

FUEL OIL COMPOSITIONS, AND METHODS AND USES RELATING THERETO

The present invention relates to fuel oil compositions and to methods and uses relating thereto. In particular the invention relates to very low sulfur fuel oil (VLSFO) compositions.

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The invention relates especially to fuel oils useful in marine applications. Fuels of this kind are commonly referred to as marine diesel oil (marine fuel oil), marine residue oil (residual fuel oil) or bunker oil (bunker fuel oil). These are typically heavy fuels containing long chain alkanes and alkenes, high molecular weight cycloalkanes and highly fused aromatics (asphaltenes).

10 Fuels of this type are often high in sulfur. New regulations (IMO 2020) have recently been introduced by the International Maritime Organization (IMO) setting a global limit for sulfur in fuel oil on board ships of 0.50 wt% (5000 ppm by weight). This is a significant reduction from the previous limit of 3.5 wt%.

15 Various approaches have been taken to reduce the sulfur content of these fuels in order to comply with the new regulations. More catalytic processing of fuels is often involved and fuels from multiple sources may be blended to provide a blended fuel with a sulfur content of less than 0.50 wt%. However the component fuels mixed into the blends may have very different properties.

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This has led to fuel stability problems for the new IMO2020 compliant very low sulfur fuel oils (VLSFO). Typically residual and low sulfur distillate streams are blended to reach the new sulfur specification, but the component fuel streams that are blended to make the fuel can be variable quality and often have a level of chemical reactivity. This can lead to oxidative and thermal stability problems over time for the blended fuel, with gums or other insolubles being formed.

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Problems due to precipitation of asphaltenes from marine fuels have been known for a long time and additives have been developed which help address these issues and reduce asphaltene deposits. These additives are known as asphaltene dispersants. However for new blended VLSFO compositions new problems with stability are occurring. It is an aim of the present invention to provide a VLSFO having improved oxidative and/or thermal stability.

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According to a first aspect of the present invention there is provided a fuel oil composition comprising a blended fuel oil having a sulfur content of less than 5000 ppm and an additive where the additive is a copolymer comprising maleic anhydride derived units and α -olefin derived units.

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The present invention relates to a fuel oil composition having a sulfur content of less than 5000 ppm. Unless otherwise mentioned all references to ppm in this specification are to parts per million by weight.

- 5 The fuel oil composition of the present invention comprises a blended fuel oil. Suitably the blended fuel oil comprises at least two component fuels. The two or more component fuel oils may be selected from residual fuel oils, distillate fuel oils, bio-derived fuel oils, cracked process streams, synthetic fuels and plastic pyrolysis oils.
- 10 Residual fuel oils are the heavy fuel components which remain after distillation or refining process. By residual fuel oils we mean to include atmospheric tower bottoms and vacuum tower bottoms. Residual fuel oils which have been subjected to hydrotreating or visbreaking processes are also regarded as residual fuel oils.
- 15 Residual fuel oils have high boiling points and high viscosity, and have high sulfur and nitrogen contents.

Unless hydrotreated residual fuel oils comprise high levels of sulfur, for example up to 5 wt%, typically 1 to 4 wt%.

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Residual fuel oils typically have a nitrogen content of at least 1000 ppm and may have a nitrogen content of at least 2000 ppm, for example up to 5000 ppm or up to 10000 ppm.

Atmospheric tower bottoms (ATB) typically have a boiling point of 340°C or above.

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Vacuum tower bottoms (VTB) typically have a boiling point of 550°C or above.

Visbreaker residue typically has a boiling range of 340 to 540°C.

- 30 The kinematic viscosity of residual fuel oils is typically in the range 10 to 15000 mm²/s, preferably 20 to 7500 mm²/s, suitably 50 to 1000 mm²/s. Visbreaker residue which is typically derived from VTB typically has a lower viscosity than VTB, often having a viscosity around a fifth of that of the VTB from which it is derived.

- 35 Kinematic viscosity may be measured according to ISO 3104 at 50°C.

The pour point of residual fuel oils may be from -10 to 85°C, preferably from -5 to 60°C, for example from 0 to 45°C.

Pour point may be measured according to ISO 3016.

The asphaltene content of the residual fuel oil is preferably less than 5 wt%, more preferably less than 2 wt%, suitably less than 1 wt%.

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Suitable methods for measuring asphaltene content include IP-469 (SARA analysis).

By distillate fuels we mean to include straight run distillate fuels, hydrotreated distillate fuels (for example low sulfur diesel fuel or very low sulfur diesel fuel), kerosene, light gas oil, heavy gas oil and vacuum gas oil.

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Distillate fuels may have a boiling point within the range 180 to 550°C.

Straight run distillate fuels are obtained directly from the distillation column and used without any further treatment.

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Middle distillate fuel oil/diesel fuel oil suitably has a boiling range of 200 to 350°C,

Kerosene typically has a boiling range of 193 to 271°C.

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Light gas oil typically has a boiling range of 271 to 321°C.

Heavy gas oil typically has a boiling range of 321 to 425°C.

Light vacuum gas oil typically has a boiling range of 425 to 510°C.

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Heavy vacuum gas oil typically has a boiling range of 510 to 564°C.

Straight run middle distillate fuels typically have a sulfur content of 0.5 to 2 wt%. However distillate fuels are commonly hydrotreated in a process which reduces the sulfur content.

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Low sulfur diesel fuels have a sulfur content of less than 500 ppm. In some countries they may have a sulfur content of less than 200 ppm.

Ultra low sulfur diesel fuels have a sulfur content of less than 50 ppm. In some countries they may have a sulfur content of less than 15 ppm or less than 10 ppm.

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By cracked process streams we mean to refer to fuels obtained from catalytic cracking of fuel oils. Such fuel components typically contain reactive groups such as olefins. By cracked

process streams we mean to include cracked light gas oil, cracked heavy gas oil, light cycle oil, heavy cycle oil and fluid catalytic cracker slurry oil.

5 Light cycle oil typically refers to the fluid catalytic cracker (FCC) product distilling in the range of 200 to 350°C.

Heavy cycle oil typically refers to the FCC product distilling in the range 350 to 500°C.

10 Slurry oil is a mixture comprising the FCC residue and catalyst fines (typically silica and/or alumina).

Suitable bio-derived fuel oils include biodiesel fuels and second generation biodiesel fuels. Biodiesel as defined by ASTM specification D-6751 (the entire teachings of which are incorporated herein by reference) and EN 14214 are fatty acid mono alkyl esters of vegetable
15 or animal oils. Suitable biofuel may be made from any fat or oil source, including tallow, but is preferably derived from a vegetable oil, for example rapeseed oil, palm oil, palm kernel oil, coconut oil, corn or maize oil, sunflower oil, safflower oil, canola oil, peanut oil, cottonseed oil, jatropha oil (physic nut), used cooking oil or soybean oil. Preferably it is a fatty acid alkyl ester (FAAE). More specifically the biofuel may comprise rapeseed methyl ester (RME) and/or
20 soybean methyl ester (SME) and/or palm oil methyl ester (PME) and/or jatropha oil methyl ester.

A biofuel may suitably be second generation biodiesel. Second generation biodiesel is derived from hydrotreatment of renewable resources such as vegetable oils and animal fats. Second
25 generation biodiesel may be similar in properties and quality to petroleum based fuel oil streams.

Biofuels typically have very low sulfur contents, suitably less than 100 ppm. They have similar boiling points to mineral distillate fuels.

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By synthetic fuel oils we mean to include any synthetically prepared hydrocarbon fuel oils, for example those obtained by Fischer Tropsch processes. Suitable fuels of this type include heavier Fisher-Tropsch fuels for example as described in US10294431.

35 Plastic pyrolysis oils are obtained from plastic waste via a thermochemical process based on pyrolysis and hydrotreatment. Plastic pyrolysis oils typically have a boiling range of 170 to 370°C and a low sulfur content, for example less than 100 ppm or less than 50 ppm.

The fuel oil composition of the present invention comprises a blended fuel oil. This is suitably obtained by blending two or more component fuels.

5 Preferably the blended fuel oil comprises at least one residual fuel component and at least one further non-residual fuel component.

Preferably the blended fuel oil comprises at least 1 wt% residual fuel components.

10 The blended fuel oil may comprise at least 5 wt% residual fuel components.

The blended fuel oil preferably comprises from 1 to 50 wt% residual fuel components.

The blended fuel oil may comprise two or more residual fuel components.

15 Preferably the blended fuel oil comprises at least one residual fuel component and at least one further fuel component.

20 In some embodiments the blended fuel oil comprises from 5 to 95 wt% residual fuel components and from 95 to 5 wt% one or more further fuel components selected from distillate fuel components and/or cracked fuel components.

In some embodiments the blended fuel oil comprises 5 to 75 wt%, preferably 10 to 50 wt % straight run distillate fuel.

25 In some embodiments the blended fuel oil comprises 5 to 75 wt%, preferably 10 to 50 wt % cracked process streams.

In some embodiments the blended fuel oil comprises 5 to 75 wt%, preferably 10 to 50 wt % light cycle oil.

30 The properties of a blended fuel depend on the properties of the component fuels from which they are made and the proportions of each fuel in the blend.

35 The stability of a blended fuel depends on the nature and relative amounts of the component fuels present in the blended fuels.

Residual and cracked components generally lead to reduced stability.

The inclusion of treated distillates for example hydrotreated distillates and synthetic fuels tends to improve the stability of the blended fuel.

5 The blended fuel oil has a sulfur content of less than 5000 ppm. It may have a sulfur content of less than 4000 ppm, for example less than 3000 ppm, less than 2000 ppm or less than 1000 ppm.

10 Preferably the blended fuel oil has a pour point as measured according to ISO 3016 of from -10 to 40°C, preferably from -10 to 25°C, more preferably from -10 to 10°C.

Preferably the blended fuel oil has a kinematic viscosity as measured by ISO 3104 at 40°C of less than 200 mm²/s, preferably less than 100 mm²/s, suitably between 1 and 20 mm²/s, preferably from 1.4 to 10 mm²/s.

15 The blended fuel oil may have a kinematic viscosity of from 0.1 to 200 mm²/s, for example 1 to 100 mm²/s, for example 1.4 to 15 mm²/s as determined by ISO 3014 at 40°C.

20 Suitably the blended fuel oil has an asphaltene content of less than 6 wt%, for example less than 2 wt%, such as less than 0.5 wt%.

The fuel oil compositions of the present invention comprise an additive which is a copolymer comprising maleic anhydride derived units and α -olefin derived units.

25 The copolymer is suitably an alternating copolymer and is prepared by reacting maleic anhydride with an α -olefin. Means for carrying out such reactions will be well known to those skilled in the art and are described, for example in US4240916, US3560456 and US4151069.

30 The copolymer additive of the invention is suitably prepared by reacting maleic anhydride with an α -olefin in a molar ratio of from 3:1 to 1:3, preferably 2:1 to 1:2, more preferably from 1.5:1 to 1:1.5, for example about 1:1.

35 Preferably the α -olefin has from 6 to 40 carbon atoms, preferably from 10 to 36 carbon atoms, preferably from 12 to 36 carbon atoms, for example from 16 to 32 carbon atoms. Most preferably the α -olefin has from 18 to 30 carbon atoms, for example from 20 to 28 carbon atoms.

To form the copolymer additive of the invention a mixture of α -olefins may be used.

In one preferred embodiment a mixture of α -olefins having 20 to 24 carbon atoms is used.

In one embodiment a mixture of α -olefins having 24 to 28 carbon atoms is used, for example a mixture having 26 to 28 carbon atoms.

5 The present invention relates to a copolymer comprising maleic anhydride derived units and α -olefin derived units.

The copolymer directly obtained from the reaction of an α -olefin and maleic anhydride comprises alkyl chains and anhydride functional groups.

10 In some embodiments the anhydride groups may be further reacted. For example in some embodiments the anhydride groups may be hydrolysed to provide carboxylic acid functional groups.

15 In some embodiments the anhydride and/or hydrolysed acid product may be partially or fully further functionalised, for example by reaction with amines and/or alcohols to incorporate ester and/or amide and/or imide functional groups into the copolymer.

20 In preferred embodiments the copolymer is not further functionalised in this way and the maleic anhydride derived units are present as underivatized anhydride moieties and/or as carboxylic acid moieties.

Most preferably the maleic anhydride derived units of the copolymer contain anhydride groups. Suitably the additive comprises a copolymer obtained directly from the reaction of an α -olefin with maleic anhydride.

25 Preferred copolymers for use herein have a number average molecular weight of from 1000 to 50000, preferably from 2000 to 40000, suitably from 2500 to 30000, for example from 3000 to 25000.

30 Preferably the copolymer has a number average molecular weight of from 5000 to 20000, in one embodiment the copolymer has a number average molecular weight of from 5000 to 10000. In one embodiment the copolymer has a number average molecular weight of from 8000 to 15000.

35 The copolymer additive is preferably present in the fuel oil composition in an amount of at least 10 ppm, preferably at least 30 ppm.

Preferably the copolymer additive is present in the fuel oil composition in an amount of from 20 to 10000 ppm, preferably 50 to 5000 ppm, suitably from 60 to 3000 ppm, more preferably from 100 to 1000 ppm.

5 In some embodiments the fuel oil composition of the present invention comprises a single component fuel. The fuel oil composition of the present invention preferably comprises a blended fuel oil formed from two or more component fuels. The copolymer additive of the invention may be added to the blended fuel or it may be added to a component fuel before it is mixed with further components.

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When formulating a blended fuel oil it is typical that one or more component fuels used to prepare the blended fuel will be less stable than other component fuels. For example some component fuels may be more susceptible to thermal and/or oxidative degradation. Thus it may be advantageous to add the copolymer additive to a particular component fuel prior to

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admixture with other component fuels.

In some cases SARA analysis may be carried out on one or more component fuels or the blended fuel.

20 SARA analysis (percent saturates, aromatics, resins and asphaltenes) can be performed to obtain information about the compositional nature of the blended fuel. SARA analysis is used to determine the properties of an oil that contribute to instability and its potential for fouling when processed or blended with other oils. Asphaltenes and saturated, straight-chained hydrocarbons (n-paraffins) can become unstable and precipitate out of an oil as a function of
25 composition, temperature, pressure and/or time. Aromatics and resins on the other hand tend to help stabilize a fuel oil sample.

According to a second aspect of the invention there is provided a method of preparing a fuel oil composition, the method comprising admixing an additive with a first component fuel and with
30 a second component fuel wherein the resultant fuel oil composition has a sulfur content of less than 5000 ppm and wherein the additive is a copolymer comprising maleic anhydride derived units and α -olefin derived units.

Preferred features of the second aspect are as defined in relation to the first aspect.

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Preferably the copolymer additive is mixed with the first component fuel before the first component fuel is mixed with the second component fuel.

The copolymer additive improves the stability of the fuel oil compositions of the invention. Thus the fuel oil composition of the invention has improved stability compared with an equivalent unadditised fuel oil.

5 According to a third aspect of the invention there is provided a method of improving the stability of a blended fuel oil having a sulfur content of less than 5000 ppm, the method comprising mixing into the fuel oil an additive which is a copolymer comprising maleic anhydride derived units and α -olefin derived units.

10 In some embodiments the additive is mixed into a component fuel used to prepare the fuel oil composition.

According to a fourth aspect of the invention there is provided a use of a copolymer comprising maleic anhydride derived units and α -olefin derived units as an additive to improve the stability
15 of a blended fuel oil having a sulfur content of less than 5000 ppm.

Preferred features of the third and fourth aspects of the invention are as defined in relation to the first aspect.

20 Further preferred features of the invention will now be described.

The present invention involves the use of an additive to improve the stability of a fuel oil having a sulfur content of less than 5000 ppm.

25 By improving the stability of the fuel oil we mean to include any means by which the additised fuel may be considered to be more stable than an equivalent unadditised fuel.

An improvement in stability may result from reduced degradation due to heat, light or oxidation.
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An improvement in stability may provide a reduction in the formation of gums, sediments or other insolubles.

An improvement in stability may reduce or inhibit precipitation.
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An improvement in stability may provide improved dispersion of insolubles in a fuel.

An improvement in stability may improve filterability and/or reduce filter blocking.

An improvement in stability may involve colour stability and/or reduced discolouration.

5 The present invention may provide improved storage stability. Improved storage stability may be measured by a reduction in sediment formation and/or reduced precipitation and/or improved filterability and/or improved colour stability.

10 The present invention may provide improved thermal stability. This may be measured by a reduction in the formation of thermal degradation products such as gums and sediments and/or reduced discolouration.

The present invention may provide improved oxidation stability. This may be measured by a reduction in the formation of oxidative degradation products such as gums and sediments and/or reduced discolouration.

15 A particular advantage of the present invention is the reduction in the levels of gums and insolubles which are not reduced by traditional asphaltene dispersants used in marine fuel oils. These additives are known to the person skilled in the art and include, for example alkylphenol resins, sulfonated alkyl, alkyl compounds and polyester polyamides/imides. Such compounds are described in WO2009/013536, US9034093 and US2017/0198174.

20 Improvement in fuel stability can be measured by any suitable means. Methods by which stability of fuels can be measured are well known to those skilled in the art.

25 One especially useful means by which the effect of the present invention can be measured is by determining total sedimentation using the methods described in ISO10307-1 and ISO10307-2. Alternatively, the effect of the present invention can be measured by determining total sedimentation using the methods described in ASTM D4870.

30 Other methods for measuring improved fuel stability include ASTN D4740 Spot Test, ASTM D7061 Turbiscan Method, ATSM D7112 PORLA Method and ASTM D7157 Rofa Method (S-value).

35 Further suitable methods for measuring improved fuel stability include ASTM D97 (modified) – Manual Pour Point; ASTM D4530 – Micro-Carbon Residue Test; ASTM D5949 – Automated Pour Point Testing; ASTM D7169 – Paraffin Content & Distribution Analysis; IP 469 – SARA Compositional Analysis; and Digital Imaging (via Cross Polar Microscopy) & Particle Size Evaluations.

The fuel oil compositions of the invention may further comprise one or more further additives. Any additives commonly incorporated into fuels for marine applications may be included. The formation of suitable fuel compositions and additive packages for fuels will be within the competence of the person skilled in the art.

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Additive classes which may be included in the fuel oil compositions of the present invention include:

- (i) conductivity improvers;
- (ii) combustion improvers;
- 10 (iii) asphaltene dispersants;
- (iv) fuel antioxidants;
- (v) cold flow improvers;
- (vi) wax anti-setting agents;
- (vii) biofuel instability inhibitors;
- 15 (viii) blended fuel separation inhibitors;
- (ix) other detergents/dispersants.

Suitable conductivity improver additives (i) for use herein include: alpha-olefin-sulfone copolymer class – polysulphone and quaternary ammonium salt (for example as described in
 20 US3811848); polysulphone and quaternary ammonium salt amine/epichlorhydrin adduct dinonylnaphthylsulphonic acid (for example as described in US3917466); copolymer of an alkyl vinyl monomer and a cationic vinyl monomer (for example as described in US5672183); alpha-olefin-maleic anhydride copolymer class (for example as described in US4416668);
 25 alpha -olefin-acrylonitrile copolymers (for example as described in US4388452); alpha-olefin-acrylonitrile copolymers and polymeric polyamines (for example as described in US4259087); copolymer of an alkylvinyl monomer and a cationic vinyl monomer and polysulfone (for example as described in US6391070); and acrylic-type ester-acrylonitrile copolymer and polymeric polyamine (for example as described in US4537601 and US4491651).

30 In some preferred embodiments the conductivity improver comprises a polysulfone component.

In some preferred embodiments the conductivity improver comprises a polymeric nitrogen-containing conductivity improver.

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In some preferred embodiments the conductivity improver comprises a polyamine compound.

In some preferred embodiments the conductivity improver is a composition comprising both a polyamine component and a polysulfone component, optionally in combination with a quaternary ammonium salt, for example as described in US3917466.

- 5 Preferred conductivity improvers for use in the fuel oil compositions of the invention are described in WO2009/013536.

Suitable combustion improvers (ii) include metal compounds, organic compounds and mixtures thereof.

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Suitable combustion improvers are described in WO2009/013536.

Some preferred combustion improvers containing a metal compound and an organic compound are described in EP1899440.

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The metal compound is preferably selected from an iron compound, a manganese compound, a calcium compound, a cerium compound, and mixtures thereof.

- 20 The organic compound is preferably selected from a bicyclic monoterpene, substituted bicyclic monoterpene and mixtures thereof.

Preferably the organic compound is camphor.

- 25 Preferred metal compounds are ferrocene and substituted ferrocenes.

Other suitable combustion improvers are cetane improvers such as alkyl nitrates or dialkyl peroxides, for example as described in US20190127657.

- 30 An especially preferred cetane improver is 2-ethylhexyl nitrate.

- 35 Suitable asphaltene dispersants (iii) for use in the fuel oil compositions of the present invention include alkoxylated fatty amines or derivatives thereof; alkoxylated polyamines; alkane sulphonic acids; aryl sulphonic acids; sarcosinates; ether carboxylic acids; phosphoric acid esters; carboxylic acids and derivatives thereof; alkylphenol-aldehyde resins; hydrophilic-lipophilic vinylic polymers; alkyl substituted phenol polyethylene polyamine formaldehyde resins; alkyl aryl compounds; alkoxylated amines and alcohols; imines; amides; zwitterionic compounds; fatty acid esters; lecithin and derivatives thereof; and derivatives of succinic anhydride and succinamide.

Suitable asphaltene dispersants are described in WO2009/013536.

5 A particularly preferred class of asphaltene dispersants for use herein are alkyl phenol aldehyde resins, for example those described in paragraphs [0017] to [0038] of US2007221539. Compounds derived from C3 to C12 alkyl or alkenyl phenols, especially nonylphenol are particularly preferred.

10 Combinations of alkyl phenol aldehyde resins and poly(meth)acrylates as described in US5021498 are useful as asphaltene dispersants.

Further suitable asphaltene dispersants include alkoxylated fatty polyamines for example as described in US6488724 and US5421993. Also useful are alkoxylated derivatives of simple polyamines, for example a block copolymer derived from ethylene diamine, ethylene oxide and propylene oxide. An example of such a compound is available from Clariant under the trade mark GENAPOL (RTM).

15 Suitable fuel antioxidants (iv) suitable for use in the present invention include phenolic antioxidants, sulphurized phenolic antioxidants and aromatic amine antioxidants.

20 Suitable antioxidants are described, for example, in WO2009/013536, US3556748 and US5509944.

Preferred antioxidants for use herein are aromatic amines, for example phenylene diamine.

25 Cold flow improvers (v) suitable for use in the present invention include copolymers of alkenes and unsaturated esters, alkylmethacrylate polymers, polyoxyalkylene esters, ethers, ester/ethers and mixtures thereof.

30 Suitable cold flow improvers for use herein are described in WO2009/013536 and US2017/0233670.

Particular preferred cold flow improvers are ethylene vinyl acetate copolymers and terpolymers. These are described for example in paragraphs [0026] to [0032] of US20170233670.

35 Typical copolymers are those of ethylene and vinyl esters such as vinyl acetate. Propene may also be included.

Terpolymers may further comprise vinyl neodecanotate, vinyl 2-ethylhexanoate, methyl acrylate or 2-ethylhexyl acrylate.

Another preferred class of cold flow improvers are comb polymers. These are known to the person skilled in the art and include:

- polyalkyl(meth) acrylates or copolymers thereof;
- maleic anhydride - α -olefin copolymers which are subsequently reacted with alcohols (eg. C10 to C28 alcohols) to form esters or subsequently reacted with primary fatty amines;
- fumarate vinyl ester copolymers, for example fumarate vinyl acetate; and
- poly(α -olefin)homo or copolymers.

Some suitable comb polymers are described in paragraphs [0067] to [0070] of US20170233670.

Wax anti-settling agents (vi) useful as stabilisers in the present invention include certain polyimide and maleic anhydride olefin copolymers.

Suitable additives of this type for use herein are described in WO2009/013536.

Other suitable wax settling additives include: those described in US4402708 such as the reaction product of phthalic anhydride and ditallow fatty amide; combinations of such additives and ethylene vinyl acetate copolymers, for example as described in US4481013; the fatty amide derivatives described in US5071445; and the copolymers described in US5391632, including in particular the compound of comparative example 25.

Further compounds which may be useful as wax anti-settling agents and/or as cold flow inhibitors are described in EP 743972 and EP 743974.

Biofuel instability inhibitors (vii) function mainly to disperse polymers or high molecular weight compounds either found in the biofuels as the bi-product of oxidation or thermal breakdown. Biofuel instability inhibitors useful herein include polymers of: ethylene and unsaturated esters; vinyl alcohols, vinyl ethers and their ester with organic acids; propylene, ethylene, isobutylene adducts with unsaturated carboxylic acids (such as maleic and fumaric acids) and their amide or imide derivatives; acrylic acids and their amide or esters derivatives; polystyrenes; and polymers made from combinations of these monomers.

A blended fuel separation inhibitor (viii) acts to maintain two or more fuels in a dispersed or blended form. Loss of uniformity and mobility of fuel may also occur when there is phase

separation within such a fuel. Fuel blends may commonly be made in-tank when ships dock and may source whatever fuel is available at the locality at a favourable price. Lack of stability may occur, for example, when two or more different distilled fuels are blended, or when a biofuel is blended with a distilled fuel.

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Many compounds as blended fuel separation inhibitors include compounds described above and selection of suitable additives will be within the competence of the person skilled in the art.

10 Detergent/dispersant compounds (ix) suitable for use herein include any commonly known nitrogen-containing or non-nitrogen containing detergent compounds. Such compounds typically include a long chain hydrophobic tail and a polar head group. Suitable hydrophobic groups are polyisobutene groups and polar head groups may contain nitrogen and/or oxygen containing functional groups such as amides, amines, succinimides, acids and esters.

15 Preferred acylated nitrogen-containing dispersants are the reaction product of a carboxylic acid derived acylating agent and an amine including at least one primary or secondary amine group.

20 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.

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Especially preferred polyisobutenyl succinimide additives include those obtained from the condensation reaction of a polyisobutenyl succinic anhydride derived from polyisobutene of Mn approximately 750 or approximately 1000 with a polyethylene polyamine mixture of average composition approximating to tetraethylene pentamine.

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Preferred further additives for inclusion in the fuel oil compositions of the invention include acylated nitrogen-containing dispersants, alkylphenol-aldehyde resins and phenylene diamine antioxidants.

35 In a preferred embodiment the phenolic resin is a substituted phenolic resin. More preferably the phenolic resin is the reaction product of substituted phenol and an aldehyde.

More preferably the phenolic resin is the reaction product of substituted phenol and an aldehyde having 1-22, preferably 1-7 carbon atoms, for example formaldehyde.

Preferably the phenolic resin is a C₉-C₂₄ phenolic resin.

5 More preferably the phenolic resin is the reaction product of a C₉-C₂₄ phenol and formaldehyde, or of t-butyl phenol and an aldehyde having 1-22, preferably 1-7, carbon atoms, for example formaldehyde.

Preferred additives for improving the low temperature properties of the fuel oil compositions are described in US2017/0233670.

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In some preferred embodiments the first, second, third or fourth aspects of the invention may relate the use of a copolymer comprising underivatized maleic anhydride derived units and units derived from a mixture of α -olefins having 20 to 24 carbons in combination with a blended fuel oil comprising at least 1 wt% residual fuel components and 5 to 75 wt%, preferably 10 to 15 50 wt% straight run distillate fuel components.

In some preferred embodiments the first, second, third or fourth aspects of the invention may relate the use of a copolymer comprising underivatized maleic anhydride derived units and units derived from a mixture of α -olefins having 26 to 28 carbons in combination with a blended 20 fuel oil comprising at least 1 wt% residual fuel components and 5 to 75 wt%, preferably 10 to 50 wt% straight run distillate fuel components.

In some preferred embodiments the first, second, third or fourth aspects of the invention may relate the use of a copolymer comprising underivatized maleic anhydride derived units and units derived from a mixture of α -olefins having 20 to 24 carbons in combination with a blended 25 fuel oil comprising at least 1 wt% residual fuel components and 5 to 75 wt%, preferably 10 to 50 wt% cracked fuel components.

In some preferred embodiments the first, second, third or fourth aspects of the invention may relate the use of a copolymer comprising underivatized maleic anhydride derived units and units derived from a mixture of α -olefins having 26 to 28 carbons in combination with a blended 30 fuel oil comprising at least 1 wt% residual fuel components and 5 to 75 wt%, preferably 10 to 50 wt% cracked fuel components.

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50 wt% straight run distillate fuel components, wherein the copolymer has a number average molecular weight of from 5000 to 10000.

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In some preferred embodiments the first, second, third or fourth aspects of the invention may relate the use of a copolymer comprising underivatised maleic anhydride derived units and units derived from a mixture of α -olefins having 26 to 28 carbons in combination with a blended fuel oil comprising at least 1 wt% residual fuel components and 5 to 75 wt%, preferably 10 to 50 wt% straight run distillate fuel components, wherein the copolymer has a number average molecular weight of from 8000 to 15000.

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In some preferred embodiments the first, second, third or fourth aspects of the invention may relate the use of a copolymer comprising underivatized maleic anhydride derived units and units derived from a mixture of α -olefins having 26 to 28 carbons in combination with a blended fuel oil comprising at least 1 wt% residual fuel components and 5 to 75 wt%, preferably 10 to 50 wt% cracked fuel components, wherein the copolymer has a number average molecular weight of from 5000 to 10000.

In some preferred embodiments the first, second, third or fourth aspects of the invention may relate the use of a copolymer comprising underivatized maleic anhydride derived units and units derived from a mixture of α -olefins having 26 to 28 carbons in combination with a blended fuel oil comprising at least 1 wt% residual fuel components and 5 to 75 wt%, preferably 10 to 50 wt% cracked fuel components, wherein the copolymer has a number average molecular weight of from 8000 to 15000.

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

Example 1

Additives A to D (inventive) were prepared by the reaction of equimolar amounts of α -olefin and maleic anhydride in the presence of radical initiator and solvent for 5 hours. The reaction conditions are summarized in Table 1. After completion of the reaction, the reaction solvents were removed under reduced pressure to provide the polymeric products, which were then diluted to a polymer concentration of 40 wt% using Aromatic 150 solvent.

GPC analysis of the molecular weight (MW) distribution is also shown in Table 1

Gel permeation chromatography (GPC) was carried out using a Waters Styragel® HR column, eluting with tetrahydrofuran (1 mL/min) at 39°C. Detection was by refractive index and the product molecular weight distribution (Mn, Mw and polydispersity) was calculated relative to polystyrene standards.

Table 1

Additive	α -olefin	Radical initiator	Reaction solvent	Reaction temp (°C)	Polymer MW by GPC		
					Mn	Mw	PD
A	C20 – 24	di(tert-butyl)peroxide	Diisobutyl ketone	160	2292	4600	2.0
B	C26 – 28	di(tert-butyl)peroxide	Diisobutyl ketone	160	4190	6424	1.53

C	C20 – 24	Trigonox 21S*	toluene	80	9769	22155	2.27
D	C26 – 28	Trigonox 21S*	toluene	80	12910	28832	2.23

*tert-Butyl peroxy-2-ethylhexanoate, commercially available from Nouryon

Example 2

- 5 Additives A to D as shown in Table 1 were added to a marine fuel complying with IMO 2020 standards. The marine fuel comprised a blend of distillate and residual fuel components, having a TSE values of 0.09% (m/m) as measured by ISO10307-1.

- Comparative fuel compositions were prepared by dosing the known asphaltene dispersants E, F, G, H and I into the same fuel.
- 10

Compositional information for the additives used in the comparative examples is shown in Table 2.

15 **Table 2**

Additive	Description
E	Marine fuel additive package containing an alkylphenol resin, an alkoxyated polyamine and an acylated nitrogen-containing stabilizer / dispersant
F	Acylated nitrogen-containing stabilizer / dispersant
G	Phenolic resin prepared from dodecyl phenol, tert-octyl phenol and formaldehyde
H	Phenolic resin prepared from tetradecylphenol and formaldehyde

The fuel compositions were then subjected to a heptane dispersant test carried out in the following manner:

- 20 The additised or unadditised fuel oil (0.1 g) was added to heptane (6.77g, 9.9 mL) in a graduated centrifuge tube. After mixing thoroughly, the centrifuge tube was allowed to stand undisturbed for 18 hours at ambient temperature. The sample was then visually evaluated and given a rating of good, moderate or poor for dispersancy.
- 25 A sample was also run in the absence of additive. The results of the heptane dispersant tests are shown in Table 3.

Table 3

Entry	Additive	Type	Treat Rate (ppm by weight Active)	Visual inspection rating 18 hours
1	A	inventive	1500	Good
2	B	inventive	1500	Good
3	E	comparative	1500	Moderate
4	F	comparative	1500	Poor
5	G	comparative	1500	Poor
5	H	comparative	1500	Poor
7	none	comparative	-	Poor*

* For the unadditised test, visual inspection took place after 1 hour

5 The additives of the invention showed superior dispersancy of the gums and sediments that were present within the IMO 2020 compliant marine fuel, when compared to the comparative examples. Figure 1 shows the centrifuge tube for entries 7 and 1 (from left to right) in Table 3 after it has been allowed to stand undisturbed for 18 hours at ambient temperature.

Example 3

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The effect of an additive of the invention on TSP (total sediment potential) was evaluated in a different VLSFO, which comprised a blend of distillate and residual fuel components.

15 Prior to testing with additives, the TSE (existent sediment without thermal aging) for the fuel was measured as 0.13 % (m/m). The SARA analysis (IP-469) provided saturates 49.8 wt%, aromatics 36.50 wt%, resins 8.80 wt% and asphaltenes 4.90 wt%]

20 Total sediment existent (TSE) was measured according to ISO 10307-1. The results are expressed as the mass percentage of total sediment, to the nearest 0.01 % (m/m).

Total sediment potential (TSP) was measured by thermally aging the test sample for 24 hours at 100 °C according to ISO 10307-2 (Procedure A) followed by hot filtration according to ISO 10307-1. The results are expressed as the mass percentage of total sediment, to the nearest 0.01 % (m/m).

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Compositional information for the additives used in the comparative examples is shown in Table 4.

Table 4

Additive	Compositional Information
J	Amine based stability additive
K	Phenolic resin, high molecular weight

The TSP was then measured and the results are shown in Table 5.

5

Table 5 TSP measurements

Entry	Additive	Type	Treat Rate (ppm by weight active)	TSP (% m/m)
1	none	comparative	-	0.42
2	B	inventive	1500	0.14
3	J	comparative	1500	0.30
4	K	comparative	1500	0.22

The results showed that the test fuel was unstable. For the unadditised fuel the TSP result (0.42 % m/m) was significantly higher than the TSE (0.13 % m/m). Unexpectedly, inventive additive B was highly effective in stabilizing the test fuel (Table 5, entry 2). For the fuel additised with additive B the measured TSP was essentially unchanged compared to the TSE of the unadditised fuel.

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Claims

- 5 1. A fuel oil composition comprising a blended fuel oil having a sulfur content of less than 5000 ppm and an additive wherein the additive is a copolymer comprising maleic anhydride derived units and α -olefin derived units.
- 10 2. A fuel oil composition according to claim 1 wherein the fuel oil comprises at least one distillate fuel component and at least one residual fuel component.
- 15 3. A fuel oil composition according to claim 2 wherein the fuel oil comprises from 5 to 95 wt% of residual fuel components and from 5 to 95 wt% of one or more fuel components selected from distillate fuel components and cracked fuel components.
- 20 4. A fuel oil composition according to any preceding claim wherein the maleic anhydride derived units of the copolymer are present as underivatized anhydride moieties and/or as carboxylic acid moieties.
- 25 5. A fuel oil composition according to any preceding claim wherein the α -olefin derived units contain 12 to 36 carbon atoms.
- 30 6. A fuel oil composition according to any preceding claim wherein the maleic anhydride/ α -olefin copolymer is present in an amount of from 50 to 5000 ppm.
- 35 7. A fuel oil composition according to any preceding claim wherein the copolymer additive has a number average molecular weight of 5000 to 20000.
8. A fuel oil composition according to any preceding claim which comprises one or more further additives selected from:
- (i) conductivity improvers;
 - (ii) combustion improvers;
 - (iii) asphaltene dispersants;
 - (iv) fuel antioxidants;
 - (v) cold flow improvers;
 - (vi) wax anti-setting agents;
 - (vii) biofuel instability inhibitors;
 - (viii) blended fuel separation inhibitors;
 - (ix) other detergents/dispersants.

9. A fuel oil composition according to any preceding claim wherein the fuel oil comprising the additive has improved stability compared with an equivalent unadditised fuel oil.
- 5 10. A method of preparing a fuel oil composition, the method comprising admixing an additive with a first component fuel and with a second component fuel wherein the resultant fuel oil composition has a sulfur content of less than 5000 ppm and wherein the additive is a copolymer comprising maleic anhydride derived units and α -olefin derived units.
- 10 11. A method according to claim 10 wherein the additive is mixed with the first component fuel before the first component fuel is mixed with the second component fuel.
12. A method according to claim 10 or claim 11 wherein one or more further component
15 fuels are mixed to provide the fuel oil composition.
13. A method of improving the stability of a blended fuel oil having a sulfur content of less than 5000 ppm, the method comprising mixing into the fuel oil an additive which is a copolymer comprising maleic anhydride derived units and α -olefin derived units.
- 20 14. A method according to claim 13 wherein the additive is mixed into a component fuel used to prepare the fuel oil composition.
- 25 15. The use of a copolymer comprising maleic anhydride derived units and α -olefin derived units as an additive to improve the stability of a blended fuel oil having a sulfur content of less than 5000 ppm.
- 30 16. A method or use according to any of claims 13 to 15 wherein the improvement in stability is measured by improved storage stability and/or improved thermal stability and/or improved oxidation stability.