

COMPOSITIONS, USES AND METHODS FOR IMPROVING THE LOW TEMPERATURE PROPERTIES OF A MIDDLE DISTILLATE FUEL

The present invention relates to additives which affect the low temperature properties of middle distillate fuel compositions. In particular the invention relates to additives which counteract negative interactions between other additive compounds in the fuel at low temperatures.

The low temperature properties of fuels have been extensively studied and it is commonplace and in many countries mandated to incorporate additives into fuels to prevent problems when fuel is stored at low temperatures.

Standardised tests have been devised to measure various low temperature properties of middle distillate fuels, including the temperature at which the fuel hazes (the cloud point - CP), the lowest temperature at which a fuel can flow (the pour point - PP) and the cold filter plugging point - CFPP.

The cloud point of a fuel is the temperature at which a cloud of wax crystals first appears in a liquid when it is cooled under prescribed conditions, for example as measured by the test method as defined in ASTM D 2500.

At temperatures below the cloud point but above the pour point, the wax crystals can reach a size and shape capable of plugging fuel lines, screens, and filters even though the fuel will physically flow. These problems are well recognized in the art and have a number of recognised test methods such as the CFPP value (cold filter plugging point, determined in accordance with DIN EN 116).

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

Fuel additives in the form of cold flow improvers (CFIs also known as middle distillate flow improvers or MDFIs) and wax anti-settling additives (WASAs) have been devised to ameliorate the problems of precipitation in fuels at low temperatures, and these are routinely added to middle distillate fuels.

Some such additives may assist in keeping the so-called "waxes" in solution in the mineral fuel; others may alter their crystal morphology or size, so that filterability and pourability are maintained in spite of precipitation. Other additives may be used to prevent precipitated waxes from settling during storage.

These additives have been generally found to be very successful, to the extent that such fuels, suitably additised, can be used even in severe low temperature conditions. In many fuels the CFPP value may be lowered by 10-20°C, compared with corresponding fuels without additives.

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It is thus common practice to include additives which improve the low temperature properties such as WASAs and/or MDFIs to middle distillate fuels. Additive packages comprising a combination of WASA and MDFI are also commonly used and known as WAFIs.

- 10 The Short Sediment Test (SST) measures the propensity of the wax content of a fuel oil to settle and can be used to determine the effectiveness of wax anti-settling additives or additive combinations. In the test the Cloud Point (CP) of a base fuel is measured. The additive(s) under study are added to the base fuel and the sample is stored at a particular temperature, typically 7° C below the measured CP, for 16 hours. The amount of wax that is judged by eye
- 15 to have settled may be noted. The bottom 20% of the fuel is then taken and the CP of this sample is measured and compared to either that of the base fuel, or that of the top 80%, depending on the particular test conditions. The difference between the CP of base fuel or the top 80% and the CP of the bottom 20% of the additized fuel (Δ CP) is a measure of the degree of wax settling. A low value of Δ CP, preferably around zero, indicates good wax dispersion.
- 20 Low levels of sediment may be used as an additional measure of good wax dispersion.

- It is also routine practice to include nitrogen-containing detergent/dispersant compounds in middle distillate fuels. These are necessary to ensure engine cleanliness and improve engine performance. Typical classes of nitrogen-containing detergents will be known to the person
- 25 skilled in the art and include, for example, succinimides, Mannich reaction products and quaternary ammonium salts.

- However in certain middle distillate fuels an antagonistic interaction can occur between nitrogen-containing detergents and wax antisetling additives and/or middle distillate flow
- 30 improvers which affects the low temperature properties of the fuel.

- The antagonism results in poorer dispersion of waxes on storage leading to unexpected poor performance when fuels are stored at low temperatures. This effect may be seen in the Short Sediment Test (SST).

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Antagonism between detergents and WASA/MDFIs is a phenomenon that is widely known in the art. However it does not occur in all fuels and it is difficult to predict whether or not it is likely to occur in a particular fuel.

A number of solutions to this problem have been proposed and various additives which can be used to ameliorate the negative interaction have been described, for example, see EP1932899, US8021444, US8153567, US8628590, US8628591, US8734542, US20100154294, US20100180492 and US20100236139.

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However due to the significant variability of fuels, the solutions that have been proposed do not always solve the problem and thus there is a continuing need for alternative solutions to this problem.

10 According to a first aspect of the present invention there is provided a method of improving the low temperature properties of a middle distillate fuel composition comprising:

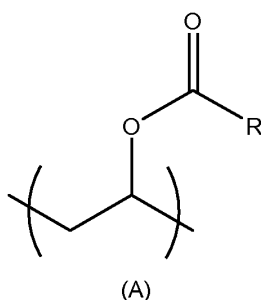
- (a) a nitrogen-containing dispersant; and
- (b) one or more low temperature property enhancers which are not fumarate vinyl ester copolymers and which are selected from: (x) wax antissettling additives; (y) middle

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distillate flow improvers; and mixtures thereof;

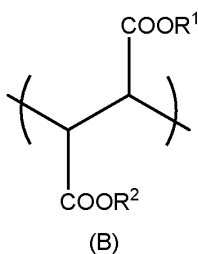
the method comprising adding to the fuel an additive (c) which is a copolymer comprising units of formula (A):

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and units of formula (B):

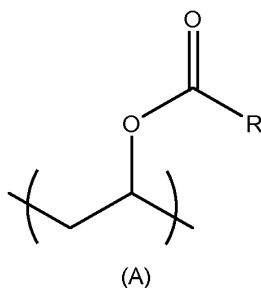
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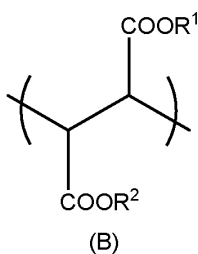
wherein R is an alkyl group and each of R^1 and R^2 is an alkyl group.

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According to a second aspect of the present invention there is provided the use of (c) a copolymer comprising units of formula (A):



and units of formula (B):



wherein R is an alkyl group and each of R¹ and R² is an alkyl group;

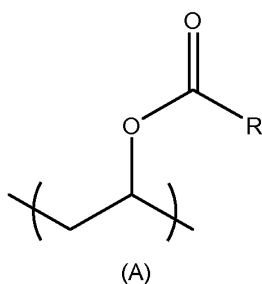
to improve the low temperature properties of a middle distillate fuel composition comprising:

- (a) a nitrogen-containing dispersant; and
- (b) one or more low temperature property enhancers which are not fumarate vinyl ester copolymers and which are selected from: (x) wax antisetling additives; (y) middle distillate flow improvers; and mixtures thereof.

According to a third aspect of the present invention there is provided an additive composition for improving the low temperature properties of a middle distillate fuel composition the additive composition comprising:

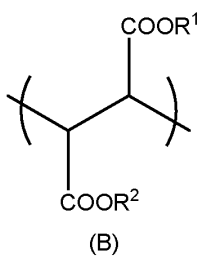
- (b) one or more low temperature property enhancers which are not fumarate vinyl ester copolymers and which are selected from: (x) wax antisetling additives; (y) middle distillate flow improvers; and mixtures thereof; and
- (c) a copolymer comprising units of formula (A):

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and units of formula (B):

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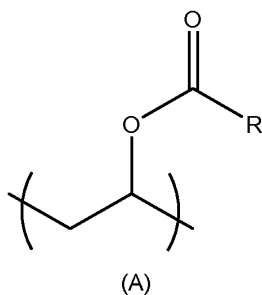
wherein R is an alkyl group and each of R¹ and R² is an alkyl group.

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According to a fourth aspect of the present invention there is provided a middle distillate fuel composition comprising:

- (a) a nitrogen-containing dispersant;
- (b) one or more low temperature property enhancers which are not fumarate vinyl ester copolymers and which are selected from: (x) wax antissettling additives; (y) middle distillate flow improvers; and mixtures thereof; and
- (c) a copolymer comprising units of formula (A):

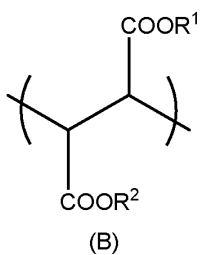
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and units of formula (B):

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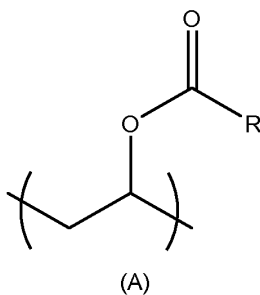


wherein R is an alkyl group and each of R¹ and R² is an alkyl group.

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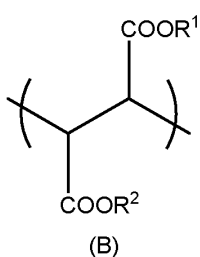
Preferred features of the first, second, third and fourth aspects of the invention will now be described.

The present invention relates to improving the low temperature properties of a middle distillate fuel composition by the addition of an additive (c) which is a copolymer comprising units of formula (A):



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and units of formula (B):



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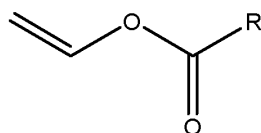
wherein each of R¹ and R² is an alkyl group.

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

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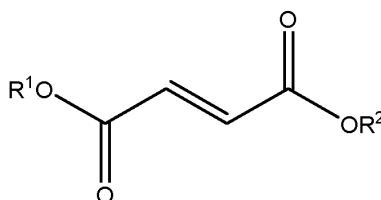
Preferably additive (c) is prepared by copolymerising vinyl ester monomers and dialkyl fumarate monomers.

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



(C)

10 and dialkyl fumarate monomers of formula (D):



(D)

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

R is alkyl group, preferably an unsubstituted alkyl group.

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

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

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

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

30 Preferably all of the monomers of formula (D) used to prepare additive (c) are the same.

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

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

- 5 Preferably each of R^1 and R^2 is an alkyl group having less than 18 carbon atoms.

Preferably each of R^1 and R^2 is an alkyl group having 6 to 17 carbon atoms, preferably 6 to 16 carbon atoms, more preferably 8 to 16 carbon atoms, preferably 10 to 16 carbon atoms, more preferably 12 to 16 carbon atoms, suitably 12 to 14 carbon atoms and most preferably 14 carbon atoms. Most preferably R^1 is $C_{14}H_{29}$ and R^2 is $C_{14}H_{29}$.

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

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

25 Suitably additive (c) comprises from 10 to 90 mol% of units of formula (A) and from 90 to 10 mol% of units of formula (B); preferably from 25 to 75 mol% of units of formula (A) and from 25 to 75 mol% of units of formula (B); more preferably from 40 to 60 mol% of units of formula (A) and from 60 to 40 mol% of units of formula (B).

30 Preferably additive (c) is a random copolymer.

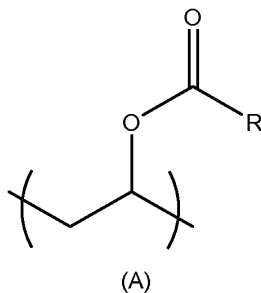
Suitably the copolymer additive (c) has a number average molecular weight of from 1000 to 100000, preferably from 2000 to 50000, more preferably from 5000 to 30000, for example from 8000 to 25000.

In some preferred embodiments copolymer additive (c) has a number average molecular weight of from 20000 to 25000.

In some especially preferred embodiments copolymer additive (c) has a number average molecular weight of from 8000 to 12000.

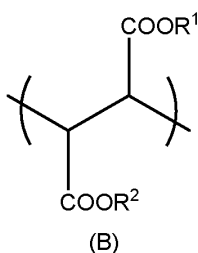
In especially preferred embodiments additive (c) is copolymer comprising units of formula (A):

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and units of formula (B):

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wherein R is an alkyl group each of R¹ and R² is an alkyl group having less than 18 carbon atoms, and preferably 12 to 16 carbon atoms and which copolymer has a number average molecular weight of from 8000 to 25000. Most preferably the copolymer comprises from 40 to 60 mol % of units of formula (A) and from 60 to 40 mol % of units of formula (B).

The additive (c) is used to improve the low temperature properties of a middle distillate fuel composition comprising:

- (a) a nitrogen-containing dispersant; and
- (b) one or more low temperature property enhancers which are not fumarate vinyl ester copolymers and which are selected from (x) wax antisetling additives; (y) middle distillate flow improvers and mixtures thereof.

Any suitable nitrogen-containing detergent may be used as component (a).

Suitable nitrogen-containing detergents for use herein include:

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- (i) a quaternary ammonium salt additive;
 - (ii) the product of a Mannich reaction between an aldehyde, an amine and an optionally substituted phenol;
 - (iii) the reaction product of a carboxylic acid-derived acylating agent and an amine;
 - (iv) the reaction product of a carboxylic acid-derived acylating agent and hydrazine;
 - 10 (v) a salt formed by the reaction of a carboxylic acid with di-n-butylamine or tri-n-butylamine;
 - (vi) the reaction product of a hydrocarbyl-substituted dicarboxylic acid or anhydride and an amine compound or salt which product comprises at least one amino triazole group; and
 - 15 (vii) a polyalkylene substituted amine.

Preferably component (a) comprises one or more of:

- 20
- (i) a quaternary ammonium salt additive;
 - (ii) the product of a Mannich reaction between an aldehyde, an amine and an optionally substituted phenol; and
 - 25 (iii) the reaction product of a carboxylic acid-derived acylating agent and an amine.

In some embodiments component (a) comprises (i) a quaternary ammonium salt additive.

- 30 The quaternary ammonium salt additive is suitably the reaction product of a nitrogen-containing species having at least one tertiary amine group and a quaternising agent.

The nitrogen containing species may be selected from:

- 35
- (p) the reaction product of a hydrocarbyl-substituted acylating agent and a compound comprising at least one tertiary amine group and a primary amine, secondary amine or alcohol group;
 - (q) a Mannich reaction product comprising a tertiary amine group; and
 - (r) a polyalkylene substituted amine having at least one tertiary amine group.
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Examples of quaternary ammonium salt and methods for preparing the same are described in the following patents, which are hereby incorporated by reference, US2008/0307698, US2008/0052985, US2008/0113890 and US2013/031827.

- 5 The preparation of some suitable quaternary ammonium salt additives in which the nitrogen-containing species includes component (p) is described in WO 2006/135881 and WO2011/095819.

- 10 Component (q) is a Mannich reaction product having a tertiary amine. The preparation of quaternary ammonium salts formed from nitrogen-containing species including component (y) is described in US 2008/0052985.

- 15 The preparation of quaternary ammonium salt additives in which the nitrogen-containing species includes component (r) is described for example in US 2008/0113890.

- 20 In preferred embodiments the nitrogen-containing species used to prepare the quaternary ammonium salt additive (i) is of type (p), the reaction product of a hydrocarbyl-substituted acylating agent and a compound having an oxygen or nitrogen atom capable of condensing with said acylating agent and further having a tertiary amino group.

- 25 The hydrocarbyl substituted acylating agent is preferably a mono-or polycarboxylic acid (or reactive equivalent thereof) for example a substituted succinic, phthalic or propionic acid.

- 30 Most preferably the acylating agent is a hydrocarbyl substituted succinic acid or anhydride.

- 35 The hydrocarbyl substituent in such acylating agents preferably comprises at least 8, more preferably at least 12, for example 30 or 50 carbon atoms. It may comprise up to about 200 carbon atoms. Preferably the hydrocarbyl substituent of the acylating agent has 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, for example from 700 to 1000.

- 40 In some preferred embodiments, the hydrocarbyl-based substituents are poly-(isobutene)s known in the art. Thus in especially preferred embodiments the hydrocarbyl substituted acylating agent is a polyisobutenyl substituted succinic anhydride.

The preparation of polyisobutenyl substituted succinic anhydrides (PIBSA) is documented in the art.

Examples of the nitrogen or oxygen containing compounds capable of condensing with the acylating agent and further having a tertiary amino group can include but are not limited to: N,N-dimethylaminopropylamine, N,N-diethylaminopropylamine, N,N-dimethylaminoethylamine, 1-(3-aminopropyl)imidazole, 4-(3-aminopropyl)morpholine, 1-(2-aminoethyl)piperidine, 3,3-diamino-N-methyldipropylamine, and 3'3'-aminobis(N,N-dimethylpropylamine), triethanolamine, trimethanolamine, N,N-dimethylaminopropanol, N,N-dimethylaminoethanol, N,N-diethylaminopropanol, N,N-diethylaminoethanol, N,N-diethylaminobutanol, N,N,N-tris(hydroxyethyl)amine, N,N,N-tris(hydroxymethyl)amine, N,N,N-tris(aminoethyl)amine, N,N-dibutylaminopropylamine and N,N,N'-trimethyl-N'-hydroxyethyl-bisaminoethylether; N,N-bis(3-dimethylaminopropyl)-N-isopropanolamine; N-(3-dimethylaminopropyl)-N,N-diisopropanolamine; N'-(3-(dimethylamino)propyl)-N,N-dimethyl 1,3-propanediamine; 2-(2-dimethylaminoethoxy)ethanol, and N,N,N'-trimethylaminoethylethanolamine.

Most preferably the alcohol or amine compound that reacts with the acylating agent and has a tertiary amino group is dimethylaminopropylamine or dimethylaminopropanol.

The quaternary ammonium salt additive (i) is formed by reacting a nitrogen-containing species having a tertiary amine group with a quaternising agent.

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The quaternising agent may suitably be selected from esters and non-esters.

The quaternizing agent is suitably selected from the group consisting of dialkyl sulphates; an ester of a carboxylic acid; alkyl halides; benzyl halides; hydrocarbyl substituted carbonates; and hydrocarbyl epoxides in combination with an acid or mixtures thereof.

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Examples of hydrocarbyl epoxides can include styrene oxide, ethylene oxide, propylene oxide, butylene oxide, stilbene oxide and C2-50 epoxide.

Suitable ester quaternising agents include esters of a carboxylic acid selected from one or more of oxalic acid, phthalic acid, salicylic acid, maleic acid, malonic acid, citric acid, nitrobenzoic acid, aminobenzoic acid and 2, 4, 6-trihydroxybenzoic acid.

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Preferred quaternising agents for use herein include dimethyl oxalate, methyl 2-nitrobenzoate, methyl salicylate and styrene oxide or propylene oxide optionally in combination with an additional acid.

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An especially preferred quaternary ammonium salt for use herein is formed by reacting methyl salicylate or dimethyl oxalate with the reaction product of a polyisobutylene-substituted

succinic anhydride having a PIB number average molecular weight of 700 to 1300 and dimethylaminopropylamine.

5 Other suitable quaternary ammonium salts include quaternised terpolymers, for example as described in US2011/0258917; quaternised copolymers, for example as described in US2011/0315107; and the acid-free quaternised nitrogen compounds disclosed in US2012/0010112.

10 Further suitable quaternary ammonium compounds for use in the present invention include the quaternary ammonium compounds described in the applicants copending applications WO2011095819, WO2013/017889, WO2015/011506, WO2015/011507, WO2016/016641 and PCT/GB2016/052312.

15 In some embodiments component (a) comprises (ii) the product of a Mannich reaction between an aldehyde, an amine and an optionally substituted phenol. This Mannich reaction product is suitably not a quaternary ammonium salt.

20 Preferably the aldehyde component used to prepare the Mannich additive is an aliphatic aldehyde. Preferably the aldehyde has 1 to 10 carbon atoms. Most preferably the aldehyde is formaldehyde.

Suitable amines for use in preparing the Mannich additive include monoamines and polyamines. One suitable monoamine is butylamine.

25 The amine used to prepare the Mannich additive is preferably a polyamine. This may be selected from any compound including two or more amine groups. Preferably the polyamine is a polyalkylene polyamine, preferably a polyethylene polyamine, especially a polyethylene polyamine having 1 to 10 ethylene groups and 2 to 11 amine groups.

30 Commercially available sources of polyamines typically contain mixtures of isomers and/or oligomers, and products prepared from these commercially available mixtures fall within the scope of the present invention.

35 Suitably the polyamine may be selected from ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenhexamine, hexaethyleneheptamine, heptaethyleneoctamine, propane-1,2-diamine, 2(2-aminoethylamino)ethanol, and N',N'-bis (2-aminoethyl) ethylenediamine (N(CH₂CH₂NH₂)₃).

40 Most preferably the polyamine comprises tetraethylenepentamine or ethylenediamine.

The optionally substituted phenol component used to prepare the Mannich additive may be substituted with 0 to 4 groups on the aromatic ring (in addition to the phenol OH). For example it may be a hydrocarbyl-substituted cresol. Most preferably the phenol component is a mono-substituted phenol. Preferably it is a hydrocarbyl substituted phenol. Preferred hydrocarbyl substituents are alkyl substituents having 4 to 28 carbon atoms, especially 10 to 14, for example 12 carbon atoms. Other preferred hydrocarbyl substituents are polyalkenyl substituents. Such polyisobutenyl substituents having a number average molecular weight of from 400 to 2500, for example from 500 to 1500.

Suitable Mannich reaction products useful herein as additives are described in the applicant's patents and applications the reaction product of a hydrocarbyl-substituted acylating agent and a compound comprising at least one tertiary amine group and a primary amine, secondary amine or alcohol group; WO2009/040582, WO2009/040583, WO2009/040584, WO2009/040585, WO2010/097624, WO2013/017884, WO2013/017886 and WO2013/017887.

Preferred Mannich reaction product additives for use herein are the reaction product of a hydrocarbyl substituted phenol, formaldehyde and a polyamine, preferably a polyethylene polyamine.

Preferably the Mannich reaction product additive is formed by the reaction of a phenol substituted with an alkyl group having 6 to 30 carbon atoms or a polyisobutenyl group having a number average molecular weight of 500 to 2000 with formaldehyde and a polyamine, preferably a polyethylene polyamine.

Especially preferred Mannich reaction products for use herein as a nitrogen-containing detergent (a) are the reaction product of dodecylphenol, formaldehyde and either ethylene diamine or tetraethylpentamine.

In some embodiments component (a) comprises (iii) the reaction product of a carboxylic acid-derived acylating agent and an amine.

These may also be referred to herein in general as acylated nitrogen-containing compounds.

Suitable acylated nitrogen-containing compounds may be made by reacting a carboxylic acid acylating agent with an amine and are known to those skilled in the art.

Preferred hydrocarbyl substituted acylating agents are polyisobutenyl succinic anhydrides. 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 are preferred

- 5 Especially preferred PIBSAs are those having a PIB molecular weight (Mn) of from 300 to 2800, preferably from 450 to 2300, more preferably from 500 to 1300.

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.

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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
15 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
20 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.

- 25 In some preferred embodiments the composition comprises a detergent of the type formed by the reaction of a polyisobutene-substituted succinic acid-derived acylating agent and a polyethylene polyamine. Suitable compounds are, for example, described in WO2009/040583.

- 30 Especially preferred additives of this type are the reaction product of a polyisobutenyl substituted succinic acid/anhydride having a PIB molecular weight (Mn) of 500 to 1300 and a polyethylene polyamine having 1 to 9 amino groups and 1 to 8 ethylene groups.

- In some embodiments component (a) comprises (iv) the reaction product of a carboxylic acid-derived acylating agent and hydrazine.
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Suitably the additive comprises the reaction product between a hydrocarbyl-substituted succinic acid or anhydride and hydrazine.

Preferably, the hydrocarbyl group of the hydrocarbyl-substituted succinic acid or anhydride comprises a C₈-C₃₆ group, preferably a C₈-C₁₈ group. Alternatively, the hydrocarbyl group may be a polyisobutylene group with a number average molecular weight of between 200 and 2500, preferably between 800 and 1200.

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Hydrazine has the formula NH₂-NH₂. Hydrazine may be hydrated or non-hydrated. Hydrazine monohydrate is preferred.

The reaction between the hydrocarbyl-substituted succinic acid or anhydride and hydrazine produces a variety of products, such as is disclosed in US 2008/0060259.

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In some embodiments component (a) comprises (v) a salt formed by the reaction of a carboxylic acid with di-n-butylamine or tri-n-butylamine. Exemplary compounds of this type are described in US 2008/0060608.

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Such additives may suitably be the di-n-butylamine or tri-n-butylamine salt of a fatty acid of the formula [R'(COOH)_x]_y, where each R' is a independently a hydrocarbon group of between 2 and 45 carbon atoms, and x is an integer between 1 and 4.

In a preferred embodiment, the carboxylic acid comprises tall oil fatty acid (TOFA).

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Further preferred features of additives of this type are described in EP1900795.

In some embodiments component (a) comprises (vi) the reaction product of a hydrocarbyl-substituted dicarboxylic acid or anhydride and an amine compound or salt which product comprises at least one amino triazole group.

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Further preferred features of additive compounds of this type are as defined in US2009/0282731.

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In some embodiments component (a) comprises (vii) a polyalkylene substituted amine.

The polyalkene-substituted amines may be derived from an olefin polymer and an amine, for example ammonia, monoamines, polyamines or mixtures thereof. They may be prepared by a variety of methods such as those described and referred to in US 2008/0113890.

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Suitably the polyalkene substituent of the polyalkene-substituted amine is derived from a polyisobutylene.

The number average molecular weight of the polyalkene-substituted amines can range from 500 to 5000, or from 500 to 3000, for example from 1000 to 1500.

Preferably component (a) comprises one or more of:

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- a quaternary ammonium salt additive formed by the reaction of a quaternising agent and the reaction product of a hydrocarbyl-substituted acylating agent and a compound comprising at least one tertiary amine group and a primary amine, secondary amine or alcohol group;

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- the product of a Mannich reaction between a hydrocarbyl substituted phenol, formaldehyde and a polyamine; and
- the reaction product of a hydrocarbyl substituted succinic acid derived acylating agent and an amine.

15

More preferably component (a) is selected from one or more of:

- a quaternary ammonium salt additive formed by the reaction of quaternising agent and the reaction product of a polyisobutenyl substituted succinic anhydride and an amine or alcohol which further includes a tertiary amino group, preferably wherein the

20

- quaternising agent is selected from the group consisting of dialkyl sulphates; an ester of a carboxylic acid; alkyl halides; benzyl halides; hydrocarbyl substituted carbonates; and hydrocarbyl epoxides in combination with an acid or mixtures thereof;
- the product of a Mannich reaction between a phenol substituted with an alkyl group having 6 to 30 carbon atoms or a polyisobutenyl group having a number average

25

- molecular weight of 500 to 2000; with formaldehyde; and a polyamine selected from ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, hexaethyleneheptamine, heptaethyleneoctamine, propane-1,2-diamine, 2(2-amino-ethylamino)ethanol, and N',N'-bis (2-aminoethyl) ethylenediamine ($N(CH_2CH_2NH_2)_3$); and

30

- the reaction product of a polyisobutenyl substituted succinic acid derived acylating agent and a polyamine.

Most preferably component (a) is selected from one or more of:

35

- a quaternary ammonium salt additive formed by reacting methyl salicylate or dimethyl oxalate with the reaction product of a polyisobutylene-substituted succinic anhydride having a PIB number average molecular weight of 700 to 1300 and dimethylaminopropylamine;

40

- the Mannich reaction product of dodecylphenol, formaldehyde and either ethylene diamine or tetraethylpentamine; and

- the reaction product of a polyisobutenyl substituted succinic acid/anhydride having a PIB molecular weight (Mn) of 500 to 1300 and a polyethylene polyamine having 1 to 9 amino groups and 1 to 8 ethylene groups.

5 Component (b) comprises one or more low temperature property enhancers which are not fumarate vinyl ester copolymers and which are selected from (x) wax antisetling additives; (y) middle distillate flow improvers and mixtures thereof.

Preferably component (b) comprises at least one wax antisetling additive (x).

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Preferably component (b) comprises at least one middle distillate flow improver (y).

More preferably component (b) comprises at least one wax antisetling additive (x) and at least one middle distillate flow improver (y).

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Preferred wax anti-settling additives (x) are the reaction product of (I) a compound containing the segment $-NR^3R^4$ where R^3 represents a group containing from 4 to 44 carbon atoms and R^4 represents a hydrogen atom or a group R^3 , and (II) a carboxylic acid having from 1 to 4 carboxylic acid groups or a reactive equivalent thereof.

20

Preferably R^3 is a hydrocarbyl group or a polyethoxylate or polypropoxylate group.

Preferably the group R^3 is a hydrocarbyl group. Preferably R^3 is a hydrocarbon group, preferably a straight chain hydrocarbon group.

25

Preferably the group R^3 comprises from 6 to 36 carbon atoms, preferably 8 to 32, preferably 10 to 24, preferably 12 to 22, most preferably 14 to 20.

30

It will be appreciated by the skilled person that commercial sources of alkylamines and dialkylamines may contain mixtures of homologues. Additives derived from such compounds are within the scope of the present invention.

R^4 may be a group according to the definition of R^3 or hydrogen.

35

R^4 preferably conforms to the same definitions as are given for R^3 . R^3 and R^4 need not be the same. Preferably, however, R^3 and R^4 are the same.

Species (II) is a carboxylic acid or a reactive equivalent thereof.

Reactive equivalents of a carboxylic acid include acid anhydrides, spirobislactones and acid halides.

5 Acid halides are not preferred. However if an acid halide is used it is preferably an acid chloride.

Suitable compounds (I) include primary, secondary, tertiary and quaternary amines. Tertiary and quaternary amines only form amine salts.

10 Secondary amines, of formula HNR^3R^4 , are an especially preferred class of compounds (I). Examples of especially preferred secondary amines include di-octadecylamine, di-cocoamine, di-hydrogenated tallow amine and methylbehanyl amine. Amine mixtures are also suitable such as those derived from natural materials. A preferred amine is a secondary hydrogenated tallow amine, the alkyl groups of which are derived from hydrogenated tallow fat composed of
15 approximately 3-5%wt C_{14} , 30-32%wt C_{16} , and 58-60%wt C_{18} .

Quaternary amines, of formula $[\text{NR}^3\text{R}^4\text{R}^5\text{R}^6-\text{An}]$, are a further preferred class of compounds (I). R^3 and R^4 are as defined above (but R^4 is not hydrogen). R^5 and R^6 independently represent a C(1-4) alkyl group, preferably propyl, ethyl or, most preferably, methyl.
20 $+\text{NR}^3\text{R}^4(\text{CH}_3)_2$ represents a preferred cation. $-\text{An}$ represents the anion. The anion may be any suitable species but is preferably a halide, especially a chloride. Where (I) comprises a quaternary amine, the reaction conditions may be adjusted to assist the reaction between (I) and (II). Preferably the reaction conditions are adjusted by the introduction of an auxiliary base. The auxiliary base is preferably a metal alkoxide or metal hydroxide. Alternatively, the
25 quaternary amine salt may be preformed as the corresponding basic salt, for example, a quaternary ammonium hydroxide or alkoxide.

Mixtures of primary and secondary amines or mixtures of secondary and quaternary amines, may be provided as species (I).
30

Preferred carboxylic acids (II) include carboxylic acids containing two, three or four carboxylic acid groups, and reactive equivalents thereof.

Examples of suitable carboxylic acids and their anhydrides include
35 aminoalkylenepolycarboxylic acids, for example nitrilotriacetic acid, propylene diamine tetraacetic acid, ethylenediamine tetraacetic acid, and carboxylic acids based on cyclic skeletons, e.g., pyromellitic acid, cyclohexane-1,2-dicarboxylic acid, cyclohexene-1,2-dicarboxylic acid, cyclopentane-1,2-dicarboxylic acid and naphthalene dicarboxylic acid, 1,4-dicarboxylic acids, and dialkyl spirobislactones. Generally, these acids have about 5 to 13
40 carbon atoms in the cyclic moiety. Preferred acids useful in the present invention are

optionally substituted benzene dicarboxylic acids, e.g. phthalic acid, isophthalic acid, and terephthalic acid, and their acid anhydrides or acid chlorides. Optional substituents include 1-5 substituents, preferably 1-3 substituents, independently selected from C(1-4)alkyl, C(1-4)alkoxy, halogen, C(1-4)haloalkyl, C(1-4)haloalkoxy, nitrile, -COOH, -CO-OC(1-4)alkyl, and -CONR³R⁴ where R³ and R⁴ are independently selected from hydrogen and C(1-4)alkyl. Preferred halogen atoms are fluorine, chlorine and bromine. However unsubstituted benzene carboxylic acids are preferred. Phthalic acid and its acid anhydride are particularly preferred.

Other suitable compounds of formula (II) are alkyl spirobislactones.

Preferably the molar ratio of compound (I) to acid, or reactive equivalent thereof (II) is such that at least 50% of the acid groups (preferably at least 75%, preferably at least 90%, and most preferably 100%) are reacted in the reaction between the compounds (I) and (II), for example to form the amide and/or the amine salt.

Where compound (II) comprises one or more free carboxylic acid groups, reaction conditions may be adjusted to allow reaction between compounds (I) and (II), for example to form the respective amide or amine salt. The reaction conditions may be adjusted as appropriate using methods known to the skilled person.

In the case of a preferred reaction, between a compound (I) and a dicarboxylic acid, or reactive equivalent thereof (e.g. acid anhydride) or preferably the molar ratio of compound (I) (or mixtures of compounds (I), in that situation) to acid, or reactive equivalent thereof (or mixed compounds (II), in that situation) is at least 0.7:1, preferably at least 1:1, preferably at least 1.5:1. Preferably it is up to 3:1, preferably up to 2.5:1. Most preferably it is in the range 1.8:1 to 2.2:1. A molar ratio of 2:1, (I) to (II) is especially preferred. In another preferred embodiment a molar ratio of 1:1 is used.

In the case of a preferred reaction, between a secondary amine as compound (I) and a dicarboxylic acid, or acid anhydride preferably the molar ratio of amine (I) to acid or acid anhydride (II) is at least 1:1, preferably at least 1.5:1. Most preferably it is in the range 1.8:1 to 2.2:1. A molar ratio of 2:1, (I) to (II) is especially preferred.

Preferably the reaction between the compound (I) and the carboxylic acid, acid anhydride or acid halide (II) forms one or more amide, imide or ammonium salts, combinations of these within the same compound, and mixtures of these compounds.

Thus, in one preferred embodiment a dicarboxylic acid, acid anhydride or acid halide (II) is reacted with a secondary amine (I), preferably in a molar ratio of 1:2 such that one mole of the amines form an amide and one mole forms an ammonium salt.

An especially preferred additive is a dialkylammonium salt of a monoamide of a dialkylamine and phthalic acid, which suitably is the reaction product of di(hydrogenated) tallow amine (I) and phthalic acid or its acid anhydride (II); preferably at a molar ratio of 2:1.

5

An especially preferred wax anti-settling additive is the reaction product of di(hydrogenated) tallow amine (I) and phthalic acid or its acid anhydride (II); preferably at a molar ratio of 1:1.

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Other preferred wax anti-settling additives are the reaction products of (hydrogenated) tallow amine (I) with EDTA (II); preferably in a molar ratio of 4:1 with removal of four moles of water or two moles of water to form respectively the tetraamide derivative or the diamide diammonium salt derivative.

15

Another preferred additive is the reaction product of an alkylspirobislactone (II), for example dodecenyl-spirobis lactone, with mono-tallow amine and/or di-tallow amine (I); preferably the reaction product of one mole of alkylspirobis lactone, for example dodecenyl-spirobis lactone with one mole of mono-tallow amine and one mole of di-tallow amine.

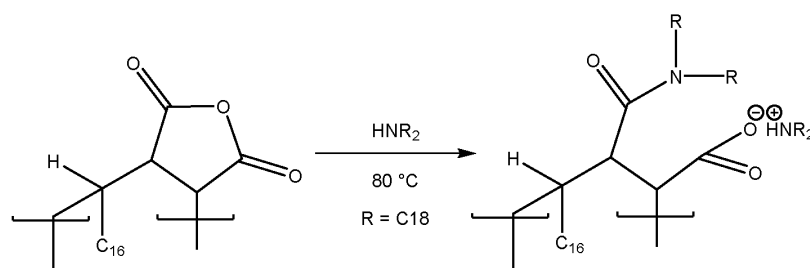
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Another preferred additive is the reaction product of the reaction product of benzene-1,2,4,5-tetracarboxylic acid or its dianhydride (II) with di(hydrogenated tallow) amine (I); preferably in a molar ratio of 1:4. This reaction product may be termed pyromellitic tetraamide but in fact may typically be a mixture of the tetraamide, triamide/mono salt and diamide/disalt.

25

Another suitable wax antisetling additive is the half amide half ammonium salt of a maleic anhydride α olefin copolymer where the α olefin has 10 to 36 carbon atoms, preferably 12 to 24 carbon atoms, for example 16 to 20 carbon atoms. The amine reacted with the maleic anhydride α olefin copolymer is suitably a dialkylamine in which the alkyl group has 6 to 30, preferably 12 to 24, for example 18 carbon atoms. Such an additive may be formed, for example according to the following reaction scheme:

30



One further class of wax antisetling additives that may be useful herein are alkylphenol aldehyde resins modified by a Mannich reaction with an alkylamine. These compounds are suitably formed by forming an alkylphenol condensate with an aldehyde and then reacting the

condensate in a Mannich reaction with an alkylamine and an aldehyde or ketone (preferably and aldehyde). The alkyl phenol suitably is monosubstituted with one alkyl group having 1 to 30 carbon atoms; the aldehyde used to prepare the resin preferably has 1 to 4 carbon atoms. Preferably the alkylamine preferably includes one primary amine group and has 12 to 24
5 carbon atoms. An aldehyde having 1 to 4 carbon atoms, preferably formaldehyde is used in the Mannich reaction. Such compounds are described in more detail in US9169452.

Preferred middle distillate flow improvers (y) are copolymers of ethylene and an olefinically unsaturated compound.

10

Preferred copolymers of ethylene and olefinically unsaturated compounds for use in the present invention are those which, in addition to ethylene, contain 1 to 23 mol %, preferably 6 to 21 mol %, more preferably 7 to 18 mol%, suitably 9 to 16 mol %, especially 10 to 15 mol %, of olefinically unsaturated compounds as co-monomers.

15

The olefinically unsaturated compounds are preferably vinyl esters, acrylic esters, methacrylic esters, alkyl vinyl ethers and/or alkenes, and the compounds mentioned may be substituted by hydroxyl groups. One or more co-monomers may be present in the polymer.

20 The vinyl esters are preferably those of the formula (1).



where R^7 is C1 to C30 alkyl group. In some embodiments R^7 may be a C4 to C16 alkyl group,
25 for example a C6 to C12 alkyl groups. In some embodiments, the alkyl groups may be substituted by one or more hydroxyl groups. In preferred embodiments R^7 is a C1 to C10 alkyl group, more preferably a C1 to C4 alkyl group, most preferably a C1 to C2 alkyl group.

Suitable vinyl esters include vinyl acetate, vinyl propionate, vinyl butyrate, vinyl isobutyrate,
30 vinyl hexanoate, vinyl heptanoate, vinyl octanoate, vinyl pivalate, vinyl 2-ethylhexanoate, vinyl laurate, vinyl stearate and Versatic esters such as vinyl neononanoate, vinyl neodecanoate, vinyl neoundecanoate. An especially preferred vinyl ester is vinyl acetate.

In some embodiments these ethylene copolymers may contain vinyl acetate and at least one
35 further vinyl ester of formula (1) where R^7 is C4 to C30 alkyl, preferably C4 to C16 alkyl, especially C6 to C12 alkyl.

In preferred embodiments, the compound of formula (1) is vinyl acetate and the middle distillate flow improver (y) comprises a copolymer of ethylene and vinyl acetate. Preferably

the copolymer comprises 76 to 63 wt% ethylene and 24 to 37 wt % vinyl acetate, more preferably from 74 to 65 wt% ethylene and 26 to 35 wt % vinyl acetate.

The acrylic esters are preferably those of the formula (2).

5



where R^8 is hydrogen or methyl and R^9 is C1- to C30-alkyl, preferably C4- to C16-alkyl, especially C6- to C12-alkyl. Suitable acrylic esters include, for example, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, n- and isobutyl (meth)acrylate, hexyl, octyl, 2-ethylhexyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl (meth)acrylate and mixtures of these comonomers. In a further embodiment, the alkyl groups mentioned may be substituted by one or more hydroxyl groups. An example of such an acrylic ester is hydroxyethyl methacrylate.

15

The alkyl vinyl ethers are preferably compounds of the formula (3).



where R^{10} is C1- to C30-alkyl, preferably C4- to C16-alkyl, especially C6- to C12-alkyl. Examples include methyl vinyl ether, ethyl vinyl ether, isobutyl vinyl ether. In a further embodiment, the alkyl groups mentioned may be substituted by one or more hydroxyl groups.

The alkenes are preferably monounsaturated hydrocarbons having 3 to 30 carbon atoms, especially 4 to 16 carbon atoms and especially 5 to 12 carbon atoms. Suitable alkenes include propene, butene, isobutylene, pentene, hexene, 4-methylpentene, octene, diisobutylene and norbornene and derivatives thereof such as methylnorbornene and vinylnorbornene. In a further embodiment, the alkyl groups mentioned may be substituted by one or more hydroxyl groups.

30

In some embodiments, the middle distillate flow improver (y) may comprise a terpolymer comprising ethylene, vinyl acetate and a further monomer, for example a longer chain vinyl ester or a longer chain alkene.

Apart from ethylene, some particularly preferred terpolymers contain 1 to 23 mol %, preferably 3 to 20 mol %, especially 8 to 15 mol %, of vinyl acetate, and 0.1 to 12 mol %, especially 0.2 to 5 mol %, of at least one relatively long-chain and preferably branched vinyl ester, for example vinyl 2-ethylhexanoate, vinyl neononanoate or vinyl neodecanoate, the total comonomer content of the terpolymers being preferably between 8 and 21 mol %, especially between 12 and 18 mol %. Other preferred copolymers contain, in addition to

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ethylene and 8 to 18 mol % of vinyl esters of C2- to C12-carboxylic acids, also 0.5 to 30 mol %, preferably 0.5 to 10 mol %, of olefins such as propene, butene, isobutylene, hexene, 4-methylpentene, octene, diisobutylene and/or norbornene.

5 In some embodiments preference is given to using mixtures of two or more of the abovementioned ethylene copolymers. More preferably, the polymers on which the mixtures are based differ in at least one characteristic. For example, they may contain different comonomers, or have different comonomer contents, molecular weights and/or degrees of branching.

10

Most preferably the middle distillate flow improvers (y) are copolymers of ethylene and vinyl acetate.

15

Preferably the weight ratio of the wax antisetling additive (x) to the middle distillate flow improver (y) present in component (b) is from 10:1 to 1:10, preferably from 5:1 to 1:10, more preferably from 2:1 to 1:10, most preferably from 1:1 to 1:10.

20

The above ratios are calculated based on the active amounts of all wax antisetling additives (x) and all middle distillate flow improvers (y) present in component (b).

The additive composition of the third aspect comprises component (b) and additive (c).

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The weight ratio of additive (c) to component (b) is preferably from 1:100 to 1:1, more preferably from 1:40 to 1:2, suitably from 1:20 to 1:3.

Preferably the additive composition of the third aspect comprises a wax antisetling additive (x), a middle distillate flow improver (y), and a copolymer additive (c).

30

Preferably the additive composition of the third aspect comprises (by weight) from 10 to 40 parts of wax antisetling additive (x); from 50 to 88 parts of middle distillate flow improver (y) and from 2 to 20 parts of copolymer additive (c), based on the total active weight of (x), (y) and (c).

35

The additive composition of the third aspect suitably further comprises a diluent or carrier. Suitable diluents and carriers will be known to the person skilled in the art and include, for example solvents, especially aromatic and aliphatic organic solvents and mixtures thereof.

The additive composition of the third aspect may further contain additional additives to improve handling, for example esters, carboxylic acids and alcohols.

40

The middle distillate fuel composition of the fourth aspect of the present invention comprises component (a), component (b) and additive (c).

5 Suitably component (a) is present in the middle distillate fuel composition in an amount of at least 0.1 ppm, preferably at least 1 ppm, more preferably at least 10 ppm, suitably at least 30 ppm, for example at least 50 ppm.

10 Suitably component (a) is present in the middle distillate fuel composition in an amount of up to 10000 ppm, preferably up to 1000 ppm, more preferably up to 500 ppm, for example up to 250 ppm or up to 200 ppm.

15 Suitably component (b) is present in the middle distillate fuel composition in an amount of at least 1 ppm, preferably at least 10 ppm, more preferably at least 50 ppm, suitably at least 80 ppm.

Suitably component (b) is present in the middle distillate fuel composition in an amount of up to 10000 ppm, preferably up to 5000 ppm, more preferably up to 1000 ppm, for example up to 500 ppm, up to 400 ppm or up to 350 ppm.

20 Suitably the wax antisetling additive (x) is present in the middle distillate fuel composition in an amount of at least 0.1 ppm, preferably at least 1 ppm, more preferably at least 5 ppm, suitably at least 10 ppm.

25 Suitably the wax antisetling additive (x) is present in the middle distillate fuel composition in an amount of up to 10000 ppm, preferably up to 1000 ppm, more preferably up to 500 ppm, for example up to 200 ppm or up to 100 ppm.

30 Suitably the middle distillate flow improver (y) is present in the middle distillate fuel composition in an amount of at least 0.1 ppm, preferably at least 1 ppm, more preferably at least 10 ppm, suitably at least 50 ppm, for example at least 60 ppm.

Suitably the middle distillate flow improver (y) is present in the middle distillate fuel composition in an amount of up to 10000 ppm, preferably up to 1000 ppm, more preferably up to 500 ppm, for example up to 350 ppm or up to 300 ppm.

35 Suitably additive (c) is present in the middle distillate fuel composition in an amount of at least 0.1 ppm, preferably at least 1 ppm, more preferably at least 5 ppm.

Suitably additive (c) is present in the middle distillate fuel composition in an amount of up to 10000 ppm, preferably up to 1000 ppm, more preferably up to 500 ppm, suitably up to 200 ppm, for example up to 100 ppm or up to 60 ppm

- 5 Each of components (a), (b) (x), (y) and (c) may contain a mixture of compounds. For the avoidance of doubt, the above amounts refer to the total amount of additives (a), (b) (x), (y) and (c) respectively present in the composition.

10 Unless otherwise specified all amounts of additive referred to herein relate to the amount of active material present in the composition and all parts per million (ppm) are by weight.

In preferred embodiments the fuel composition of the present invention comprises from 10 to 250 ppm, preferably 30 to 200 ppm component (a); from 40 to 400 ppm, preferably 50 to 350 ppm component (b); and from 1 to 100 ppm, preferably 5 to 60 ppm additive (c).

15 The base fuel used in the present invention may comprise or consist of a petroleum-based middle distillate fuel oil. Such middle 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 from conversion units such as thermally and/or catalytically cracked and hydro-cracked distillates.

20 The fuel composition of the present invention may comprise or consist of 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).

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

30 Such first generation biofuels may be termed fatty acid alkyl esters (FAAEs), preferably fatty acid methyl esters (FAMEs).

35 The fuel composition may comprise second generation biofuel. Second generation biofuel 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 biofuel may be similar in properties and quality to petroleum

based fuel oil streams, for example renewable fuel produced from vegetable oils, animal fats etc. and marketed by ConocoPhillips as Renewable Diesel and by Neste as NExBTL.

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

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

In some embodiments the fuel composition of the present invention may be a blended fuel comprising biofuel, and a second fuel. In such blends the biofuel may be present in an amount of from 0.1% to 99% (vol/vol), preferably from 0.1 to 25%. In such blends the biofuel
15 component may include a mixture of first generation biofuel and second generation biofuel. First generation biofuel preferably FAAEs, especially FAMEs, suitably provides from 0.1 to 25 % (vol/vol), preferably 0.1 to 20 %, more preferably 0.1 to 12 %, for example 0.1 to 10% of the fuel composition. The second fuel may be a petroleum-based fuel oil, especially a middle distillate fuel oil, including a non-renewable Fischer-Tropsch fuel.

20 All such fuels may be used in embodiments of the invention.

In some embodiments the fuel composition of the present invention may comprise a petroleum based middle distillate fuel oil and optionally from 0.1% to 25% (vol/vol) of a biofuel
25 wherein the fuel composition optionally comprises from 0.1% to 12% (vol/vol) of FAAEs.

The fuel composition of the present invention may contain a relatively high sulphur content, for example greater than 0.05% by weight, such as 0.1%, or 0.2%, 0.5% or more.

30 However in preferred embodiments the fuel 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.

35 The fuel composition of the present invention may be utilized as a fuel for locomotion in motor vehicles, ships and boats; as burner fuel in home heating and power generation and as fuel in multi purpose stationary engines.

40 The fuel composition may include one or more further additives such as those which are commonly found in the fuels of use in this invention. These include, for example,

antioxidants, further dispersants and/or detergents, cetane improvers, dehazers, stabilisers, demulsifiers, antifoams, corrosion inhibitors, lubricity improvers, dyes, markers, combustion improvers and odour masks, and further additives useful in achieving improvements in cold temperature performance.

5

In preferred embodiments of the present invention component (a) is selected from one or more of:

- a quaternary ammonium salt additive formed by the reaction of a quaternising agent and the reaction product of a hydrocarbyl-substituted acylating agent and a compound comprising at least one tertiary amine group and a primary amine, secondary amine or alcohol group;
- the product of a Mannich reaction between a hydrocarbyl substituted phenol, formaldehyde and a polyamine; and
- the reaction product of a hydrocarbyl substituted succinic acid derived acylating agent and an amine;

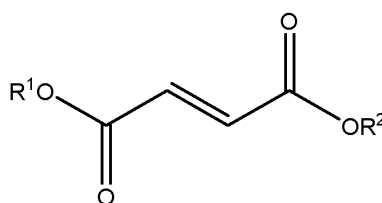
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component (b) comprises:

- a copolymer of ethylene and vinyl acetate; and
- the reaction product of (I) a compound containing the segment $-NR_3R_4$ where R_3 represents a group containing from 4 to 44 carbon atoms and R_4 represents a hydrogen atom or a group R_3 , and (II) a carboxylic acid having from 1 to 4 carboxylic acid groups or an acid anhydride or acid halide thereof; and

20

additive (c) comprises a copolymer of vinyl acetate and monomers of formula (D):



25

(D)

in which each of R^1 and R^2 is an alkyl group having less than 18 carbons.

In the present invention the copolymer additive (c) improves the low temperature properties of the middle distillate fuel composition.

30

Preferably the additive reduces the value of ΔCP as measured by a short sediment test.

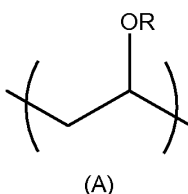
A number of short sediment tests are known. However all of these seek to minimise the difference between the cloud point (CP) of the bottom portion of a fuel and another portion of the additised fuel or base fuel (ΔCP).

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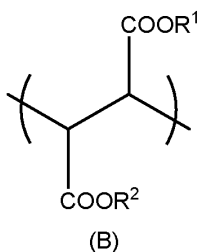
Suitably the copolymer additive (c) provides ΔCP in a short sediment test of less than 5°C, preferably less than 3°C, more preferably less than 2°C. Suitably a ΔCP of less than 3°C, preferably less than 2°C is provided according to the short sediment test protocol described in example 2, procedure A.

Preferably the copolymer additive (c) improves the low temperature properties of the middle distillate fuel composition by influencing the antagonistic interaction between component (a) and component (b).

According to a fifth aspect of the present invention there is provided the use of an additive (c) which is a copolymer comprising units of formula (A):



and units of formula (B):



wherein R is an alkyl group and each of R¹ and R² is an alkyl group; to ameliorate an antagonistic interaction in a middle distillate fuel composition between (a) a nitrogen-containing dispersant; and (b) one or more low temperature property enhancers which are not vinyl ester copolymers and which are selected from (x) wax antissettling additives; (y) middle distillate flow improvers and mixtures thereof.

By ameliorating the antagonistic interaction in a middle distillate fuel composition, we mean to refer to preventing and/or inhibiting the antagonistic effect and/or providing a further effect which counteracts the antagonism. Thus the addition of the copolymer additive (c) may prevent or reduce the negative interactions between component (a) and component (b) from occurring or it may provide a further effect which means that the antagonistic interactions

between component (a) and component (b) do not have such a negative effect on the low temperature properties of the fuel.

5 Suitably the addition of the copolymer additive (c) improves the low temperature properties of the middle distillate fuel composition as measured by the Short Sediment Test (SST). This test is suitably as described in Example 2, procedure A. Suitably the improvement in performance is measured by a reduction in the value of ΔCP . Suitably a ΔCP of less than 3°C, preferably less than 2°C is provided according to the short sediment test protocol described in example 2, procedure A.

10

Thus the present invention may further provide the use of copolymer additive (c) as defined herein to improve the performance in the Short Sediment Test of a middle distillate fuel composition comprising:

15

- (a) a nitrogen-containing dispersant; and
- (b) one or more low temperature property enhancers selected from (x) wax antissettling additives; (y) middle distillate flow improvers and mixtures thereof.

20

Advantageously the copolymer additive (c) is highly effective at ameliorating antagonistic interactions between component (a) and component (b) even at low treat rates. Thus the present invention may provide the use of less than 120 ppm of a copolymer additive (c) to ameliorate the antagonistic interactions between component (a) and component (b) in a middle distillate fuel composition.

25

Suitably the invention may provide the use of less than 100 ppm of additive (c) to ameliorate the antagonistic interaction between component (a) and component (b) in a middle distillate fuel composition.

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In some embodiments the present invention may provide the use of less than 75 ppm or less than 50 ppm of additive (c) to ameliorate antagonistic interactions between component (a) and component (b) in a middle distillate fuel composition.

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

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Examples

In the examples, the following additive are dosed into middle distillate fuels:

- A – an ethylene vinyl acetate copolymer comprising 30 to 32% wt% vinyl acetate units and having a number average MW of approximately 4-5000 supplied in aromatic solvent.
- 5 B – the reaction product of 2 moles di(hydrogenated) tallow amine and 1 mole phthalic anhydride reacted to form the half amide half ammonium salt supplied in aromatic solvent.
- C – a copolymer of a 1:1 mole ratio of vinyl acetate and the diester of fumaric acid and tetradecanol having a number average MW of approximately 10,000 supplied in aromatic solvent.
- 10 D – the reaction product of a polyisobutenyl succinic anhydride with a PIB number average molecular weight of 750 and a mixture of polyethylene polyamines corresponding to tetraethylenepentamine reacted to form the polyisobutylene succinimide supplied in aromatic solvent.
- 15 E – the Mannich reaction product of dodecyl phenol, formaldehyde and ethylene diamine supplied in aromatic solvent.
- F – the reaction product of a polyisobutene-substituted succinic anhydride with a PIB number average molecular weight of 1000 and dimethylamino propylamine reacted to form an imide and then quaternised by reaction with methyl salicylate supplied in aromatic solvent.
- 20 G – an ethylene vinyl acetate copolymer comprising 28 wt% vinyl acetate units and having a number average MW of approximately 3-4000 supplied in aromatic solvent.
- 25 H – a copolymer of a 1:1 mole ratio of vinyl acetate and the diester of fumaric acid and tetradecanol with a number average MW of approximately 21,000 supplied in aromatic solvent.
- 30 I (Comparative) – a copolymer of α olefin and behenyl maleate supplied in aromatic solvent.
- J (Comparative) – C16/18 diester of C24/26 α olefin maleic anhydride copolymer supplied in aromatic solvent.
- 35 K (Comparative) – a C16/C18 alkyl imide of C14/C16 α olefin maleic anhydride copolymer supplied in aromatic solvent.
- L – a copolymer of a 1:1 mole ratio of vinyl acetate and the diester of fumaric acid and dodecanol with a number average MW of approximately 30,000 supplied in aromatic solvent.
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M – a copolymer of a 1:1 mole ratio of vinyl acetate and the diester of fumaric acid and dodecanol with a number average MW of approximately 33,000 supplied in aromatic solvent.

Example 1

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Fuel compositions were prepared by adding the amounts as specified in Table 4 and Table 5 to a fuel composition as described below.

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Compositions 1 to 10 were prepared in Fuel 1, a middle distillate fuel composition having a specification which corresponds to EN 590 and having properties shown in Table 1.

Compositions 11 and 12 were prepared in Fuel 2, a middle distillate fuel composition having a specification which corresponds to EN 590 and having properties shown in Table 2.

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Compositions 13 to 16 were prepared in Fuel 3, a middle distillate fuel composition having a specification which corresponds to EN 590 and having properties shown in Table 3 blended with 7% vol Fatty Acid Methyl Ester to give a fuel having a cloud point of -9°C and a CFPP of -9°C.

20 **Table 1 – Properties of Fuel 1**

Test	Units	Results
Density	g/cm ³	0.8386
Cloud Point	°C	-6
CFPP	°C	-8
Distillation		
IBP	°C	170.6
10%	°C	195.7
20%	°C	208.3
30%	°C	226.1
40%	°C	243.8
50%	°C	261.2
60%	°C	279.5
70%	°C	298.3
80%	°C	316.5
90%	°C	335.3
FBP	°C	358.8

Table 2 – Properties of Fuel 2

Test	Units	Results
Density	g/cm3	0.8312
Cloud Point	°C	-8.5
CFPP	°C	-10
Distillation		
IBP	°C	166
10%	°C	205
20%	°C	223
30%	°C	237
40%	°C	251
50%	°C	267
60%	°C	283
70%	°C	299
80%	°C	317
90%	°C	338
FBP	°C	362

Table 3 – Properties of Fuel 3

Test	Units	Results
Density	g/cm3	0.8312
Cloud Point	°C	-7.5
CFPP	°C	- 10
Distillation		
IBP	°C	168
10%	°C	205
20%	°C	221
30%	°C	237
40%	°C	251
50%	°C	267
60%	°C	282
70%	°C	299
80%	°C	317
90%	°C	338
FBP	°C	360

Table 4

	Additive concentration (ppm active)						
Composition	A	B	C	D	E	F	G
1	280	62.4	0	180	0	0	0
2	280	62.4	0	0	195	0	0
3	280	62.4	0	0	0	180	0
4	280	62.4	50	180	0	0	0
5	280	62.4	20	0	195	0	0
6	280	62.4	20	0	0	180	0
7	280	62.4	0	0	61.7	69.0	0
8	280	62.4	20	0	61.7	69.0	0
9	280	62.4	0	0	26.0	36.0	0
10	280	62.4	20	0	26.0	36.0	0
11	0	14.4	0	0	26.0	36.0	69.1
12	0	14.4	5	0	26.0	36.0	69.1

Table 5

	Additive concentration (ppm active)									
Composition	B	G	E	F	H	I comp	J comp	K comp	L	M
13	24.0	115.2	61.7	69.0	10					
14	24.0	115.2	61.7	69.0		10				
15	24.0	115.2	61.7	69.0			10			
16	24.0	115.2	61.7	69.0				10		
17	24.0	115.2	61.7	69.0					10	
18	24.0	115.2	61.7	69.0						10

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Example 2

Fuel compositions 1 to 17 were tested in a short sediment test according to procedure A and/or procedure B. Results are shown in Table 6

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Procedure A

450g of base fuel is mixed with the appropriate amount of additive and the cloud point of the treated fuel is determined. 500ml of the treated fuel is transferred into a 500ml measuring cylinder and cooled in a climate chamber or cooling bath to the test temperature and then held at that temperature for 16 hours. After the 16 hour period the upper 80% and the lower 20% of the fuel are separated and heated to redissolve the precipitated wax. The cloud point

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of the two portions is determined. ΔCP is recorded as the difference between the cloud point of the upper 80% and that of the lower 20% portion of the fuel.

Procedure B

- 5 150g of base fuel is mixed with the appropriate amount of additive and stored at 40°C for one hour. 100ml is transferred into a 100ml graduated cylinder. The cloud point of the treated fuel is determined. The sample is cooled in a cooling bath/climate chamber to the test temperature and then held at that temperature for 16 hours. After the 16 hour period, appearance of the fuel and the amount of sediment is recorded. The upper 50% and the
- 10 lower 50% of the fuel are separated and the bottom 50% is stored at 40° for 1 hour and the cloud point is determined. ΔCP is recorded as the difference between the cloud point of the lower 50% portion of the fuel and the original cloud point of the treated fuel prior to cooling.

Table 6

Composition	Procedure	Test Temp (°C)	(A) CP Treated fuel (°C)	(B) CP Top Layer (°C)	(C) CP Bottom Layer (°C)	(C)-(B) ΔCP (°C)	(C)-(A) ΔCP (°C)	Appearance	Sediment	Result
1	A	-13	-5.3	-8.3	-0.3	8.0				Fail
2	A	-13	-5.2	-8.0	-0.2	7.8				Fail
3	A	-13	-6.1	-7.1	-1.0	6.1				Fail
4	A	-13	-6.4	-7.3	-5.2	2.1				Pass
5	A	-13	-6.4	-6.8	-5.6	1.2				Pass
6	A	-13	-6.1	-6.6	-5.2	1.4				Pass
7	A	-13	-5.9	-6.6	-0.9	5.7				Fail
8	A	-13	-6.4	-6.8	-5.2	1.6				Pass
9	A	-13	-5.2	-6.7	-1.2	5.5				Fail
10	A	-13	-6.0	-6.3	-5.4	0.9				Pass
11	B	-14.5	-8.5		-4.5		4.0	clear	16ml	Fail
12	B	-14.5	-8.5		-7.5		1.0	turbid	none	Pass
12	A	-14.5	-8.5	-8.0	-7.0	1.0		turbid	none	Pass
13	B	-15	-8.5		-8.0		0.5	turbid	none	Pass
14	B	-15	-8.0		-3.0		5.0	flocculated	28ml	Fail
15	B	-15	-8.5		-4.0		4.5	flocculated	26ml	Fail
16	B	-15	-9.0		-4.5		4.5	almost clear	10ml	Fail
17	B	-15	-8.0		-8.0		0.0	turbid	trace	Pass
18	B	-15	-8.0		-7.5		0.5	turbid	trace	Pass