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(71) Applicant: **Infineum International Limited**

Abingdon, Oxfordshire OX13 6BB (GB)

(72) Inventors:

- **Jackson, Graham**
Caversham, Reading, Berkshire, RG4 7NE (GB)

• **Waterson, Carl**

Didcot, Oxfordshire, OX11 0AN (GB)

• **Morton, Colin**

Coventry, West Midlands, CV5 6DY (GB)

(74) Representative: **Capaldi, Michael Joseph et al**

Infineum UK Limited

Law Department

P.O. Box 1

Milton Hill

Abingdon, Oxfordshire OX13 6BB (GB)

(54) **Cold flow improver compositions for fuels**

(57) A fuel oil composition having improved low temperature properties comprising a fuel oil and a polymeric substance selected from the group consisting of:

(a)

(i) copolymers of one or more monoesters of maleic acid, itaconic acid or citraconic acid with one or more branched monohydric alcohols having 1 to 18 carbon atoms and more than a single methyl branch, or one or more straight-chain monohydric alcohols having less than 10 carbon atoms; and one or more vinyl esters of carboxylic acids having 2 to 18 carbon atoms; or

(ii) copolymers of a C₄ to C₆ dicarboxylic acid anhydride and one or more vinyl esters of carboxylic acids having 2 to 18 carbon atoms, esterified with one or more monohydric alcohols having 1 to 18 carbon atoms;

(b) copolymers of one or more alkylacrylates or alkylmethacrylates, where the alkyl groups have 1 to 18 carbon atoms, and acrylic or methacrylic acid;

(c) copolymers of one or more acrylic acids or meth-

acrylic acids and one or more vinyl esters of carboxylic acids having 2 to 18 carbon atoms; and,

(d)

(i) homopolymers of one or more monoesters of an unsaturated C₄ to C₆ dicarboxylic acid with a branched monohydric alcohol having 1 to 18 carbon atoms and more than a single methyl branch, or a straight-chain monohydric alcohol having less than 10 carbon atoms, or

(ii) homopolymers of an C₄ to C₆ dicarboxylic acid anhydride, followed by esterification with one or more monohydric alcohols having 1 to 18 carbon atoms,

the polymeric substance being present in the fuel oil in combination with two or more cold flow additives selected from the group consisting of: ethylene-unsaturated monomer copolymers; comb polymers; polar nitrogen compounds; polyoxyalkylene compounds and di-block hydrocarbon polymers.

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Description

[0001] This invention relates to novel compositions useful as fuel additive compositions, use of the additive compositions to improve cold flow characteristics of fuel oils, fuel oil compositions comprising the additive compositions and additive concentrates of the additive compositions.

[0002] Fuel oils, whether derived from petroleum or from vegetable sources, contain components, e.g., n-alkanes, that at low temperatures tend to precipitate as large 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.

[0003] As the temperature of the 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 recognized 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 to pass through a filter than are platelets. The additives may also have the effect of retaining in suspension in the fuel the crystals that have formed, the resulting reduced settling also assisting in prevention of blockages.

[0004] US 5,487,763 describes additives for distillate fuels which are copolymers of an alpha olefin or an aromatic substituted olefin with an ester of a dicarboxylic acid.

[0005] EP 0356256 describes the use of an additive to improve the low temperature properties of distillate fuels, wherein the additive may include a comb polymer which is a copolymer of a fumarate ester and vinyl acetate.

[0006] US 3,982,909 describes the use, in combination, of nitrogen compounds, hydrocarbons, such as waxes, and pour point depressants as cold flow improvers for middle distillate fuel oils. The pour point depressant is preferably an ethylene backbone polymer derived from the copolymerization of ethylene with e.g. an ester of a dicarboxylic acid.

[0007] US 5,094,666 describes a three or more component additive comprising an ethylene backbone polymer, and two nitrogen compounds.

[0008] EP 0308176 describes an additive for adding to a fuel oil which is a fused mixture of a paraffin wax and a flow improver. The flow improver may be a copolymer of an ester of fumaric acid and a vinyl ester. The additive may be in the form of solid slabs or blocks to aid effective distribution and handling.

[0009] The present invention is concerned with the problem of providing an improved additive composition for improving cold flow characteristics of fuel oils.

[0010] More particularly, the present invention is concerned with the problem of improving cold flow characteristics of fuel oils having a 90% - 20% boiling temperature range, as measured in accordance with ASTM D-86, of preferably from 80 to 150°C, and a final boiling point of from 320 to 390°C.

[0011] The present invention is based on the discovery of a three additive system for improving the cold flow properties of distillate fuels oils using certain copolymers or homopolymers not heretofore used as fuels additives in combination with at least two conventional cold flow additives.

[0012] In accordance with this invention, there is provided a fuel oil composition having improved low temperature properties comprising a fuel oil and an effective amount of a polymeric substance selected from the group consisting of:

(a)

(i) copolymers of one or more monoesters of maleic acid, itaconic acid or citraconic acid with one or more branched monohydric alcohols having 1 to 18 carbon atoms and more than a single methyl branch, or one or more straight-chain monohydric alcohols having less than 10 carbon atoms; and one or more vinyl esters of carboxylic acids having 2 to 18 carbon atoms; or

(ii) copolymers of a C₄ to C₆ dicarboxylic acid anhydride and one or more vinyl esters of carboxylic acids having 2 to 18 carbon atoms, esterified with one or more monohydric alcohols having 1 to 18 carbon atoms;

(b) copolymers of one or more alkylacrylates or alkylmethacrylates, where the alkyl groups have 1 to 18 carbon atoms, and acrylic or methacrylic acid;

(c) copolymers of one or more acrylic acids or methacrylic acids and one or more vinyl esters of carboxylic acids having 2 to 18 carbon atoms; and,

(d)

(i) homopolymers of one or more monoesters of an unsaturated C₄ to C₆ dicarboxylic acid with a branched monohydric alcohol having 1 to 18 carbon atoms and more than a single methyl branch, or a straight-chain monohydric alcohol having less than 10 carbon atoms, or

(ii) homopolymers of an C₄ to C₆ dicarboxylic acid anhydride, followed by esterification with one or more monohydric alcohols having 1 to 18 carbon atoms,

said polymeric substance being present in the fuel oil in combination with two or more other cold flow additives selected from the group consisting of: ethylene-unsaturated monomer copolymers; comb polymers; polar nitrogen compounds; polyoxyalkylene compounds and di-block hydrocarbon polymers.

[0013] The preferred two additional cold flow additives are (1) ethylene-unsaturated ester copolymers, particularly a copolymer of ethylene and vinyl acetate or a terpolymer of ethylene, vinyl acetate and vinyl 2-ethylhexanoate, and (2) polar nitrogen compounds, particularly the reaction product of di-hydrogenated tallow amine and phthalic anhydride, or the free amine.

[0014] Suitable dicarboxylic acid anhydrides for use in preparing the copolymer include maleic anhydride, itaconic anhydride and citraconic anhydride, and the like, with maleic anhydride being preferred. Suitable dicarboxylic acids for use in preparing the copolymer include maleic acid, fumaric acid, itaconic acid, and the like, with maleic acid being preferred. Preferred alcohols include those alcohols having 6 to 14 carbon atoms, especially the branched alkanols, with 2-ethylhexanol and isodecyl alcohol being particularly preferred. Mixed esters can also be used.

[0015] The preferred vinyl ester for use in preparing the copolymeric additive is vinyl 2-ethylhexanoate, also preferred are vinyl acetate and the vinyl esters of branched chain carboxylic acids having 9 to 11 carbon atoms. Mixed vinyl esters can also be used.

[0016] Methacrylic and acrylic acids can also be copolymerized with alkylmethacrylates and alkylacrylates, where the alkyl groups are branched or straight chained and include of 1-18 carbon atoms. Again, mixed esters can also be used.

[0017] The copolymers or homopolymers of this invention will have a number average molecular weight (Mn) ranging from about Mn 1,000 to about Mn 20,000, preferably about Mn 2,000 to Mn 8,000. The copolymers will contain about 25 to 75, preferably 40 to 60, most preferably about 50 mole % of dicarboxylic acid half ester or alkylacrylate ester or alkylmethacrylate ester.

[0018] The copolymers or homopolymers of this invention are prepared using conventional synthesis techniques well known in the art. For example, the monoesters of the dicarboxylic acids are polymerized by use of a suitable polymerization initiator, such as an organic perester initiator, at temperatures of about 50 to 120°C in a suitable solvent such as toluene. They can also be prepared by copolymerization or homopolymerization of the dicarboxylic acid anhydrides followed by esterification with a monohydric alcohol.

[0019] In an embodiment, the copolymers or homopolymers of the invention may be post-reacted with one or more amines. Primary, secondary, tertiary and branched amines, including mixtures thereof, are suitable.

[0020] The invention still further provides an additive concentrate comprising a solvent or carrier liquid miscible with fuel oil and the three additive system comprising the copolymer or homopolymer and at least two additional cold flow additives as described above.

[0021] The fuel oil may be, e.g., a petroleum-based fuel oil, especially a middle distillate fuel oil. Such distillate fuel oils generally boil within the range of from 110°C to 500°C, e.g. 150°C to 400°C.

[0022] The invention is applicable to middle distillate fuel oils of all types, including the broad-boiling distillates, i.e., those having a 90%-20% boiling temperature difference, as measured in accordance with ASTM D-86, of 80°C or more.

[0023] 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, hydro-cracking and hydroisomerisation to yield a variety of hydrocarbons such as iso-paraffins, cyclo-paraffins 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 oil, either used alone or in admixture with a petroleum

distillate oil.

[0024] The concentration of the copolymer or homopolymer additives of the invention and each of the additional cold flow additives in the oil may each be in the range of 0.1 to 1,000 ppm of additive (active ingredient) by weight per weight of fuel, preferably 1 to 500 ppm, more preferably 1 to 100 ppm.

[0025] A concentrate comprising the additive dispersed in carrier liquid (e.g. in solution) is convenient as a means of incorporating the additive. The concentrates of the present invention are convenient as a means for incorporating the additives into bulk oil such as distillate fuel, which incorporation may be done by methods known in the art. The concentrates may also contain other additives as required and preferably contain from 3 to 75 wt.%, more preferably 3 to 60 wt.%, most preferably 10 to 50 wt.% of the additives preferably in solution in oil. Examples of carrier liquid are organic solvents including hydrocarbon solvents, for example petroleum fractions such as naphtha, kerosene, diesel and heater oil; aromatic hydrocarbons such as aromatic fractions, e.g. those sold under the 'SOLVESSO' tradename; alcohols and/or esters; and paraffinic hydrocarbons such as hexane and pentane and isoparaffins. Alkylphenols, such as nonylphenol and 2,4-di-t-butylphenol, either alone or in combination with any of the above, have also been found to be particularly useful as carrier solvents. The carrier liquid must, of course, be selected having regard to its compatibility with the additive and with the fuel.

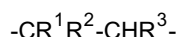
[0026] The additives of the invention may be incorporated into bulk oil by other methods such as those known in the art. If co-additives are required, they may be incorporated into the bulk oil at the same time as the additives of the invention or at a different time.

[0027] The copolymers or homopolymers of this invention are used in fuel oils in combination with two or more conventional cold flow additives as defined in categories (A) - (E) below to achieve enhanced low temperature properties.

(A) Ethylene Polymers

[0028] Each polymer may be a homopolymer or a copolymer of ethylene with another unsaturated monomer. Suitable co-monomers include hydrocarbon monomers such as propylene, n- and iso- butylenes, 1-hexene, 1-octene, methyl-1-pentene vinyl-cyclohexane and the various alpha-olefins known in the art, such as 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene and 1-octadecene and mixtures thereof.

[0029] Preferred co-monomers are unsaturated ester or ether monomers, with ester monomers being more preferred. Preferred ethylene unsaturated ester copolymers have, in addition to units derived from ethylene, units of the formula:



wherein R^1 represents hydrogen or methyl, R^2 represents COOR^4 , wherein R^4 represents an alkyl group having from 1-12, preferably 1-9 carbon atoms, which is straight chain, or, if it contains 3 or more carbon atoms, branched, or R^2 represents OOCR^5 , wherein R^5 represents R^4 or H, and R^3 represents H or COOR^4 .

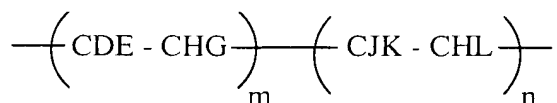
[0030] These may comprise a copolymer of ethylene with an ethylenically unsaturated ester, or derivatives thereof. An example is a copolymer of ethylene with an ester of a saturated alcohol and an unsaturated carboxylic acid, but preferably the ester is one of an unsaturated alcohol with a saturated carboxylic acid. An ethylene-vinyl ester copolymer is advantageous; an ethylene-vinyl acetate, ethylene-vinyl propionate, ethylene-vinyl hexanoate, ethylene-vinyl 2-ethylhexanoate, ethylene-vinyl octanoate or ethylene-vinyl versatate copolymer is preferred. Preferably, the copolymer contains from 5 to 40 wt% of the vinyl ester, more preferably from 10 to 35 wt% vinyl ester. A mixture of two copolymers, for example, as described in US Patent No. 3,961,916, may be used. The M_n of the copolymer is advantageously 1,000 to 10,000. If desired, the copolymer may contain units derived from additional comonomers, e.g. a terpolymer, tetrapolymer or a higher polymer, e.g. where the additional comonomer is isobutylene or diisobutylene or a further unsaturated ester.

(B) A Comb Polymer.

[0031] Comb polymers are discussed in "Comb-Like Polymers. Structure and Properties", N. A. Platé and V. P. Shibaev, J. Poly. Sci. Macromolecular Revs., 8, p 117 to 253 (1974).

[0032] Generally, comb polymers consist of molecules in which long chain branches such as hydrocarbyl branches, optionally interrupted with one or more oxygen atoms and/or carbonyl groups, having from 6 to 30 such as 10 to 20, carbon atoms, are pendant from a polymer backbone, said branches being bonded directly or indirectly to the backbone. Examples of indirect bonding include bonding via interposed atoms or groups, which bonding can include covalent and/or electrovalent bonding such as in a salt. Generally, comb polymers are distinguished by having a minimum molar proportion of units containing such long chain branches.

[0033] As examples of preferred comb polymers there may be mentioned those containing units of the general formula



where

D represents R^{11} , COOR^{10} , OCOR^{10} , $\text{R}^{11}\text{COOR}^{10}$ or OR^{10} ;

E represents H or D;

G represents H or D;

J represents H, R^{11} , $\text{R}^{11}\text{COOR}^{10}$, or a substituted or unsubstituted aryl or heterocyclic group;

K represents H, COOR^{11} , OCOR^{11} , OR^{11} or COOH ;

L represents H, R^{11} , COOR^{11} , OCOR^{11} or substituted or unsubstituted aryl;

R^{10} representing a hydrocarbyl group having 10 or more carbon atoms, and

R^{11} representing a hydrocarbylene (divalent) group in the $\text{R}^{11}\text{COOR}^{10}$ moiety and otherwise a hydrocarbyl (monovalent) group, and m and n represent mole ratios, their sum being 1 and m being finite and being up to and including 1 and n being from zero to less than 1, preferably m being within the range of from 1.0 to 0.4 and n being in the range of from 0 to 0.6. R^{10} advantageously represents a hydrocarbyl group with from 10 to 30 carbon atoms, preferably 10 to 24, more preferably 10 to 18. Preferably, R^{10} is a linear or slightly branched alkyl group and R^{11} advantageously represents a hydrocarbyl group with from 1 to 30 carbon atoms when monovalent, preferably with 6 or greater, more preferably 10 or greater, preferably up to 24, more preferably up to 18 carbon atoms. Preferably, R^{11} , when monovalent, is a linear or slightly branched alkyl group. When R^{11} is divalent, it is preferably a methylene or ethylene group. By "slightly branched" is meant having a single methyl branch.

[0034] The comb polymer may contain units derived from other monomers if desired or required, examples being CO, vinyl acetate and ethylene. It is within the scope of the invention to include two or more different comb copolymers.

[0035] The comb polymers may, for example, be copolymers of maleic anhydride acid and another ethylenically unsaturated monomer, e.g. an α -olefin or an unsaturated ester, for example, vinyl acetate as described in EP-A-214,786. It is preferred but not essential that equimolar amounts of the comonomers be used although molar proportions in the range of 2 to 1 and 1 to 2 are suitable. Examples of olefins that may be copolymerized with e.g. maleic anhydride, include 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, and styrene. Other examples of comb polymers include polyalkyl(meth)acrylates.

[0036] Copolymer may be esterified by any suitable technique and although preferred it is not essential that the maleic anhydride or fumaric acid be at least 50% esterified. Examples of alcohols that may be used include n-decan-1-ol, n-dodecan-1-ol, n-tetradecan-1-ol, n-hexadecan-1-ol, and n-octadecan-1-ol. The alcohols may also include up to one methyl branch per chain, for example, 2-methylpentadecan-1-ol, 2-methyltridecan-1-ol as described in EP-A-213,879. The alcohol may be a mixture of normal and single methyl branched alcohols. It is preferred to use pure alcohols rather than alcohol mixtures such as may be commercially available; if mixtures are used, the number of carbon atoms in the alkyl group is taken to be the average number of carbon atoms in the alkyl groups of the alcohol mixture; if alcohols that contain a branch at the 1 or 2 positions are used, the number of carbon atoms in the alkyl group is taken to be the number in the straight chain backbone segment of the alkyl group of the alcohol.

[0037] The copolymer may also be reacted with a primary and/or secondary amine, for example, a mono- or di-hydrogenated tallow amine.

[0038] The comb polymers may especially be fumarate or itaconate polymers and copolymers such as for example those described in European Patent Applications 153 176, 153 177, 156 577 and 225 688, and WO 91/16407. The comb polymers are preferably C_8 to C_{12} dialkylfumarate-vinyl acetate copolymers.

[0039] Other suitable comb polymers are the polymers and copolymers of α -olefins and esterified copolymers of styrene and maleic anhydride, and esterified copolymers of styrene and fumaric acid as described in EP-A-282,342; mixtures of two or more comb polymers may be used in accordance with the invention and, as indicated above, such use may be advantageous.

[0040] Other examples of comb polymers are hydrocarbon polymers such as copolymers of at least one short chain 1-alkene and at least one long chain 1-alkene. The short chain 1-alkene is preferably a C_3 - C_8 1-alkene, more preferably a C_4 - C_6 1-alkene. The long chain 1-alkene preferably includes greater than 8 carbon atoms and at most 20 carbon

atoms. The long chain 1-alkene is preferably a C₁₀-C₁₄ 1-alkene, including 1-decene, 1-dodecene and 1-tetradecene (see, for example, WO 93/19106). The comb polymer is preferably a copolymer of at least one 1-dodecene and at least one 1-butene in the ratio of 60-90 mole % 1-dodecene to 40-10 mole % 1-butene, preferably in the ratio of 75-85 mole % 1-dodecene to 25-15 mole % 1-butene. Preferably, the comb polymer is a mixture of two or more comb polymers made from a mixture of two or more 1-alkenes. Preferably, the number average molecular weight measured by Gel Permeation Chromatography against polystyrene standards of such a copolymer is, for example, up to 20,000 or up to 40,000, preferably from 4,000 to 10,000, preferably 4,000 to 6,000. The hydrocarbon copolymers may be prepared by methods known in the art, for example using a Ziegler-Natta type, Lewis acid or metallocene catalyst.

(C) Polar Nitrogen Compounds.

[0041] Such compounds are oil-soluble polar nitrogen compounds carrying one or more, preferably two or more, substituents of the formula >NR¹³, where R¹³ represents a hydrocarbyl group containing 8 to 40 atoms, which substituent or one or more of which substituents may be in the form of a cation derived therefrom. The oil soluble polar nitrogen compound is generally one capable of acting as a wax crystal growth inhibitor in fuels. It comprises for example one or more of the following compounds:

[0042] An amine salt and/or amide formed by reacting at least one molar proportion of a hydrocarbyl-substituted amine with a molar proportion of a hydrocarbyl acid having from 1 to 4 carboxylic acid groups or its anhydride, the substituent(s) of formula >NR¹³ being of the formula -NR¹³R¹⁴ where R¹³ is defined as above and R¹⁴ represents hydrogen or R¹³, provided that R¹³, and R¹⁴ may be the same or different, said substituents constituting part of the amine salt and/or amide groups of the compound.

[0043] Ester/amides may be used, containing 30 to 300, preferably 50 to 150, total carbon atoms. These nitrogen compounds are described in US Patent No. 4,211,534. Suitable amines are predominantly C₁₂ to C₄₀ primary, secondary, tertiary or quaternary amines or mixtures thereof but shorter chain amines may be used provided the resulting nitrogen compound is oil soluble, normally containing about 30 to 300 total carbon atoms. The nitrogen compound preferably contains at least one straight chain C₈ to C₄₀, preferably C₁₄ to C₂₄, alkyl segment.

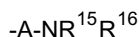
[0044] Suitable amines include primary, secondary, tertiary or quaternary, but are preferably secondary. Tertiary and quaternary amines only form amine salts. Examples of amines include tetradecylamine, cocoamine, and hydrogenated tallow amine. Examples of secondary amines include di-octadecylamine, di-cocoamine, di-hydrogenated tallow amine and methylbehenyl 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 approximately 4% C₁₄, 31% C₁₆, and 59% C₁₈.

[0045] Examples of suitable carboxylic acids and their anhydrides for preparing the nitrogen compounds 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 about 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. The particularly preferred compound is the amide-amine salt formed by reacting 1 molar portion of phthalic anhydride with 2 molar portions of dihydrogenated tallow amine. Another preferred compound is the diamide formed by dehydrating this amide-amine salt.

[0046] Other examples are long chain alkyl or alkylene substituted dicarboxylic acid derivatives such as amine salts of monoamides of substituted succinic acids, examples of which are known in the art and described in US Patent No. 4,147,520, for example. Suitable amines may be those described above.

[0047] Other examples are condensates, for example, those described in EP-A-327427.

[0048] Other examples of polar nitrogen compounds are compounds containing a ring system carrying at least two substituents of the general formula below on the ring system



where A is a linear or branched chain aliphatic hydrocarbylene group optionally interrupted by one or more hetero atoms, and R¹⁵ and R¹⁶ are the same or different and each is independently a hydrocarbyl group containing 9 to 40 atoms optionally interrupted by one or more hetero atoms, the substituents being the same or different and the compound optionally being in the form of a salt thereof. Advantageously, A has from 1 to 20 carbon atoms and is preferably a methylene or polymethylene group. Such compounds are described in WO 93/04148 and WO9407842.

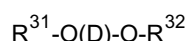
[0049] Other examples are the free amines themselves as these are also capable of acting as wax crystal growth inhibitors in fuels. Suitable amines include primary, secondary, tertiary or quaternary, but are preferably secondary.

Examples of amines include tetradecylamine, cocoamine, and hydrogenated tallow amine. Examples of secondary amines include di-octadecylamine, di-cocoamine, di-hydrogenated tallow amine and methylbehenyl 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 approximately 4% C₁₄, 31% C₁₆, and 59% C₁₈.

(D) A Polyoxyalkylene Compound.

[0050] Examples are polyoxyalkylene esters, ethers, ester/ethers and mixtures thereof, particularly those containing at least one, preferably at least two, C₁₀ to C₃₀ linear alkyl groups and a polyoxyalkylene glycol group of molecular weight up to 5,000, preferably 200 to 5,000, the alkyl group in said polyoxyalkylene glycol containing from 1 to 4 carbon atoms. These materials form the subject of EP-A-0061895. Other such additives are described in United States Patent No. 4,491,455.

[0051] The preferred esters, ethers or ester/ethers are those of the general formula



where R³¹ and R³² may be the same or different and represent

- (a) n-alkyl-
- (b) n-alkyl-CO-
- (c) n-alkyl-O-CO(CH₂)_x- or
- (d) n-alkyl-O-CO(CH₂)_x-CO-

x being, for example, 1 to 30, the alkyl group being linear and containing from 10 to 30 carbon atoms, and D representing the polyalkylene segment of the glycol in which the alkylene group has 1 to 4 carbon atoms, such as a polyoxymethylene, polyoxyethylene or polyoxytrimethylene moiety which is substantially linear; some degree of branching with lower alkyl side chains (such as in polyoxypropylene glycol) may be present but it is preferred that the glycol is substantially linear.

D may also contain nitrogen.

[0052] Examples of suitable glycols are substantially linear polyethylene glycols (PEG) and polypropylene glycols (PPG) having a molecular weight of from 100 to 5,000, preferably from 200 to 2,000. Esters are preferred and fatty acids containing from 10-30 carbon atoms are useful for reacting with the glycols to form the ester additives, it being preferred to use a C₁₈-C₂₄ fatty acid, especially behenic acid. The esters may also be prepared by esterifying polyethoxylated fatty acids or polyethoxylated alcohols.

[0053] These materials may also be prepared by alkoxylation of a fatty acid ester of a polyol (e.g. ethoxylated sorbitan tristearate having the trade name TWEEN 65, which is available from Uniqema).

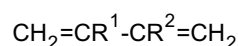
[0054] Polyoxyalkylene diesters, diethers, ether/esters and mixtures thereof are suitable as additives, diesters being preferred for use in narrow boiling distillates, when minor amounts of monoethers and monoesters (which are often formed in the manufacturing process) may also be present. It is preferred that a major amount of the dialkyl compound be present. In particular, stearic or behenic diesters of polyethylene glycol, polypropylene glycol or polyethylene/ polypropylene glycol mixtures are preferred.

[0055] Other examples of polyoxyalkylene compounds are those described in Japanese Patent Publication Nos. 2-51477 and 3-34790, and the esterified alkoxyated amines described in EP-A-117108 and EP-A-326356.

(E) Di-block Hydrocarbon Polymers.

[0056] These polymers may be an oil-soluble hydrogenated block diene polymer comprising at least one crystallizable block, obtainable by ene-to-end polymerization of a linear diene, and at least one non-crystallizable block being obtainable by 1,2-configuration polymerization of a linear diene, by polymerization of a branched diene, or by a mixture of such polymerizations.

[0057] Advantageously, the block copolymer before hydrogenation comprises units derived from butadiene only, or from butadiene and at least one comonomer of the formula



wherein R¹ represents a C₁ to C₈ alkyl group and R² represents hydrogen or a C₁ to C₈ alkyl group. Advantageously,

the total number of carbon atoms in the comonomer is 5 to 8, and the comonomer is advantageously isoprene. Advantageously, the copolymer contains at least 10% by weight of units derived from butadiene.

[0058] In addition, the additive composition may comprise one or more other conventional co-additives known in the art, such as detergents, antioxidants, corrosion inhibitors, dehazers, demulsifiers, metal deactivators, antifoaming agents, cetane improvers, co-solvents, package compatibilizers, lubricity additives and anti-static additives.

EXAMPLES

[0059] The invention will now be particularly described, by way of example only, as follows.

[0060] The cold flow improvement properties of the additives of this invention were evaluated in the two petroleum distillate fuels which are disclosed in Table 1 below.

Table 1

Fuel	A	B
Country	Germany	Germany
Sulphur, wt. %	10 ppm	10 ppm
Density at 15°C (g/l)	0.8294	0.8439
Cloud Point (°C)	-6.3	-4.4
CFPP (°C)	-13	-7.5
ASTM D86 (°C)		
IBP	200.3	203
5%	216.5	222
10%	222.9	233
20%	232.1	250
30%	242.6	261
40%	253.1	270
50%	264.2	280
60%	275.8	291
70%	287.9	303
80%	301.8	317
90%	320.3	334
95%	337.7	347
FBP	352.6	357

[0061] Table 2 below reports the results using Fuel A in the Cold Filter Plugging Point (CFPP) test, the details of which are specified in the European Standard method EN116. The CFPP test is acknowledged as a standard bench test for determining fuel performance at low temperatures and, as such, has been adopted in many national fuel specifications. "ai" means active ingredient, i.e., without regard to solvent or carrier oil and "ppm" is parts per million by weight

[0062] In Table 2 below, "EVX" is a terpolymer of ethylene, vinyl acetate and vinyl 2-ethylhexanoate of Mn 4300; "WASA" is the reaction product of dihydrogenated tallow amine and phthalic anhydride, and the copolymers of varying Mn's in the invention are the isodecyl or 2-ethylhexyl maleic half esters copolymerized with vinyl 2-ethylhexanoate, e. g. "Isodecyl MEVE", as indicated in the Table. The copolymers of the invention consistently improved the CFPP value of the fuel containing only EVX and WASA.

Table 2

Treat Rate (ppm al)							CFPP (°C)
EVX	WASA	Isodecyl MEVE Mn 5694	Isodecyl MEVE Mn 4279	2-Ethylhexyl MEVE Mn 4162	2-Ethylhexyl MEVE Mn 4871	2-Ethylhexyl MEVE Mn 5553	average
240	40						-19.0
270	45						-18.5
300	50						-20.0

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Table 2 (continued)

Treat Rate (ppm al)							CFPP (°C)
EVX	WASA	Isodecyl MEVE Mn 5694	Isodecyl MEVE Mn 4279	2-Ethylhexyl MEVE Mn 4162	2-Ethylhexyl MEVE Mn 4871	2-Ethylhexyl MEVEMn 5553	average
330	55						-20.0
360	60						-19.0
240	40	40					-20.7
270	45	45					-20.5
300	50	50					-26.5
330	55	55					-23.8
360	60	60					-25.0
270	45		45				-23.1
300	50		50				-23.5
330	55		55				-26.5
360	60		60				-27.0
240	40			40			-23.3
270	45			45			-23.0
300	50			50			-27.2
330	55			55			-24.0
360	60			60			-20.5
240	40				40		-21.5
270	45				45		-24.0
300	50				50		-26.4
330	55				55		-24.0
360	60				60		-26.5
240	40					40	-24.4
270	45					45	-20.4
300	50					50	-24.1
330	55					55	-26.5
360	60					60	-25.0

Table 3, which used Fuel B, reports the results of the Aral Short Sediment Test run at -13°C. This test was developed by the German oil company, Aral, and measures the degree of wax settling. The fuel is stored at -13°C for 16 hours and the amount of wax that is judged by eye to have settled out is noted. The bottom 20% of the fuel is then taken and the Cloud Point (CP) of this sample is measured and compared to that of the base fuel. The greater the difference ("delta CP"), the greater the degree of wax settling.

[0063] The additives used in Table 3 were as described in Table 2 except that "PEPEB" is a di-block hydrocarbon polymer of Mn 8000; "FVA" is a copolymer of mixed n-C₁₂ and n-C₁₄ alkyl fumarate and vinyl acetate and "EVA" is an ethylene-vinyl acetate copolymer having 29 wt.% vinyl acetate and "A2HT" is di-hydrogenated tallow amine. Additionally, iC10 PI is a homopolymer of the isodecyl half ester of itaconic acid having a Mn of 2000.

Table 3

Treat Rates (ppm ai)											WAS Test
(EVA)	(EVX)	(PEPEB)	(FVA)	(WASA)	A2Ht	2-Ethylhexyl MEVE Mn 3994	2-Ethylhexyl MEVE Mn 4630	2-Ethylhexyl MEVE Mn 5005	2-Ethylhexyl MEVE Mn 4669	iC10 PI Mn 2000	delta CP (°C)
67	61	12	50	22.5							9.1
67	61	12	50	22.5		22.5					1.9
67	61	12	50	22.5			22.5				1.9
67	61	12	50	22.5				22.5			2.3
67	61	12	50	22.5					22.5		2.1
67	61	12	50	22.5						22.5	2.3
67	61	12	50		22.5						7.1
67	61	12	50		22.5	22.5					2.4
67	61	12	50		22.5		22.5				2
67	61	12	50		22.5			22.5			2

Table 4 below reports additional CFPP data for Fuel A. Six copolymers of the invention were tested. Tested were three copolymers of the 2-ethylhexyl half ester of maleic acid ("2EHMEA") where the comonomers were vinyl esters of branched C₉, C₁₀ and C₁₁ carboxylic acids ("VeoVa9", "VeoVa10" and "VeoVa11") as well as three copolymers each of the isodecyl half ester of maleic acid ("iC10MEA").

Table 4

(EVX)	(WASA)	2EHMEA			iC10MEA			CFPP (°C) average
		VeoVa9 Mn 3550	VeoVa10 Mn 3877	VeoVa11 Mn 4432	VeoVa9 Mn 3099	VeoVa10 Mn 3557	VeoVa11 Mn 4025	
240	40							-19
270	45							-18.5
300	50							-20
330	55							-20
360	60							-19
270	45	45						-19.5
300	50	50						-25.5
330	55	55						-24.5
360	60	60						-24.5
300	50		50					-25
330	55		55					-24.5
360	60		60					-24.5
240	40			40				-20.25
270	45			45				-26.5
330	55			55				-26.5
360	60			60				-25.5
270	45				45			-19
300	50				50			-21.25
330	55				55			-24
360	60				60			-26

Table 4 (cont'd.)

(EVX)	(WASA)	2EHMEA			iC10MEA			CFPP (°C) average
		Veova9 Mn 3550	Veova10 Mn 3877	Veova11 Mn 4432	Veova9 Mn 3099	Veova10 Mn 3557	Veova11 Mn 4025	
240	40					40		-18.5
270	45					45		-19.5
300	50					50		-21
330	55					55		-25.5
360	60					60		-24
240	40						40	-19.5
270	45						45	-20.5
330	55						55	-22
360	60						60	-26.5

Table 5 reports CFPP data for Fuel B wherein the copolymers of the invention have been post-reacted with amines. In the table, "CX" represents a primary amine with X carbon atoms, e.g. C8 = primary C₈ amine.

[0064] Table 6 reports data for the test reported in Table 3 for copolymers of the invention have been post-reacted with amines.

Table 5

2EHMEA/V2EH post reacted with...										
EVX/WASA (ppm/ppm)	C8	C10	C12	C14	C16	dihexylamine	isobutylamine	2ethylhexylamine	CFPP (°C) average	
320/40									-20.0	
320/40	40								-23.5	
320/40		40							-22.8	
320/40			40						-24.5	
320/40				40					-21.0	
320/40					40				-22.3	
320/40						40			-24.0	
320/40							40		-24.5	
320/40								40	-23.0	
	iC10MEA/V2EH+	iC10MEA/VA +..					iC10MEA/V2EH+	2EHMEA/V2EH +...		
	C14	C12	C14	dihexylamine	t- butylamine	C8	dihexylamine	C12	C16	
320/40									-20.0	
320/40	40								-22.0	
320/40		40							-23.0	
320/40			40						-21.8	
320/40				40					-23.0	
320/40					40				-21.0	
320/40						40			-25.0	
320/40							40		-22.5	
320/40								20	20	
320/40								30	30	
320/40								40	40	
320/40									-22.0	

Table 6

EVA	EVX	PEPEB	WASA	FVA	2EHMEA/V2EH post-reacted with...						iC10MEA/VA +...			2EHMEA/V2EH +...		Delta CP (°C)
					C16	C14	C12	C10	C8	C6	C8	C12	C16			
100	125	25	45	30												8.8
100	125	25	45	30	45											2.1
100	125	25	45	30		45										1.6
100	125	25	45	30			45									6.2
100	125	25	45	30				45								6.5
100	125	25	45	30					45							7.0
100	125	25	45	30						45						2.4
100	125	25	45	30							45					1.1
100	125	25	45	30								22.5	22.5	22.5	34	1.9
100	125	25	45	30								34	34	45	45	1.7
100	125	25	45	22.5												3.2
100	125	25	45	22.5	22.5											8.2
100	125	25	45	22.5												2.3
100	125	25	45	22.5		22.5										2.8
100	125	25	45	22.5			22.5									3.4
100	125	25	45	22.5				22.5								6.3
100	125	25	45	22.5					22.5							3.9
100	125	25	45	22.5						22.5						3.7
100	125	25	45	22.5							22.5			22.5		2.9
100	125	25	45	22.5											11.5	1.5
100	125	25	45	22.5										17	17	2.6
100	125	25	45	22.5										22.5	22.5	2.9

Claims

1. A fuel oil composition comprising a fuel oil and a polymeric substance selected from the group consisting of:

(a)

(i) copolymers of one or more monoesters of maleic acid, itaconic acid or citraconic acid with one or more branched monohydric alcohols having 1 to 18 carbon atoms and more than a single methyl branch, or one or more straight-chain monohydric alcohols having less than 10 carbon atoms; and one or more vinyl esters of carboxylic acids having 2 to 18 carbon atoms; or

(ii) copolymers of a C₄ to C₆ dicarboxylic acid anhydride and one or more vinyl esters of carboxylic acids having 2 to 18 carbon atoms, esterified with one or more monohydric alcohols having 1 to 18 carbon atoms;

(b) copolymers of one or more alkylacrylates or alkylmethacrylates, where the alkyl groups have 1 to 18 carbon atoms, and acrylic or methacrylic acid;

(c) copolymers of one or more acrylic acids or methacrylic acids and one or more vinyl esters of carboxylic acids having 2 to 18 carbon atoms; and,

(d)

(i) homopolymers of one or more monoesters of an unsaturated C₄ to C₆ dicarboxylic acid with a branched monohydric alcohol having 1 to 18 carbon atoms and more than a single methyl branch, or a straight-chain monohydric alcohol having less than 10 carbon atoms, or

(ii) homopolymers of an C₄ to C₆ dicarboxylic acid anhydride, followed by esterification with one or more monohydric alcohols having 1 to 18 carbon atoms,

the polymeric substance being present in the fuel oil in combination with two or more cold flow additives selected from the group consisting of: ethylene-unsaturated monomer copolymers; comb polymers; polar nitrogen compounds; polyoxyalkylene compounds and di-block hydrocarbon polymers.

2. The composition of claim 1, wherein the branched alcohol has 6 to 14 carbon atoms.

3. The composition of claims 1 or 2, wherein the vinyl ester is vinyl 2-ethylhexanoate.

4. The composition of any one of the preceding claims, wherein polymeric substance has an Mn of 1,000 to 20,000.

5. The composition of any one of the preceding claims, wherein the alcohol is 2-ethylhexyl alcohol or isodecyl alcohol.

6. The composition of any one of the preceding claims, wherein the polymeric substance is post-reacted with one or more amines.

7. The composition of any one of the preceding claims, wherein the two other cold flow additives are an ethylene-unsaturated monomer copolymer and a polar nitrogen compound.

8. The composition of any one of claims 1 to 7, wherein the polymeric substance is present in an amount of from 0.1 to 1,000 ppm by weight.

9. The composition of any one of claims 1 to 8, wherein the fuel oil is a petroleum based middle distillate boiling in the range of 110 to 500°C.

10. An additive concentrate comprising a solvent miscible with fuel oil and an additive system comprising the polymeric substance and the two or more additional cold flow additives as defined in any one of claims 1 to 7; the two or more additional cold flow additives preferably being an ethylene-unsaturated monomer copolymer and a polar nitrogen compound.

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11. Use of the polymeric substance defined in any one of claims 1 to 6 in combination with two or more cold flow additives selected from the group consisting of: ethylene-unsaturated monomer copolymers, comb polymers, polar nitrogen compounds, polyoxyalkylene compounds, and di-block hydrocarbon polymers, to improve the low temperature properties of a fuel oil.

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Application Number
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