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(54) **Fuel oil compositions**

(57) A middle-distillate fuel oil composition comprises minor amounts of

(A) a quaternary ammonium salt of a polycarboxylic acid; and

(B) a polyalkylene amine detergent.

The concentrations of (A) and (B) endow the composition with better low temperature properties than a

corresponding composition in which (A) is replaced with (Aref), an amine salt of a polycarboxylic acid analogous to (A) and which is not a quaternary ammonium salt; and the concentration of (B) is such that it would adversely affect the low temperature properties of (Aref) in the corresponding composition.

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Description**FIELD OF THE INVENTION**

5 **[0001]** This invention relates to improvements in fuel oil compositions, more especially to fuel oil compositions containing detergent species and that are susceptible to wax formation at low temperatures.

BACKGROUND OF THE INVENTION

10 **[0002]** Fuel oils, whether derived from petroleum or from vegetable sources, contain components, e.g., n-alkanes or methyl n-alkanoates, that at low temperature tend to precipitate as large, plate-like crystals or spherulites of wax in such a way as to form a gel structure which causes the fuel to lose its ability to flow. The lowest temperature at which the fuel will still flow is known as the pour point.

15 **[0003]** As the temperature of a fuel falls and approaches the pour point, difficulties arise in transporting the fuel through lines and pumps. Further, the wax crystals tend to plug fuel lines, screens, and filters at temperatures above the pour point. These problems are well recognised in the art, and various additives have been proposed, many of which are in commercial use, for depressing the pour point of fuel oils. Similarly, other additives have been proposed and are in commercial use for reducing the size and changing the shape of the wax crystals that do form. Smaller size crystals are desirable since they are less likely to clog a filter. The wax from a diesel fuel, which is primarily an alkane wax, crystallizes as platelets. Certain additives inhibit this and cause the wax to adopt an acicular habit, the resulting needles being more likely than platelets to pass through a filter or to form a porous layer of crystals on the filter. Other additives may also have the effect of retaining the wax crystals in suspension in the fuel, reducing settling and thus also assisting in preventing blockages. These types of additives are often termed 'wax anti-settling additives' (WASA) and are commonly polar nitrogen species.

25 **[0004]** Many additives have been described for enhancing engine cleanliness, e.g. for reducing or removing deposits in the intake system (e.g. carburettors, intake manifold, inlet valves) or combustion chamber surfaces of spark-ignition engines, or for reducing or preventing injector nozzle fouling in compression-ignition engines.

30 **[0005]** For example, UK Patent No 960,493 describes incorporating metal-free detergents, in the form of polyolefin-substituted succinimides of tetraethylene pentamine, in base fuels for internal combustion engines. The use of such metal-free detergents is now widespread. Most commonly used are polyisobutylene-substituted succinimides, which are the reaction products of polyisobutylene-substituted acylating agents such as succinic acid or anhydride with polyamines. Such materials and their methods of production are known to those skilled in the art. They may be generally described as metal-free polyalkylene amine detergents.

35 **[0006]** A trend in modern diesel engine technology is to increase power output and efficiency by increasing injection pressures and decreasing injector nozzle diameters. Under these conditions, the build-up of injector deposits is more likely and the deposition which occurs is more severe. This has led fuel manufacturers to produce new types of fuels which are often sold as 'premium' grades and promoted as being especially effective to improve engine cleanliness. To meet this performance claim, such premium fuels usually contain significantly higher levels of detergent than non-premium grade fuels.

40 **[0007]** Although largely effective with regard to engine cleanliness, a drawback has been identified in the use of high levels of detergent in fuel oils. Specifically, it has been observed that the presence of high levels of polyalkylene amine detergents in premium grade fuels can interfere with the cold-flow performance of wax anti-settling additives when these are also present in the fuel. So, although the fuel may be satisfactory for engine cleanliness, its low temperature properties in terms of wax anti-settling and cold filter plugging point (CFPP) may not be adequate.

45 **[0008]** EP-A-0 908 507 describes the use of additives for improving the cold flow properties of fuel oils, such as middle distillate fuel oil boiling within the range of 110°C to 500°C. In the examples it describes fuels containing as additives an N,N-dialkylammonium salt of 2-N',N'-dialkyl-amido benzoate, being the reaction product of reacting one mole of phthalic anhydride with two moles of dihydrogenated tallow amine to form a half amide/half amine salt (additive C and a constituent of components BX and BY therein); and a polyaminated polyisobutylene succinic anhydride detergent (a constituent of component AY therein). EP-A-0 908 507 describes the results of simulated filter plugging point (SFPP) tests carried out on such fuels. Additive C is an example of a conventional wax anti-settling additive.

50 **[0009]** The present invention is based on the discovery that the use of a quaternary ammonium salt of a polycarboxylic acid as a wax anti-settling additive in place of a conventional wax anti-settling additive can improve the low temperature properties of the fuel containing a polyalkylene amine detergent.

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SUMMARY OF THE INVENTION

[0010] Thus, in accordance with a first aspect, the present invention provides a fuel oil composition comprising a major

amount of a middle-distillate fuel oil composition comprising minor amounts of

(A) at least one oil-soluble polar nitrogen compound effective as a wax anti-settling additive in the form of a quaternary ammonium salt of a polycarboxylic acid; and

(B) at least one oil-soluble polyalkylene amine detergent,

wherein the concentrations of (A) and (B) are such that one or more of the low temperature properties of said fuel oil composition are better than those of an otherwise identical fuel oil composition that contains, in place of (A), (Aref), which is not a quaternary ammonium salt and is an oil-soluble amine salt of a polycarboxylic acid analogous to (A); and wherein the concentration of (B) in said fuel oil composition is such that it would adversely affect one or more of the low temperature properties of (Aref) in said otherwise identical fuel oil composition.

[0011] In accordance with a second aspect, the present invention provides the use, in a middle distillate fuel oil composition comprising a minor amount of (B), which is at least one oil-soluble polyalkylene amine detergent, of a minor amount of (A), which is at least one oil-soluble polar nitrogen compound effective as a wax anti-settling additive in the form of a quaternary ammonium salt of a polycarboxylic acid, to improve one or more of the low temperature properties of said fuel oil composition in comparison with one or more of the low temperature properties of an otherwise identical fuel oil composition that contains, in place of (A), (Aref), which is not a quaternary ammonium salt and is an amine salt of a polycarboxylic acid analogous to (A), wherein the concentration of (B) in said fuel oil composition is such that it would adversely affect one or more of the low temperature properties of (Aref) in said otherwise identical fuel oil composition.

[0012] In accordance with a third aspect, the present invention provides a method of making a middle distillate fuel oil composition comprising minor amounts of at least one polar nitrogen compound effective as a wax anti-settling additive and at least one polyalkylene amine detergent, which method comprises

(i) determining concentrations of (B), as defined in the first aspect of the invention, and of (Aref), as defined in the first aspect of the invention, at which (B) adversely effects one or more of the low temperature properties of (Aref) in a middle distillate fuel oil composition;

(ii) determining concentrations of (A), as defined in the first aspect of the invention, at which one or more of the low temperature properties of a middle distillate fuel oil composition containing (B) at concentrations determined in step

(i) are better than those of an otherwise identical middle distillate fuel oil composition containing (Aref) and (B); and

(iii) blending a middle distillate fuel oil composition containing (A) and (B) in the concentrations determined in steps (i) and (ii).

[0013] The observed loss in wax anti-settling and CFPP performance appears to be limited to the use of metal-free polyalkylene amine detergents in combination with conventional WASA components. It is noteworthy that a similar loss in performance may not be observed when detergents other than polyalkylene amine detergents are used in combination with conventional WASA components. The addition of the quaternary ammonium salt mitigates this loss in performance thereby allowing higher levels of polyalkylene amine detergents to be used together with WASA species without compromising the low temperature properties of the additised fuel.

[0014] As indicated above, the combined presence in a fuel oil of a polyalkylene amine detergent and a conventional WASA may lead to a reduction in performance in terms of wax anti-settling and/or CFPP. Better low temperature properties refers to either wax anti-settling performance or CFPP, or, preferably, to both properties. Preferably one or more low temperature properties of a fuel oil composition that contains a conventional WASA, but does not contain a polyalkylene amine detergent, are restored or improved by the present invention.

[0015] It should be noted that it is not required that either low temperature property necessarily reaches the level which would be expected without the presence of a polyalkylene amine detergent.

[0016] The use of the term 'restore' should be taken to include the situation where, although the precise numerical value of the property may not be regained, the difference is not practically significant.

[0017] In accordance with a further aspect, the present invention provides a middle-distillate fuel oil composition comprising minor amounts of

(A) at least one oil-soluble polar nitrogen compound effective as a wax anti-settling additive in the form of a quaternary ammonium salt of a phthalic acid; and

(B) at least one polyalkylene amine detergent in the form of an N-(polyamine-substituted) polyalkenyl succinimide.

[0018] In this specification, 'hydrocarbyl' means a group containing carbon and hydrogen atoms that is bonded to the remainder of the molecule via a carbon atom and that may include hetero atoms that do not detract from the essentially hydrocarbon nature of the group.

DETAILED DESCRIPTION OF THE INVENTION

[0019] Features of the invention, applicable where appropriate to various aspects of the invention, will now be described in more detail.

(A) QUARTERNARY AMMONIUM SALT

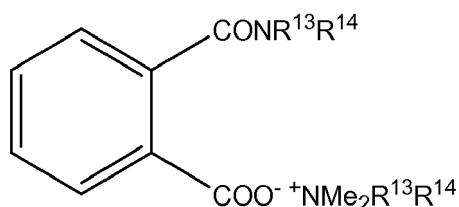
[0020] As stated, this is an oil-soluble nitrogen compound effective as a wax anti-settling additive in the form of a quaternary ammonium salt of a polycarboxylic acid. The nitrogen atom of the ammonium cation carries, for example, four hydrocarbonyl groups. The salt is for example monomeric.

[0021] The quaternary ammonium cation in the compound preferably carries a segment of the formula $\text{NR}^{13}\text{R}^{14}$, where R^{13} independently represents a hydrocarbonyl group, such as an alkyl group, containing from 8 to 40 carbon atoms, and R^{14} independently represents a hydrocarbonyl group, such as an alkyl group, containing up to 40 carbon atoms. R^{13} and R^{14} may be straight chain or branched, and/or may be the same or different. Preferably, each of R^{13} and R^{14} represents a C_{12} to C_{24} straight-chain alkyl group.

[0022] The quaternary ammonium cation is preferably represented by the formula $\oplus \text{NR}^{13}\text{R}^{14}\text{R}_2$, where R represents an alkyl group having from one to four carbon atoms such as a methyl, ethyl or propyl group.

[0023] Suitably, the segment $\text{NR}^{13}\text{R}^{14}$ is derived from a secondary amine such as di-octadecylamine, di-cocoamine, di-hydrogenated tallow amine and methylbehenylamine. The amine may be a mixture such as derived from natural materials, preferably a secondary hydrogenated tallow amine, the alkyl groups of which are derived from hydrogenated tallow fat composed of approximately 4% C_{14} , 31% C_{16} and 59% C_{18} .

[0024] Examples of suitable polycarboxylic acids and their anhydrides for preparing the quaternary ammonium salts include ethylenediamine tetraacetic acid, and carboxylic acids based on cyclic skeletons, e.g., cyclohexane-1,2-dicarboxylic acid, cyclohexene-1,2-dicarboxylic acid, cyclopentane-1,2-dicarboxylic acid and naphthalene dicarboxylic acid, and 1,4-dicarboxylic acids including dialkyl spirobis lactones. Generally, these acids have 5 to 13 carbon atoms in the cyclic moiety. Preferred acids useful in the present invention are benzene dicarboxylic acids, e.g. phthalic acid, isophthalic acid, and terephthalic acid. Phthalic acid and its anhydride are particularly preferred. A particularly preferred quaternary ammonium salt is represented by the formula



where R^{13} and R^{14} each independently represent alkyl groups derived from hydrogenated tallow fat, which compound may, for example, be made by reacting N,N-dimethyl-N,N-dihydrogenated tallow ammonium chloride (one mole) with dihydrogenated tallow amine (one mole), phthalic anhydride (one mole) and sodium methoxide (one mole).

(Aref) AMINE SALT

[0025] As stated, this is an oil-soluble amine salt of the same polycarboxylic acid as described above in respect of (A), the quaternary ammonium salt. It is a polar nitrogen compound effective as a wax anti-settling additive but is not a quaternary ammonium salt. It may be a primary, secondary or tertiary amine salt.

[0026] Such salts may carry the segment of the formula $\text{NR}^{13}\text{R}^{14}$ as defined above, but differ in not being quaternary ammonium salts. They are described in, for example, US Patent No. 4,211,534.

[0027] As particular examples, there may be mentioned amide-amine salts formed by reacting phthalic anhydride (one mole) with dihydrogenated tallow amine (two moles) to give an N,N-dialkylammonium salt of a 2-N',N'-dialkylamidobenzoic acid; reacting an alkylphenol formaldehyde condensate (APFC) with a dicoco- and dihydrogenated tallow amine mixture; and reacting ethylene diamine tetra-acetic acid with dihydrogenated tallow amine.

[0028] In the practice of the present invention, (Aref) is analogous to (A) in that both are derived from the same polycarboxylic acid and that the same hydrocarbonyl groups carried by the nitrogen atom(s) of (Aref) are also carried by nitrogen atoms of (A).

[0029] It will be clear that (Aref) is not a component of the present invention, but is for reference purposes in order to

define the scope of the invention.

(B) POLYALKYLENE AMINE DETERGENT

5 **[0030]** Polyalkylene amines are for example derived from polyalkylenes of greater than 250 mass units, which are themselves preferably derived from C₂-C₁₀ alkenes and more preferably from butene and/or isobutene. They are prepared by linking ammonia, amines, polyamines, alkylamines or alkanolamines to and/or between these polymers. A variety of methods can be used to achieve this, for example routes via chlorination, hydroformylation, epoxidation and ozonolysis
10 such as are known in the art. Typical examples, which are also known in the art, are polyisobutene monoamine ("PIBA") and polyisobutene-ethylenediamine ("PIB-EDA"). Further examples are described in EP 244616 and WO 98/28346. The ratio of hydrocarbyl units to amine units may be 1:1 to 2.5:1, preferably 1.2:1 to 1.5:1. A number of acylated, nitrogen-containing compounds having a hydrocarbyl substituent of at least 10 carbon atoms and made by reacting a carboxylic acid acylating agent, for example an anhydride or ester, with an amino compound, are known to those skilled in the art.
15 In such compositions, the acylating agent is linked to the amino compound through an imido, amido, amidine or acyloxy ammonium linkage. The hydrocarbyl substituent of at least 10 carbon atoms may be found either in the portion of the molecule derived from the carboxylic acid acylating agent, or in the portion derived from the amino compound, or in both. Preferably, however, it is found in the acylating agent portion. The acylating agent can vary from formic acid and its acylating derivatives to acylating agents having high molecular weight hydrocarbyl substituents of up to 50, 75, 100 or 200 carbon atoms. The amino compounds can vary from ammonia itself to amines having hydrocarbyl substituents
20 of up to about 30 carbon atoms.

[0031] Polyalkylene amines are normally regarded as metal-free.

[0032] A preferred class of detergent may be those made by reacting an acylating agent having a hydrocarbyl substituent of at least 10 carbon atoms and a nitrogen compound characterized by the presence of at least one -NH- group. Typically, the acylating agent is a mono- or polycarboxylic acid (or reactive equivalent thereof), such as a substituted
25 succinic or propionic acid, and the amino compound is a polyamine or mixture of polyamines, most typically, a mixture of ethylene polyamines. The amine also may be a hydroxyalkyl-substituted polyamine. The hydrocarbyl substituent in such acylating agents preferably contains an average of at least 30 or 50 and up to 200 carbon atoms.

[0033] Illustrative of hydrocarbyl substituent groups containing at least 10 carbon atoms are n-decyl, n-dodecyl, tetrapropenyl, n-octadecyl, oleyl, chlorooctadecyl and tricontanyl. Generally, the hydrocarbyl substituents are made from
30 homo- or interpolymers (e.g. copolymers such as terpolymers) of mono- and di-olefins having 2 to 10 carbon atoms, such as ethylene, propylene, 1-butene, isobutene, butadiene, isoprene, 1-hexene and 1-octene. Typically, these olefins are 1-monoolefins. This substituent can also be derived from halogenated (e.g. chlorinated or brominated) analogues of such homo- or interpolymers.

[0034] The hydrocarbyl substituents are predominantly saturated. The hydrocarbyl substituents are also predominantly aliphatic in nature, that is, they contain no more than one non-aliphatic moiety (cycloalkyl, cycloalkenyl or aromatic)
35 group of 6 or less carbon atoms for every 10 carbon atoms in the substituent. Usually, however, the substituents contain no more than one such non-aliphatic group for every 50 carbon atoms, and in many cases they contain no such non-aliphatic groups at all, that is, the typical substituents are purely aliphatic. Typically, these purely aliphatic substituents are alkyl or alkenyl groups.

[0035] A preferred source of the substituents are poly(isobutene)'s obtained by polymerization of a C₄ refinery stream having a butene content of 35 to 75 weight per cent and an isobutene content of 30 to 60 weight per cent in the presence of a Lewis acid catalyst such as aluminium trichloride or boron trifluoride. These polybutenes predominantly contain monomer repeating units of the configuration -C(CH₃)₂CH₂-.
40

[0036] The hydrocarbyl substituent is attached to the succinic acid moiety or derivative thereof via conventional means, for example the reaction between maleic anhydride and an unsaturated substituent precursor such as a polyalkene, as described for example in EP-B-0 451 380.
45

[0037] One procedure for preparing the substituted succinic acylating agents involves first chlorinating the polyalkene until there is an average of at least one chloro group for each molecule of polyalkene. Chlorination involves contacting the polyalkene with chlorine gas until the desired amount of chlorine is incorporated into the chlorinated polyalkene.
50 Chlorination is generally carried out at a temperature of 75 to 125°C. If desired, a diluent can be used in the chlorination procedure. Suitable diluents for this purpose include poly- and perchlorinated and/or fluorinated alkanes and benzenes.

[0038] The second step in the procedure is to react the chlorinated polyalkene with the maleic reactant at a temperature usually within the range of 100 to 200°C. The mole ratio of chlorinated polyalkene to maleic reactant is usually 1:1. However, a stoichiometric excess of maleic reactant can be used, for example, a mole ratio of 1:2. If an average of more
55 than one chloro group per molecule of polyalkene is introduced during the chlorination step, then more than one mole of maleic reactant can react per molecule of chlorinated polyalkene. It is normally desirable to provide an excess of maleic reactant, for example, an excess of 5 to 50, for example 25%, by weight. Unreacted excess maleic reactant may be stripped from the reaction product, usually under vacuum.

[0039] Another procedure for preparing substituted succinic acid acylating agents utilizes a process described in U.S. Patent No. 3,912,764 and U.K. Patent No. 1,440,219. According to that process, the polyalkene and the maleic reactant are first reacted by heating them together in a direct alkylation procedure. When the direct alkylation step is completed, chlorine is introduced into the reaction mixture to promote reaction of the remaining unreacted maleic reactants. According to these patent specifications, 0.3 to 2 or more moles of maleic anhydride are used in the reaction for each mole of polyalkene. The direct alkylation step is conducted at temperatures of 180 to 250°C. During the chlorine-introducing stage, a temperature of 160 to 225°C is employed.

[0040] The attachment of the hydrocarbyl substituent to the succinic moiety may alternatively be achieved via the thermally-driven 'ene' reaction in the absence of chlorine. Use of such a material as the acylating agent leads to products having particular advantages, for example, to chlorine-free products having excellent detergency and lubricity properties. In such products, the reactant is preferably formed from a polyalkene having at least 30, preferably 50 or more such as 75, % of residual unsaturation in the form of terminal, e.g. vinylidene, double bonds.

[0041] Suitable polyalkylene amines are those comprising amino nitrogens linked by alkylene bridges, which amino nitrogens may be primary, secondary and/or tertiary. The polyamines may be straight chain, wherein all the amino groups are primary or secondary, or may contain cyclic or branched regions or both, in which case tertiary amino groups may also be present. The alkylene groups are preferably ethylene or propylene groups, most preferably ethylene. Such materials may be prepared from the polymerization of lower alkylene diamines such as ethylene diamine, a mixture of polyamines being obtained, or via the reaction of dichloroethane and ammonia.

[0042] Specific examples of polyalkylene polyamines (1) are ethylene diamine, tetra(ethylene)pentamine, tri-(trimethylene)tetramine, and 1,2-propylene diamine. Specific examples of hydroxyalkyl-substituted polyamines include N-(2-hydroxyethyl) ethylene diamine, N,N-bis-(2-hydroxyethyl) ethylene diamine and N-(3-hydroxybutyl) tetramethylene diamine. Specific examples of heterocyclic-substituted polyamines (2) are N-2-aminoethyl piperazine, N-2 and N-3 amino propyl morpholine, N-3-(dimethylamino) propyl piperazine, 2-heptyl-3-(2-aminopropyl) imidazoline, 1,4-bis (2-aminoethyl) piperazine, 1-(2-hydroxy ethyl) piperazine and 2-heptadecyl-1-(2-hydroxyethyl)-imidazoline. Specific examples of aromatic polyamines (3) are isomeric phenylene diamines and isomeric naphthalene diamines.

[0043] Many patent specifications describe suitable polyalkylene amine detergents including US Patents 3 172 892; 3 219 666; 3 272 746; 3 310 492; 3341542; 3 444 170; 3 455 831; 3 455 832; 3 576 743; 3 630 904; 3 632 511; 3 804 763 and 4 234 435, and including EP 0 336 664 and EP 0 263 703. A typical and preferred detergent of this class is that made by reacting a poly(isobutylene)-substituted succinic anhydride acylating agent (e.g. anhydride, acid or ester.) wherein the poly(isobutene) substituent has between 50 to 200 carbon atoms with a mixture of ethylene polyamines having 3 to 10 amino nitrogen atoms per ethylene polyamine and 1 to 6 ethylene groups.

[0044] The polyalkylene amine may be defined by the average number of nitrogen atoms per molecule of the component, which may preferably be in the range of 4 to 8.5, more preferably 6.8 to 8, especially 6.8 to 7.5, nitrogen atoms per molecule.

[0045] Also suitable are materials made from amine mixtures comprising polyamines having seven and eight, and optionally nine, nitrogen atoms per molecule (so-called 'heavy' polyamines). Preferably, the polyamine mixture comprises at least 45, and preferably 50, % by weight of polyamines having seven nitrogen atoms per molecule, based on the total weight of polyamines. In addition to polyamine mixtures, single species may also be used, for example tetraethylene pentamine (TEPA) and triethylene tetramine (TETA).

[0046] Preferred polyalkylene amine detergents are those made by reacting a poly(isobutene)-substituted succinic anhydride acylating agent with mixtures of ethylene polyamines as hereinbefore described, wherein the polyisobutene has a Mn of 400-2500, preferably 700-400, such as 950. Generally, they may be described as polyalkenyl succinimides (such as polybutenyl succinimides, preferably polyisobutenyl succinimides) or as N-(polyamine-substituted) polyalkenyl succinimides.

THE FUEL OIL

[0047] The fuel oil is a petroleum-based fuel oil in the form of a middle distillate fuel oil, generally boiling within the range of from 110 to 500, e.g. 150 to 400, °C.

[0048] The invention is applicable to middle distillate fuel oils of all types, including broad-boiling distillates, i.e., those having a 90%-20% boiling temperature difference, as measured in accordance with ASTM D-86, of 50°C or more.

[0049] The fuel oil may comprise atmospheric distillate or vacuum distillate, cracked gas oil, or a blend in any proportion of straight-run and thermally and/or catalytically cracked distillates. The most common petroleum distillate fuels are kerosene, jet fuels, diesel fuels, heating oils and heavy fuel oils. The heating oil may be a straight atmospheric distillate, or may also contain vacuum gas oil or cracked gas oil or both. The fuels may also contain major or minor amounts of components derived from the Fischer-Tropsch process. Fischer-Tropsch fuels, also known as FT fuels, include those that are described as gas-to-liquid fuels, coal and/or biomass conversion fuels. To make such fuels, syngas (CO + H₂) is first generated and then converted to normal paraffins and olefins by a Fischer-Tropsch process. The normal paraffins

may then be modified by processes such as catalytic cracking/reforming or isomerisation, hydrocracking and hydroisomerisation to yield a variety of hydrocarbons such as iso-paraffins, cycloparaffins and aromatic compounds. The resulting FT fuel can be used as such or in combination with other fuel components and fuel types such as those mentioned in this specification. The above-mentioned low temperature flow problem is most usually encountered with diesel fuels and with heating oils. The invention is also applicable to fuel oils containing fatty acid methyl esters derived from vegetable oils, for example, rapeseed methyl ester, either used alone or in admixture with a petroleum distillate oil. **[0050]** The fuel oil is preferably a low sulphur-content fuel oil. Typically, the sulphur content of the fuel oil is less than 500ppm (parts per million) by weight. Preferably, the sulphur content of the fuel is less than 100, for example less than 50, ppm. Fuel oils with even lower sulphur contents, for example less than 20ppm or less than 10ppm are also suitable.

TREAT RATES

[0051] The amounts of each component present in the fuel oil depend on the nature of the species used, the properties of the fuel oil and the low temperature performance required. As discussed above, the present invention is based on the observation of a negative impact on the low temperature behaviour of the wax anti-settling additive when present in premium diesel fuels which contain relatively high levels of polyamine detergent.

[0052] Typically, the amount of (B), at least one polyalkylene amine detergent, in the fuel oil composition is in excess of 50ppm by weight based on the weight of the fuel oil, for example in excess of 75 or 100, ppm by weight. Some premium diesel fuels may contain up to 500 ppm by weight of polyalkylene amine detergent. This can be compared with a treat rate of around 10 to 75 ppm for more conventional, non-premium diesel fuels.

[0053] The amount of (A), at least one polar nitrogen compound in the form of the quaternary ammonium compound effective as a wax anti-settling additive, is typically in the range of 10 to 500, preferably 20 to 250, more preferably 20 to 150, ppm by weight based on the weight of the fuel oil. Alternatively, the preferments may be 10 to 200, more preferably 10 to 100.

OTHER ADDITIVES

[0054] It is commonplace in the art to use polar nitrogen compounds effective as a wax anti-settling additives in combination with other additional cold-flow improving additives. Suitable materials will be well known to those skilled in the art and include for example, ethylene-unsaturated ester copolymers such as ethylene:vinyl acetate copolymers and similar polymers. The present invention contemplates the addition of such additional cold-flow improving additives, their application in terms of treat rate also being well-known to those skilled in the art. In an embodiment of all aspects of the invention, the fuel oil further comprises an ethylene-unsaturated ester copolymer.

EXAMPLES OF THE INVENTION

[0055] The invention will now be described in the examples which are not intended to limit the scope of the claims hereof.

CONSTITUENTS

[0056] The following were used:

WASA (Aref): a monomeric polar nitrogen compound effective as a wax anti-settling additive in the form of an N,N-dialkylammonium salt of 2-N',N'-dialkylamidobenzoic acid, made by reacting phthalic anhydride (one mole) and dihydrogenated tallow) amine (two moles).

WASA (A): a monomeric polar nitrogen compound effective as a wax anti-settling additive in the form of an N,N-dimethyldi-dihydrogenated tallow ammonium salt of 2-(N',N'-dihydrogenated tallow amido)benzoic acid, made by reacting N,N-dimethyl-N,N-dihydrogenated ammonium chloride (one mole) with dihydrogenated tallow amine (one mole), phthalic anhydride (one mole) and sodium methoxide (one mole). Sodium chloride (a by-product) was separated by washing with water and removing the aqueous solution.

DETERGENT (B): a succinimide detergent made by reacting polyisobutene-substituted succinic anhydride, in which the polyisobutene group has a molecular weight of about 1000, with a poly-ethyleneamine mixture predominating in species having at least seven nitrogen atoms per molecule.

FUELS: the fuel used was a middle-distillate diesel fuel, Fuel X:
Fuel X is characterised by

D86 Distillation	IBP	199°C
	20%	231°C

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(continued)

90% 319°C
FBP 352°C

Cloud Point -6°C
CFPP -13°C

TESTS

[0057] Additives (A), (Aref) and (B) were blended into Fuel X in proportions indicated below to give middle distillate fuel oil compositions. The compositions also contained additives routinely used in diesel fuels such as ethylene unsaturated ester copolymers (EVE), dialkyl fumarate vinyl acetate copolymers (FVA), polyethylene glycol esters (PEGE) and alkyl phenol formaldehyde condensates (APFC). Such additives will be referred to below by the above-indicated abbreviations.

[0058] All additive proportions below are expressed as ppm of active ingredient (i.e. ingredient which is not solvent or carrier) by mass based on the mass of the fuel.

[0059] Low temperature properties of the compositions were measured as follows:

The Aral Short Sediment Test

[0060] The Aral Short Sediment Test (ASST) is a measurement of the propensity of the wax content of a fuel oil to settle and thus a determination of the effectiveness of a wax anti-settling additive. This test was developed by the German oil company Aral and is widely accepted throughout Europe. The ASST metric is the " Δ CP", delta Cloud Point, which is measured as follows: the Cloud Point (CP) of a base fuel oil is measured. The wax anti-settling additive combination under study is added to the base fuel and the sample is stored a temperature 7 °C below the measured CP, namely, usually for German winter diesel fuels, -13°C, for 16 hours. The amount of wax that is judged by eye to have settled is noted. The bottom 20% of the fuel is then taken and the CP of this sample is measured and compared to that of the base fuel. Δ CP is the difference [CP of base fuel] minus [CP of additized fuel]; thus, the greater the Δ CP, the greater the degree of wax settling. A small value of Δ CP, preferably around zero, indicates good wax dispersion.

Cold Filter Plugging Point ("CFPP")

[0061] CFPP is a standard industry test to evaluate the ability of a fuel oil sample to flow through a filter at reduced temperature. The test, which is carried out by the procedure described in detail in "Jn. Of the Institute of Petroleum", vol. 52, No. 510 (1996), p 173-285, is designed to correlate with the cold flow of a middle distillate fuel oil in automotive diesels. In brief, a sample of the oil to be tested (40 cm³) is cooled in a bath which is maintained at about -34°C to give an average cooling rate of about 1°C/min. Periodically (at each one degree centigrade starting from above the cloud point), the oil is tested for its ability to flow through a fine screen in a prescribed time period using a test device which is a pipette to whose lower end is attached an inverted funnel which is positioned below the surface of the oil to be tested. Stretched across the mouth of the funnel is a 350 mesh screen having an area defined by a 12 mm diameter. The periodic tests are initiated by applying a vacuum to the upper end of the pipette whereby oil is drawn through the screen up into the pipette to a mark indicating 20 cm³ of oil. After each successful passage, the oil is returned immediately to the CFPP tube. The test is repeated with each one degree drop in temperature until the oil fails to fill the pipette within 60 seconds, the temperature at which failure occurs being reported as the CFPP temperature.

RESULTS

[0062] Results of test carried out on fuel oil compositions based on Fuel X are set out in Table 1 below.

[0063] In a first set of tests, three groups of fuel oil compositions were used at respective EVE concentrations of 220, 290 and 365 ppm. Each of those three groups included oils with respective detergent, (B), concentrations of 0, 50 and 100 ppm, and each of those oils included oils containing 100 ppm of the reference WASA, (Aref), or of the WASA, (A), of the invention. Thus, eighteen oils based on Fuel X were tested.

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Table 1

EVE (ppm)	Detergent (B) (ppm)	WASA (Aref)	WASA (A)
220	0	0.1	0.4
220	50	5.8	0.6
220	100	4.5	0.9
290	0	0.1	0.1
290	50	6	0.5
290	100	4.4	1.1
365	0	0.5	0.4
365	50	4.4	0.8
365	100	3.8	1.2

[0064] The results, shown in the right-hand columns, are of ΔCP . A small value such as around zero indicates a good performance, whereas a larger value, e.g. 4 to 6 degC, indicates a poor performance. They demonstrate that, when detergent (B) is present, the wax anti-settling performance of reference WASA (Aref) is almost completely lost. In contrast, when WASA (A) of the invention is used, its wax anti-settling performance is substantially retained in the presence of detergent (B).

[0065] Results of a second set of tests carried out on fuel oil compositions based on Fuel X are set out in Table 2 below. All compositions based on Fuel X contained a didodecyl fumarate: vinyl acetate copolymer (25 ppm) and an APFC (25 ppm), both being known cold flow improver additives.

[0066] Three groups of fuel oil compositions were used at respective EVE concentrations of 220, 290 and 365 ppm.

[0067] Each of these three groups included oils with either 0 or 100 ppm detergent, (B), and with either 0 or 20 ppm of a polyethylene glycol ester ("PEGE") cold flow improver. Each oil contained 50 ppm of the reference WASA, (Aref), or of the WASA, (A), of the invention. Thus, twenty-four oils based on Fuel X were tested.

Table 2

EVE (ppm)	PEGE (ppm)	Detergent (B) (ppm)	WASA (Aref)	WASA (A)
220	0	0	-19.5	-19
220	0	100	-18.5	-20
220	20	0	-25.25	-18.5
220	20	100	-18	-20
290	0	0	-24	-19.7
290	0	100	-18	-24
290	20	0	-25.75	-22
290	20	100	-19.5	-27
365	0	0	-26.3	-27
365	0	100	-19.5	-28
365	20	0	-26.5	-25.3
365	20	100	-22.5	-26

[0068] The results, shown in the two adjacent right-hand columns, are of CFPP in °C. They demonstrate that, in the absence of detergent, (B), the CFPP of oils containing the reference WASA, (Aref), is either better than or comparable to the CFPP of oils containing the WASA of the invention, (A). However, they also demonstrate that, in the presence of detergent, (B), the CFPP advantage is lost and that there is a further CFPP advantage in including (A) in place of (Aref).

Claims

1. A middle-distillate fuel oil composition comprising minor amounts of

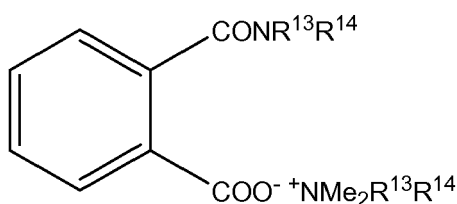
(A) at least one oil-soluble polar nitrogen compound effective as a wax anti-settling additive in the form of a quaternary ammonium salt of a polycarboxylic acid; and

(B) at least one oil-soluble polyalkylene amine detergent,

wherein the concentrations of (A) and (B) are such that one or more of the low temperature properties of said fuel oil composition are better than those of an otherwise identical fuel oil composition that contains, in place of (A), (Aref), which is not a quaternary ammonium salt and is an oil-soluble amine salt of a polycarboxylic acid analogous to (A); and

wherein the concentration of (B) in said fuel oil composition is such that it would adversely affect one or more of the low temperature properties of (Aref) in said otherwise identical fuel oil composition.

2. A fuel oil composition according to claim 1 where one or more of the low temperature properties of said fuel oil composition are the same as or better than an other identical fuel oil composition that contains (Aref) in place of (A) and does not contain (B).
3. A fuel oil composition according to claim 1 or claim 2 wherein the quaternary ammonium cation in the or each polar nitrogen compound carries a segment of the formula $\text{NR}^{13}\text{R}^{14}$, where R^{13} represents a hydrocarbyl group, such as an alkyl group, containing from 8 to 40 carbon atoms, and R^{14} represents a hydrocarbyl group, such as an alkyl group containing up to 40 carbon atoms, provided that R^{13} and R^{14} may be straight chain or branched, and/or may be the same or different.
4. A fuel oil composition according to claim 3 wherein the quaternary ammonium cation is represented by the formula $\text{NR}^{13}\text{R}^{14}\text{R}_2$, where R represents a methyl, ethyl or propyl group.
5. A fuel oil composition according to claim 3 or claim 4 wherein R^{13} and optionally R^{14} represent alkyl groups derived from hydrogenated tallow fat.
6. A fuel oil composition according to any of claims 1 to 5 wherein the polycarboxylic acid is phthalic acid.
7. A fuel oil composition as claimed in any of claims 1 to 6 wherein (A) is represented by the formula



where R^{13} and R^{14} each represent alkyl groups derived from hydrogenated tallow fat, and (Aref) is an amide-amine salt obtainable by reacting one molar proportion of phthalic anhydride with two molar portions of dihydrogenated tallow amine.

8. A fuel oil composition as claimed in any of claims 1 to 7 wherein the at least one polyalkylene amine detergent is the reaction product of a poly(isobutene)-substituted succinic anhydride and a polyamine.
9. A fuel oil composition as claimed in claim 8 wherein the poly(isobutene) substituent has a number average molecular weight in the range of 400 to 2500, preferably of 700 to 1400.
10. The use, in a middle distillate fuel oil composition comprising a minor amount of (B), which is at least one oil-soluble polyalkylene amine detergent, of a minor amount of (A), which is at least one oil-soluble polar nitrogen compound effective as a wax anti-settling additive in the form of a quaternary ammonium salt of a polycarboxylic acid, to improve one or more of the low temperature properties of said fuel oil composition in comparison with one or more of the low temperature properties of an otherwise identical fuel oil composition that contains, in place of (A), (Aref), which is not a quaternary ammonium salt and is an amine salt of a polycarboxylic acid analogous to (A), wherein the concentration of (B) in said fuel oil composition is such that it would adversely affect one or more of the low temperature properties of (Aref) in said otherwise identical fuel oil composition.
11. The use of claim 10 in which the low temperature properties that are improved are ΔCP or CFPP or both.

12. A method of making a middle distillate fuel oil composition comprising minor amounts of at least one polar nitrogen compound effective as a wax anti-settling additive and at least one polyalkylene amine detergent, which method comprises

- 5 (i) determining concentrations of (B), as defined in claim 1, and of (Aref), as defined in claim 1, at which (B) adversely effects one or more of the low temperature properties of (Aref) in a middle distillate fuel oil composition;
- (ii) determining concentrations of (A), as defined in claim 1, at which one or more of the low temperature properties of a middle distillate fuel oil composition containing (B) at concentrations determined in step (i) are better than those of an otherwise identical middle distillate fuel oil composition containing (Aref) and (B); and
- 10 (iii) blending a middle distillate fuel oil composition containing (A) and (B) in the concentrations determined in steps (i) and (ii).

13. A middle-distillate fuel oil composition comprising minor amounts of

- 15 (A) at least one oil-soluble polar nitrogen compound effective as a wax anti-settling additive in the form of a quaternary ammonium salt of a phthalic acid; and
- (B) at least one polyalkylene amine detergent in the form of an N-(polyamine-substituted) polyalkenyl succinimide.

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Place of search		Date of completion of the search	Examiner
Munich		9 April 2008	Bertrand, Samuel
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