivating compounds, when present, may be included in the composition of the first aspect in an amount of up to 5000 ppm, preferably up to 3000 ppm, more preferably up to 1000 ppm, for example up to 500 ppm, as proportion of the middle distillate fuel oil obtained from the distillation of a pyrolysis oil.

10

The metal deactivating compounds, when present, are preferably included in the composition of the first aspect in an amount of from 0.1 to 1000, preferably 1 to 100 ppm, as proportion of the middle distillate fuel oil obtained from the distillation of a pyrolysis oil.

15

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

In one preferred embodiment the composition of the present invention comprises an antioxidant, an acylated nitrogen compound and a metal deactivating compound.

20

Preferably the composition of the present invention comprises from 1 to 500 ppm, preferably from 20 to 150 ppm of an antioxidant; from 1 to 500 ppm, preferably from 20 to 150 ppm of an acylated nitrogen compound; and from 1 to 250 ppm, preferably 1 to 100 ppm of a metal deactivating compound.

25

Preferably the composition of the present invention comprises from 1 to 500 ppm, preferably from 20 to 150 ppm of a polyisobutenyl succinimide; from 1 to 500 ppm, preferably from 20 to 150 ppm of a phenylene diamine compound; and from 1 to 250 ppm, preferably 1 to 100 ppm of a metal deactivating compound, as proportion of the middle distillate fuel oil obtained from the distillation of a pyrolysis oil.

30

In one especially preferred embodiment the composition of the present invention comprises a polyisobutenyl succinimide; N,N'-di-secondary-butyl-para-phenylenediamine and N,N'-disalicylidene-1,2-propane diamine.

35

In one especially preferred embodiment the composition of the present invention comprises from 1 to 500 ppm, preferably from 20 to 150 ppm of a polyisobutenyl succinimide; from 10 to 500 ppm, preferably from 20 to 150 ppm of N,N'-di-secondary-butyl-para-phenylenediamine; and from 1 to 250 ppm, preferably 1 to 100 ppm of a N,N'-disalicylidene-1,2-propane diamine, as proportion of the middle distillate fuel oil obtained from the distillation of a pyrolysis oil.

The stabilising additive may also comprise a carrier or diluent. Preferred carriers and diluents are aromatic hydrocarbon compounds, especially C₁₀ alkyl naphthalene.

5 In a preferred embodiment, the composition of the first aspect comprises from 1 to 1000 ppm, preferably 2 to 500 ppm of an antioxidant and/or from 1 to 1000 ppm, preferably 2 to 500 ppm of a stabilising additive selected from (x) alkoxyated amine compounds; (y) aldehyde-alkylphenol copolymers; (z) acylated nitrogen compounds and mixtures thereof, as proportion of the middle distillate fuel oil obtained from the distillation of a pyrolysis oil.

10

In a preferred embodiment, the composition of the first aspect comprises from 1 to 1000 ppm, preferably 2 to 500 ppm of an antioxidant and/or from 1 to 1000 ppm, preferably 2 to 500 ppm of alkoxyated amine compounds and/or from 1 to 1000 ppm, preferably 2 to 500 ppm aldehyde-alkylphenol copolymers and/or from 1 to 1000 ppm, preferably 2 to 500 ppm acylated
15 nitrogen compounds, as proportion of the middle distillate fuel oil obtained from the distillation of a pyrolysis oil.

20

The fuel composition of the first aspect is a middle distillate fuel oil. Thus the fuel composition 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
25 the person skilled in the art.

30

The inclusion of (a) an antioxidant; and/or (b) a stabilising additive selected from (x) alkoxyated amine compounds, (y) aldehyde-alkylphenol copolymers, (z) acylated nitrogen compounds or mixtures thereof has surprisingly been found to improve the storage stability of
fuel compositions comprising middle distillate fuel oils obtained from the distillation of pyrolysis
oils.

35

According to a second aspect of the present invention there is provided a method of improving the stability of a fuel composition comprising a middle distillate fuel oil obtained from the
distillation of a pyrolysis oil, the method comprising adding to the fuel composition one or more
additives selected from:

(a) an antioxidant; and

(b) a stabilising additive selected from (x) alkoxyated amine compounds; (y) aldehyde-alkylphenol copolymers; (z) acylated nitrogen compounds; and mixtures thereof.

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

- (a) an antioxidant; and
 - 5 (b) a stabilising additive selected from (x) alkoxyated amine compounds; (y) aldehyde-alkylphenol copolymers; (z) acylated nitrogen compounds, and mixtures thereof;
- to improve the stability of a fuel composition comprising a middle distillate fuel oil obtained from the distillation of a pyrolysis oil.

- 10 Preferred features of the second and third aspects are as defined in relation to the first aspect. Further preferred features of the invention will now be described.

The one or more additives may be added to the fuel composition at any time.

- 15 The method and use of the present invention improve the stability of a composition comprising a middle distillate fuel oil obtained from the distillation of a pyrolysis oil.

Preferably the method and use improve the stability of a fuel composition comprising a middle distillate fuel oil obtained from the distillation of a plastic pyrolysis oil.

20

Preferably the method and use improve the storage stability of fuel compositions comprising a middle distillate fuel oil obtained from the distillation of a pyrolysis oil.

- 25 Preferably the method and use improve the storage stability of fuel composition comprising a middle distillate fuel oil obtained from the distillation of a plastic pyrolysis oil.

An improvement in storage stability suitably results in a reduction in degradation of the oil on storage. This may be observed in a number of ways.

- 30 In some embodiments the improvement in stability may provide reduced discolouration on storage.

In some embodiments the improvement in stability may provide reduced sedimentation.

- 35 In some embodiments the improvement in stability may reduce or prevent increases in viscosity.

In some embodiments the improvement in stability may reduce the formation of gums and particulates in the fuel composition comprising a middle distillate fuel oil obtained from the distillation of a pyrolysis oil.

- 5 In some embodiments the improvement in stability may provide improved filterability, particularly after storage.

- In some embodiments the improvement in stability may provide an improvement in low temperature properties of the composition comprising a middle distillate fuel oil obtained from the distillation of a pyrolysis oil.
- 10

Preferably the method and use of the present invention improves the stability of the fuel composition as measured by ASTM D6468.

- 15 ASTM D6468 is standard for measuring the high temperature stability of middle distillate fuels under ageing conditions. In the test, the fuel is aged at elevated temperature and then filtered through a filter pad. The amount of filterable insolubles in the fuel sample is estimated by measuring the light reflectance of the filter pads. The lower the reflectance, the more filterable insoluble deposits the fuel sample contained and therefore lower the stability of the fuel sample to aging.
- 20

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

25 **Example 1**

Two middle distillate fuel oils obtained from different plastic pyrolysis oils were tested.

Fuel I had the following properties:

Element	Concentration
P 15	14.10 ppm
S 16	19.62 ppm
Cl 17	54.81 ppm
K 19	0.50 ppm
Ca 20	ND< 0.21 ppm
V 23	ND< 0.05 ppm
Cr 24	12.15 ppm
Mn 25	0.35 ppm
Fe 26	5.77 ppm
Co 27	0.08 ppm

Ni 28	ND< 0.02 ppm
Cu 29	ND< 0.03 ppm
Zn 30	ND< 0.06 ppm

Fuel II had the following properties:

Element	Concentration
P 15	10.79 ppm
S 16	30.55 ppm
Cl 17	190 ppm
K 19	0.40 ppm
Ca 20	ND< 0.21 ppm
V 23	ND< 0.04 ppm
Cr 24	ND< 0.03 ppm
Mn 25	0.17 ppm
Fe 26	3.72 ppm
Co 27	0.06 ppm
Ni 28	ND< 0.02 ppm
Cu 29	0.18 ppm
Zn 30	0.35 ppm

The following additive compositions were prepared:

5

Additive composition A

Component	Wt% active
PIBSI X	16.8
N,N'-di-secondary-butyl-para-phenylenediamine	20
N,N'-disalicylidene-1,2-propane diamine	7.5
Aromatic solvents	balance

10 PIBSI X is a polyisobutenyl succinimide obtained from the condensation reaction of a polyisobutenyl succinic anhydride derived from polyisobutene of Mn approximately 750 with a polyethylene polyamine mixture of average composition approximating to tetraethylene pentaamine.

Additive composition B

15

Component	Wt% active
PIBSI X	9

N,N'-di-secondary-butyl-para-phenylenediamine	15
imidazoline	18
diethylhydroxylamine	25
Aromatic solvents	balance

The imidazoline component was provided by the reaction product of a fatty acid and a polyethylene polyamine comprising diethylene triamine (DETA).

5 **Additive composition C**

Component	Wt% active
PIBSI X	60
Aromatic solvents	balance

Additive composition D

Component	Wt% active
N,N'-disalicylidene-1,2-propane diamine	2.25
2,6-ditertbutyl phenol	58.75
N,N-di-sec-butyl-1,4,benzenediamine	39

10

Additive composition E

Component	Wt% active
Dodecyl lphenol resin Y	50
Aromatic solvents	Balance

15 Dodecyl phenol resin Y is a formaldehyde dodecyl phenol polymer having a number average molecular weight of 4500 to 5000.

Additive composition F

20 Additive composition F is a commercially available polyisobutenyl succinimide comprising 30-70 wt% aromatic solvents.

Example 2

The additive compositions of example 1 were dosed into the fuel oils I and II and the stability of the resultant fuel compositions was assessed using the method of ASTM D6468. The results are shown in table 1:

Table 1

Composition	Fuel	Additive	Treat rate (mg/L)	Accelerated Stability, % reflectance (ASTM D6468)
1	I	None		53.8
2	I	A	524	80.3
3	II	None		30.2
4	II	A	500	81.1
5	II	B	500	56.9
6	II	C	500	82.6
7	II	D	500	38.7
8	II	E	500	46.2
9	II	F	500	52.6

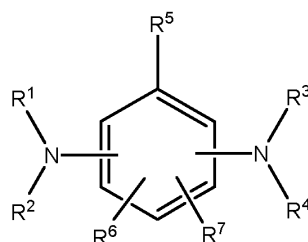
Each test fuel comprising an additive composition as disclosed herein showed increase in light reflectance of the filter pad used to filter the sample compared to the corresponding filter pad used to filter the unadditised base fuel, which corresponds to lower deposits formed in the sample during the test and therefore increased stability. These results show that the additive compositions disclosed herein can improve the stability of middle distillate fuel oil obtained from the distillation of a pyrolysis oil, as measured by the method of ASTM D6468.

Claims

1. A fuel composition comprising a middle distillate fuel oil obtained from the distillation of a pyrolysis oil and, as an additive, one or more of:
 - 5 (a) an antioxidant; and
 - (b) a stabilising additive selected from (x) alkoxyated amine compounds; (y) aldehyde-alkylphenol copolymers; (z) acylated nitrogen compounds; and mixtures thereof.
- 10 2. A method of improving the stability of a fuel composition comprising a middle distillate fuel oil obtained from the distillation of a pyrolysis oil, the method comprising adding to the composition one or more additives selected from:
 - (a) an antioxidant; and
 - 15 (b) a stabilising additive from (x) alkoxyated amine compounds; (y) aldehyde-alkylphenol copolymers; (z) acylated nitrogen compounds; and mixtures thereof.
- 20 3. Use of one or more additives selected from:
 - (a) an antioxidant; and
 - (b) a stabilising additive selected from (x) alkoxyated amine compounds; (y) aldehyde-alkylphenol copolymers; (z) acylated nitrogen compounds; and mixtures thereof;to improve the stability of a fuel composition comprising a middle distillate fuel oil obtained from the distillation of a pyrolysis oil.
- 25 4. The fuel composition, method or use according to any preceding claim wherein the pyrolysis oil is a plastic pyrolysis oil.
5. The fuel composition, method or use according to any preceding claim wherein the middle distillate fuel oil comprises paraffins and at least 50 wt% of the paraffin compounds present have at least 18 carbons.
- 30 6. The fuel composition, method or use according to any preceding claim wherein the fuel composition comprises the antioxidant (a).
7. The fuel composition, method or use according to claim 6 wherein the antioxidant is a phenolic antioxidant.
- 35 8. The fuel composition, method or use according to claim 7 wherein the phenolic antioxidant is selected from tertiarybutylhydroquinone (TBHQ or MTBHQ), 2,5-di-

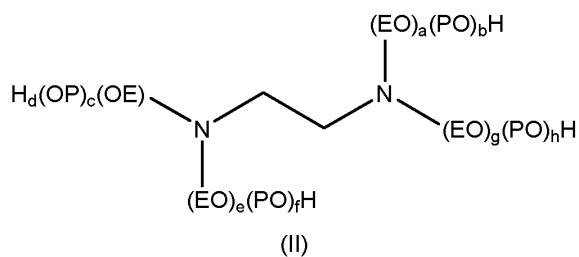
tertiarybutylhydroquinone (DTBHQ), pyrogallol, pyrocatechol 2,6-di-*tert*-butyl-4-methylphenol (BHT), 2,6-ditertiary-butyl-phenol, propylgallate and tertiarybutylcatechol.

9. The fuel composition, method or use according to any preceding claim wherein the antioxidant comprises a nitrogen containing antioxidant.
10. The fuel composition, method or use according to any preceding claim wherein the fuel composition comprises one or more nitrogen containing antioxidants selected from:
 - (i) phenylenediamines;
 - (ii) substituted hydroxylamines; and
 - (iii) mixtures thereof.
11. The fuel composition, method or use according to claim 10 wherein the fuel composition comprises phenylene diamine of formula:



- wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 are independently selected from hydrogen, an optionally substituted alkyl, alkenyl, aryl, alkaryl or aralkyl group, an ester, a carboxylic acid, an aldehyde, a ketone, an ether, an alcohol, an amine or an amide.
12. The fuel composition, method or use according to claim 10 or claim 11 wherein the fuel composition comprises a compound of formula R_2NOH in which each R is independently hydrogen or an optionally substituted hydrocarbyl group.
 13. The fuel composition, method or use according to any preceding claim wherein the fuel composition comprises the stabilising additive (b).
 14. The fuel composition, method or use according to claim 13 wherein the stabilising additive comprises (x) alkoxyated amine compounds.
 15. The fuel composition, method or use according to claim 14 wherein the alkoxyated amine compounds comprise compounds of formula (II):

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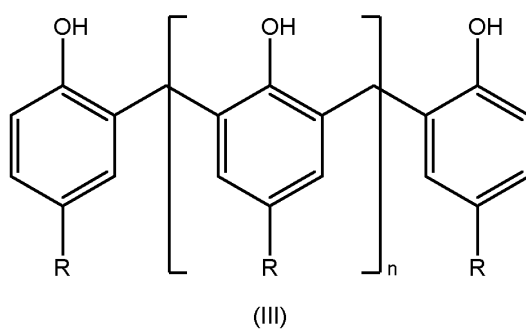


wherein EO represents an ethylene oxide residue, PO represents a propylene oxide residue and at least one of a, b, c, d, e, f, g and h is not 0.

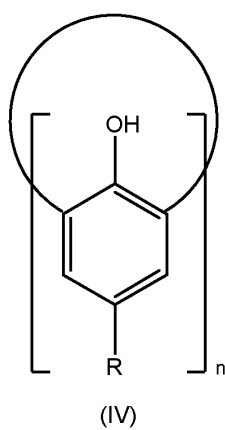
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16. The fuel composition, method or use according to any of claims 13 to 15 wherein the stabilising additive comprises (y) aldehyde-alkylphenol copolymers.

10 17. The fuel composition, method or use according to claim 16 wherein the aldehyde-alkylphenol copolymers have the structures (III) or (IV):



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wherein R is hydrogen or an alkyl group and n is at least 1.

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18. The fuel composition method or use according to any of claims 13 to 17 wherein the stabilising additive comprises (z) acylated nitrogen compounds.
- 5 19. The fuel composition, method or use according to claim 18 wherein the fuel composition comprise an acylated nitrogen compound (z) which is the reaction product of a polyisobutene-substituted succinic acid or succinic anhydride and a polyethylene polyamine.
- 10 20. The fuel composition, method or use according to any proceeding claim wherein the fuel composition comprises a metal deactivator.
21. The method or use according to any of claims 2 to 20 wherein the improvement in stability is an improvement in storage stability.
- 15 22. The method or use according to any of claims 2 to 21 which provides one or more of:
- a reduction in discolouration on storage;
 - reduced sedimentation;
 - a reduction in the formation of gums and particulates;
 - improved filterability; and

20 - an improvement in low temperature properties.