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(54) Title: IMPROVEMENT IN THE COLD FLOW PROPERTIES OF FUELS

(57) Abstract: There is described a method of combating antagonism between a first component, namely a cold flow improver, and a second component, namely a drag reducing agent, in a liquid fuel composition, the antagonism being a reduction in the low temperature benefit achieved by the first component, by including in the fuel composition a third component, namely a compound selected from: a copolymer of one or more alkenes and sulphur dioxide; a copolymer of one or more alkenes with acrylonitrile; a copolymer of alkyl vinyl monomers and cationic monomers; a conductivity improver; and mixtures thereof. Related compositions and uses are also described.



## IMPROVEMENT IN THE COLD FLOW PROPERTIES OF FUELS

5 This invention relates to improvements in fuels, and in fuel additives therefor.

Fuels may require any one or more of a wide range of different chemical additives in order to deliver acceptable performance. Examples include: additives to enhance lubricity and prevent premature wear of engine parts; additives to inhibit corrosion; detergents or dispersants to  
10 keep particulate matter mobile and keep engine parts clean, and prevent sludging; additives to improve conductivity of fuels and reduce the risk of spark hazards; additives to improve the cold temperature operability of fuels; and additives to reduce the drag forces arising when fuels are conveyed by pipeline. A fuel may contain several such additives.

15 The invention derives from the finding that the action of a first additive may be compromised by a second additive; but that a further additive unexpectedly reverses the detrimental effect, at least in part.

The first additive is a cold flow improver (CFI). Certain untreated fuels may freeze, wholly or  
20 partially, under ambient conditions. Freezing can be partial, yet sufficient to cause blocking of fuel filters by wax crystal precipitates. A cold flow improver is added to such a fuel to maintain operability under such conditions. If the effectiveness of the cold flow improver is reduced filter blocking may occur, under cold conditions. We are aware that this has occurred, on occasion, at temperatures which are higher than one would expect from the Cold Filter Plugging Point  
25 (CFPP) value for the given cold flow improver, in the given fuel.

The second additive is a drag reducing agent (DRA). When a liquid fuel is transported through a pipeline, the drag forces resulting from the fluid flow within the pipeline causes a pressure drop increasing with the distance from the point(s) of feeding. Such drag forces lead to high  
30 fluid transportation energy and costs. A drag reducing agent (DRA) is added to a fuel prior to such transportation.

EP-A-0436151 teaches a paraffin dispersant based on a polymer or copolymer comprising structural units of general formula  $-\text{CH}(\text{CO NR}^3\text{R}^4)\text{CH}(\text{COOH})-$  and their use as additives to  
35 middle distillates together with conventional ethylene copolymers as flow improvers and conductivity improvers

US-A-5071445 teaches reaction products of amino alkylene polycarboxylic acids with secondary amines and their use as additives to middle distillates together with conventional ethylene copolymers as flow improvers and conductivity improvers.

- 5 Both EP-A-0436151 and US-A-5071445 teach the benefits of the additive compositions in sedimentation tests in which fuels were stored at temperatures below the cloud point for 24 hours.

10 Drag reducing agents are typically high molecular weight polymers, added to fuel prior to transportation by pipeline. The drag reducing agent is used in fuel to reduce energy losses resulting in lower energy costs and/or to increase throughput of fuel through the pipeline. It is well known that during use, the drag reducing agent polymer can degrade and lose its effectiveness. This may occur simply because of the shear forces experienced in the pipeline or more particularly due to the shear forces experienced as the fuel containing drag reducing  
15 agent passes through pumps. It is common practice when pipelines have more than one pump along the length of the pipeline that the drag reducing agent is injected after each pumping station. Treat rates of the drag reducing agent tend to be optimised to match the operating conditions of the pipeline so that the drag reducing effectiveness is experienced throughout the whole length of the pipeline but avoiding unnecessary overtreatment of the  
20 drag reducing agent. Development of drag reducing agents which are more resistant to shear degradation has also taken place.

We have found that the drag reducing agent sometimes reduces the effectiveness of the cold flow improver. We have also found that in some circumstances this antagonism may be  
25 absent when the fuel has been subjected to high shear. It is thought that the high shear may destroy the drag reducing agent or reduce the molecular weight to one that no longer causes antagonism with the cold flow improver.

Nevertheless, there are circumstances when the drag reducing agent is present in the fuel in  
30 sufficient quantities to have an antagonistic effect on the cold flow improver, and it would be useful to be able to treat or prevent this antagonism through use of an additive.

Antagonism between one additive and another additive is known.

35 For example EP-A-1932899 describes a problem wherein a particular polyamine detergent was antagonistic towards a polar nitrogen compound effective as a wax anti-settling additive. Specifically, it was observed that the presence of high levels of polyamine detergent species 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 from an

engine cleanliness viewpoint, its low temperature properties, in terms of wax anti-settling and cold filter plugging point (CFPP) may not be adequate. In EP-A-1932899, a solution to this antagonism was to add to the composition at least one organic acid such as a fatty acid or neodecanoic acid.

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EP-A-2162512 recognises the same problem as EP-A-1932899 but solves the problem in a different way, by the addition of a substantially linear hydrocarbon having at least 20 carbon atoms such as mixtures of n-paraffins having 26-30 carbon atoms

10 This invention concerns the finding of an antagonism between drag reducing agents and cold flow improvers; and the combating of this antagonism.

The present invention is predicated on the discovery that a drag reducing agent may reduce the effectiveness of a cold flow improver in a fuel; and on the devising of a solution, enabling a  
15 cold flow improver and a drag reducing agent to be used together, with assurance that the intended level of cold weather performance will be provided.

Thus, it is an object of preferred aspects of the present invention to provide fuel compositions containing a cold flow improver and a drag reducing agent, in which both additives are  
20 effective.

The present invention is defined and explained with particular reference (but not exclusively) to Cold Filter Plugging Point values – CFPP. At certain low temperatures wax crystals will form and reach a size and shape in sufficient quantity to plug fuel lines, screens, and filters even  
25 though the fuel will physically flow. These problems are well recognized in the art and have a number of recognised test methods. The method we use herein defines CFPP in accordance with the DIN EN 116 standard test.

In accordance with a first aspect of the present invention there is provided a method of  
30 combating antagonism between a first component, namely a cold flow improver, a second component, namely a drag reducing agent, in a liquid fuel composition, the antagonism being a reduction in the low temperature benefit achieved by the first component;  
by including in the fuel composition a third component, namely an additive selected from: a copolymer of one or more alkenes and sulphur dioxide; a copolymer of one or more alkenes  
35 with acrylonitrile; a copolymer of alkyl vinyl monomers and cationic monomers; a conductivity improver; and mixtures thereof.

It should be noted, in considering the present invention, that EP-A-0436151 and US-A-5071445 contain examples in which CFPP tests before storage show that fuel compositions

comprising conductivity improvers sometimes showed a worse CFPP, sometimes showed the same CFPP and sometimes showed a better CFPP than the fuels absent the conductivity improver.

- 5 Neither EP-A-0436151 nor US-A-5071445 disclose or otherwise address any antagonism between drag reducing agents and cold flow improvers. Neither patent teaches any method of combating the antagonism between drag reducing agents and cold flow improvers.

10 The first component has a benefit on the cold temperature properties of the fuel, when added to the fuel; that is the function of a cold flow improver. However when a second component is also present the benefit is reduced or entirely lost, or the cold temperature properties of the fuel may be even worse than that of the base fuel, and the fuel is at risk of causing filter blocking when this would not normally be expected.

15 It should be noted that in the definition above, and throughout this specification, where comparisons are made between fuel compositions containing any of the first, second or third components, the identical base fuel and first, second or third components are used, and the concentrations of the first, second or third components are the same, between the compared samples, except where expressly stated otherwise.

20

Antagonism may be described as the reduction in the effectiveness of the first component, when the second component is also present. More specifically antagonism may be described as the situation wherein the cold temperature properties of the fuel comprising the first and second components are poorer than the cold temperature properties of the fuel comprising the first component without the second component.

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In accordance with a second aspect of the present invention there is provided a liquid fuel composition comprising a base fuel, a first component, namely a cold flow improver, a second component, namely a drag reducing agent, and a third component as defined above in the first aspect of the invention;

30

wherein the cold temperature properties of a first reference fuel composition which comprises the base fuel and the first component are better than those of the base fuel;

wherein the cold temperature properties of a second reference fuel composition which comprises the base fuel, the first component and the second component are worse than those of the first reference fuel composition;

35

wherein the cold temperature properties of said liquid fuel composition which comprises the base fuel, the first component, the second component and the third component are better than those of the second reference fuel composition.

It will be appreciated that the term "reference fuel" is commonly used in the industry to mean a specific fuel of known characteristics used to provide repeatable results in fuel tests. However, throughout this specification, the terms "first reference fuel composition", "second reference fuel composition", "third reference fuel composition" etc. are used only as a convenient description of fuels comprising certain components and absent other components. This means of description does not imply that these fuels are Reference Fuels as the term is commonly used in the industry.

Cold temperature properties may be defined by any convenient measure, for example cloud point, pour point or cold filter plugging point (CFPP). The inventors favour CFPP for the assessment of the invention and for convenience the references which follow are to CFPP, determined by the DIN EN 116 test protocol.

The definitions which follow may be applied to the different aspects of the present invention.

The following terminology applies, in relation to all aspects:

- first CFPP : of the base fuel without the first component, the second component or third component ("base fuel")
- second CFPP : of the fuel with the first component, but without the second component and without the third component ("first reference fuel composition")
- third CFPP : of the fuel with the first component and the second component, but without the third component ("second reference fuel composition")
- fourth CFPP : of the fuel with the first component, the second component and the third component ("liquid fuel composition" or "liquid fuel composition of the invention" or "target fuel composition")
- fifth CFPP: of the fuel with the third component and the first component but without the second component ("third reference fuel composition").

A fuel composition referred to in the first aspect of the present invention or provided by the second aspect preferably has the following characteristics:

- the second CFPP is lower than the first CFPP;
- the third CFPP is higher than the second CFPP;
- the fourth CFPP is lower than the third CFPP.

Further definitions which may be useful to describe the present invention, in the first aspect, the second aspect or any further aspect defined herein are:-

- the difference between the fourth CFPP and the third CFPP – which difference we call  $\Delta\text{CFPP}_{\text{INV}}$  herein (for  $\Delta\text{CFPP}_{\text{INVENTION}}$ ) – is the benefit provided by the third

component when used in a fuel composition which contains the base fuel, the first component and the second component. This is the benefit of the invention.

- the difference between the fifth CFPP and the second CFPP – which we call  $\Delta\text{CFPP}_2$  herein - is the benefit (if any) provided by the third component when used in a fuel composition which contains the base fuel and the first component. In the absence of the second component any benefit would be a cold flow benefit attributed to the third component, in addition to that of the first component.

In preferred embodiments, the fuel composition referred to in the first aspect of the present invention or provided by the second aspect preferably has the following characteristics:

- $\Delta\text{CFPP}_{\text{INV}}$  is greater than  $\Delta\text{CFPP}_2$ . Preferably  $\Delta\text{CFPP}_{\text{INV}}$  is greater than  $\Delta\text{CFPP}_2$  by at least 1°C, more preferably at least 2°C preferably at least 3°C.

In some preferred embodiments,  $\Delta\text{CFPP}_2$  is zero.

A fuel composition referred to in the first aspect of the present invention or provided by the second aspect preferably has the following characteristics:

- the base fuel alone, without the first component, the second component and the third component, has a first CFPP;
- a first reference fuel composition comprising the base fuel and the first component, but without the second component and the third component, has a second CFPP, which is lower than the first CFPP;
- a second reference fuel composition comprising the base fuel, the first component, and the second component, but without the third component, has a third CFPP, which is higher than the second CFPP;
- said liquid fuel composition comprising the base fuel, the first component, the second component, and the third component, has a fourth CFPP, which is lower than the third CFPP.

A fuel composition referred to in the first aspect of the present invention or provided by the second aspect preferably has the following characteristics:

- a third reference fuel composition comprising the base fuel, the first component, and the third component, but without the second component, has a fifth CFPP; and
- the difference between the fourth CFPP and the third CFPP is greater than the difference between the fifth CFPP and the second CFPP.

The third component provides a low temperature performance benefit when added to a second reference fuel composition herein, in which the benefit of the first component has been

reduced or removed by the second component. In fuel compositions of the present invention, this benefit of the third component is significantly greater than any benefit that may be seen when the third component is added in the absence of the second component. In some embodiments, the third component provides substantially no low temperature performance benefit, or only a small low temperature performance benefit, when the second component is absent.

Accordingly we believe that the second component is implicated in the problem the invention seeks to address, and that the third component combats the negative action of the second component. If the third component also has some effect on the cold flow performance in the absence of the second component, then this effect is not relevant to the present invention. To avoid any misunderstanding we state that the effect of the invention as defined herein is larger than the effect (if any) on the cold flow performance in the absence of the second component. We believe the third component exerts its beneficial influence in a particular circumstance, where a second component is acting as an antagonist, compromising the behaviour of the first component.

Thus the fuel composition referred to in the first aspect of the present invention or provided by the second aspect preferably has the following characteristics

- there is an improvement in low temperature properties of the fuel composition comprising the first, second and third components compared to the fuel composition absent the third component
- and the improvement is greater than would be expected from measurement of low temperature properties of the fuel composition comprising the first and third components and absent the second component compared to the fuel composition comprising the first component and absent the second and third components.

Preferably the CFPP of the third reference fuel composition is within  $\pm 4^{\circ}\text{C}$  of the CFPP of the first reference fuel, preferably within  $\pm 2^{\circ}\text{C}$ , most preferably within  $\pm 1^{\circ}\text{C}$ .

In accordance with a third aspect of the present invention there is provided a combination of fuel composition components, comprising a liquid base fuel which has a first CFPP; a first component which is a cold flow improver; a second component which is a drag reducing agent; and a third component which is a third component as defined in the first aspect of the invention;

wherein:

the base fuel has a first CFPP;

a first reference fuel composition provided by addition of the first component to the base fuel has a second CFPP, lower than the first CFPP;



a second reference fuel composition provided by addition of the second component to the first reference fuel composition has a second CFPP, higher than the third CFPP, higher than the second CFPP;

5 a target fuel composition provided by addition of the third component to the second reference fuel composition has a fourth CFPP, lower than the third CFPP.

10 In accordance with a fourth aspect of the present invention there is provided the use of a third component as defined in the first aspect of the invention to reduce the CFPP of a fuel composition which contains a first component which is a cold flow improver and a second component which is a drag reducing agent.

15 In accordance with a fifth aspect of the present invention there is provided the use of a third component as defined in the first aspect of the invention, to reduce the CFPP of a fuel which contains a first component, namely a cold flow improver, and a second component, namely a drag reducing agent, and whose CFPP, absent the third component, has been raised by the presence of the second component.

20 In accordance with a sixth aspect of the present invention there is provided a method of reducing the CFPP of a fuel composition containing a first component, namely a cold flow improver, and a second component, namely a drag reducing agent, by addition of a third component as defined in the first aspect of the invention.

25 The invention may therefore logically be defined and examined in terms of the sequenced addition of these additives, to assess (1) the effect of adding the first component to the base fuel, (2) the effect, subsequently, of adding the second component, and (3) the effect, subsequently, of adding the third component.

30 However in the actual practice of the invention these additives can be added in any order, or together (including as an additive package containing two or three of the first component, the second component, and third component; and if wished further additive compounds providing other functional benefits).

35 The invention concerns the use of a cold flow improver to lower the CFPP of a fuel composition; the use of a the drag reducing agent to achieve drag reduction; its propensity to sometimes give rise to detrimental antagonism towards the CFPP, thereby compromising the cold flow properties of the fuel composition; and the use of a third component to counteract such antagonism, when it arises.

As noted above, the antagonism between the drag reducing agent (second component) and the cold flow improver (first component) does not always occur. The intermittent nature of the problem is not fully understood. One reason for the intermittent nature may be that high shear experienced in use may destroy the drag reducing agent or reduce the molecular weight to one that no longer causes antagonism with the cold flow improver. There may be other reasons.

In some situations the third component may be added after the fuel has left the pipeline and the antagonism has been observed or in the knowledge that it will be needed to combat this antagonism, for example in a fuel composition which is not expected to undergo high shear forces in pipeline transportation. On other occasions it may be added as a preventive or precautionary measure.

The fuel compositions to which the present invention relates are intended to be sold in regions which may experience cold weather, such that the first CFPP (that of the base fuel only) is too high to provide assurance that there will not be problems in the field, arising from blocking of fuel filters by wax crystals. For guidance, the first CFPP, of a typical base fuel, may typically be in the range +10°C to -10°C. However the absolute value of the first CFPP is not of significance in the present invention.

The second CFPP is indicative of a desired effect (the intended effect of the first component). The second CFPP is preferably at least 4°C lower than the first CFPP, preferably at least 6°C lower, and in especially preferred cases, at least 8°C lower. The second CFPP may typically be up to 20°C lower than the first CFPP, but could be still lower.

The third CFPP is indicative of the unwanted side-effect which may be caused by the DRA. The third CFPP may be at least 2°C higher, preferably at least 4°C higher, preferably at least 6°C higher, than the second CFPP. In some embodiments it may be at least 12°C higher. The third CFPP may be up to 20°C higher than the second CFPP or higher still.

The third CFPP may in some embodiments be higher than the first CFPP and in such cases it appears that the second component is not only counteracting the CFPP-lowering effect of the first component but is having some further detrimental effect, not yet understood. In general, it is found that the third CFPP is in the range from 10°C lower than the first CFPP to 14°C higher (but in all cases higher than the second CFPP).

The fourth CFPP is indicative of the advantageous effect of the third component. The fourth CFPP is preferably at least 2°C lower, preferably at least 4°C lower, than the third CFPP,

preferably at least 6°C lower, more preferably at least 8°C lower. Typically the fourth CFPP may be up to 20°C lower than the third CFPP, or lower still.

5 The fourth CFPP is preferably within  $\pm 6^\circ\text{C}$ , of the second CFPP, more preferably within  $\pm 4^\circ\text{C}$ , more preferably within  $\pm 2^\circ\text{C}$ .

10 In the following definitions of additive concentrations and ratios of additives, weights of active materials are referenced. When there is more than one cold flow improver, or drag reducing agent, or third component the definitions refer to the summated amount thereof.

Preferably the concentration of the cold flow improver (or first component) in the fuel composition is at least 10 ppm, preferably at least 25 ppm, preferably at least 50 ppm, preferably at least 100 ppm, preferably at least 150 ppm, and in some preferred embodiments at least 200 ppm.

15 Preferably the concentration of the first component in the fuel composition is up to 10,000 ppm, preferably up to 2000 ppm, preferably up to 1200 ppm, preferably up to 800 ppm.

20 Preferably the concentration of the drag reducing agent (or second component) in the fuel composition is at least 0.1 ppm, preferably at least 1 ppm, preferably at least 8 ppm, preferably at least 12 ppm.

25 Preferably the concentration of the second component in the fuel composition is up to 1,000 ppm, preferably up to 500 ppm, preferably up to 200 ppm, preferably up to 150 ppm, preferably up to 100 ppm. In particularly preferred embodiments, the concentration of the second component in the fuel composition is up to 80 ppm, preferably up to 60ppm, preferably up to 50ppm, preferably up to 40ppm.

30 Preferably the concentration of the third component in the fuel is at least 0.1 ppm, preferably at least 0.5 ppm, preferably at least 2 ppm, preferably at least 5 ppm.

Preferably the concentration of the third component in the fuel composition is up to 400 ppm, preferably up to 200 ppm, preferably up to 150 ppm.

35 Preferably the ratio of the second component to the first component is in the range 1 part second component to 2-100 parts first component, preferably 5-50 parts first component, preferably 10-30 parts first component.

Preferably the ratio of the third component to the first component is in the range 1 part third component to 1-200 parts first component, preferably 2-100 parts first component, preferably 4-60 parts first component.

- 5 Preferably the ratio of the third component to the second component is in the range 1 part third component to 0.1 - 30 parts second component, preferably 0.1-10 parts second component, preferably 0.2-6 parts second component.

10 Unless otherwise stated the concentrations and ratios are of active compounds, e.g. active cold flow improver content.

#### First component

Cold flow improvers of interest in the present invention include:

- 15 1. copolymers of ethylene and olefinically unsaturated compounds  
2. oil-soluble polar nitrogen compounds  
20 3. alkylphenol-aldehyde resins  
4. comb polymers  
5. oil-soluble polyoxyalkylene compounds  
25 6. hydrogenated polymers of alkenes

#### **1. Copolymers of ethylene and olefinically unsaturated compounds**

30 Preferred copolymers of ethylene and olefinically unsaturated compounds are those which, in addition to ethylene, contain 1 to 22 mol %, preferably 8 to 21 mol %, especially 9 to 18 mol %, of olefinically unsaturated compounds as co-monomers.

35 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.

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



40

where R<sup>1</sup> is C1- to C30-alkyl, preferably C4- to C16-alkyl, especially C6- to C12-alkyl. In a further embodiment, the alkyl groups mentioned may be substituted by one or more hydroxyl groups.

In a further preferred embodiment, R<sup>1</sup> is a branched alkyl radical or a neoalkyl radical having 7 to 11 carbon atoms, especially having 8, 9 or 10 carbon atoms. Particularly preferred vinyl esters derive from secondary and especially tertiary carboxylic acids whose branch is in the alpha-position to the carbonyl group. Suitable vinyl esters include vinyl acetate, vinyl propionate, vinyl butyrate, vinyl isobutyrate, 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.

In a further preferred embodiment, these ethylene copolymers contain vinyl acetate and at least one further vinyl ester of the formula 1 where R<sup>1</sup> is C4- to C30-alkyl, preferably C4- to C16-alkyl, especially C6- to C12-alkyl.

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



where R<sup>2</sup> is hydrogen or methyl and R<sup>3</sup> 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.

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



where R<sup>4</sup> 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.

Apart from ethylene, particularly preferred terpolymers contain 1 to 22 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 %. Further particularly preferred copolymers contain, in addition to 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.

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.

## 2. Oil-soluble polar nitrogen compounds

These are preferably reaction products of fatty amines with compounds which contain an acyl group.

Particularly useful oil-soluble polar nitrogen compounds are those which are obtained by reaction of aliphatic or aromatic amines, preferably long-chain aliphatic amines, with aliphatic or aromatic mono-, di-, tri- or tetracarboxylic acids or their anhydrides (cf. U.S. Pat. No. 4,211,534). Equally suitable as oil-soluble polar nitrogen compounds are amides and ammonium salts of aminoalkylenepolycarboxylic acids such as nitrilotriacetic acid or ethylenediamine-tetraacetic acid with secondary amines (cf. EP-A-0 398 101). Other oil-soluble polar nitrogen compounds are copolymers of maleic anhydride and  $\alpha,\beta$ -unsaturated compounds which may optionally be reacted with primary monoalkylamines and/or aliphatic alcohols (cf. EP-A-0 154 177, EP-A-0 777 712), the reaction products of alkenyl-spiro-bis lactones with amines (cf. EP-A-0 413 279 B1) and, according to EP-A-0 606 055 A2, reaction products of terpolymers based on  $\alpha,\beta$ -unsaturated dicarboxylic anhydrides,  $[\alpha], [\beta]$ -unsaturated compounds and polyoxyalkylene ethers of lower unsaturated alcohols. Preferred examples of polar nitrogen compounds include reaction products of: dodecenyl-spiro-bis lactone with a mixture of tallow fatty amines; terpolymers of C14/C16  $\alpha$  olefin, maleic anhydride and allyl polyglycols with di tallow fatty amine; phthalic anhydride with 2 equivalents of di (hydrogenated tallow fatty) amine; and EDTA with 4 equivalents of di tallow fatty amine.

### 3. Alkylphenol-aldehyde resins

These are especially those alkylphenol-aldehyde resins which derive from alkylphenols having one or two alkyl radicals in ortho and/or para positions to the OH group. Particularly preferred starting materials are alkylphenols which bear, on the aromatic ring, at least two hydrogen atoms capable of condensation with aldehydes, and especially monoalkylated phenols. The alkyl radical is more preferably in the para-position to the phenolic OH group. The alkyl radicals (for constituent V, this refers generally to hydrocarbon radicals as defined below) may be the same or different in the alkylphenol-aldehyde resins usable in the process according to the invention, they may be saturated or unsaturated and have preferably 1-20, especially 4-16, for example 6-12, carbon atoms; they are preferably n-, iso- and tert-butyl, n- and isopentyl, n- and isohexyl, n- and isooctyl, n- and isononyl, n- and isodecyl, n- and isododecyl, tetradecyl, hexadecyl, octadecyl, tripropenyl, tetrapropenyl, poly(propenyl) and poly(isobutenyl) radicals. In a preferred embodiment, the alkylphenol resins are prepared by using mixtures of alkylphenols with different alkyl radicals. For example, resins based firstly on butylphenol and secondly on octyl-, nonyl- and/or dodecylphenol in a molar ratio of 1:10 to 10:1 have been found to be particularly useful.

### 4. Comb polymers

Suitable comb polymers are, for example, copolymers of ethylenically unsaturated dicarboxylic acids, such as maleic acid or fumaric acid, with other ethylenically unsaturated monomers, such as olefins or vinyl esters, for example vinyl acetate. Particularly suitable olefins in this context are  $\alpha$ -olefins having 10 to 20 and especially 12 to 18 carbon atoms, for example 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and mixtures thereof. Longer-chain olefins based on oligomerized C2-C6-olefins, for example poly(isobutylene) having a high content of terminal double bonds, are also suitable as co-monomers. Typically, these copolymers are esterified to an extent of at least 50% with alcohols having 10 to 20 and especially 12 to 18 carbon atoms. Suitable alcohols include n-decan-1-ol, n-dodecan-1-ol, n-tetradecan-1-ol, n-hexadecan-1-ol, n-octadecan-1-ol and mixtures thereof. Particular preference is given to mixtures of n-tetradecan-1-ol and n-hexadecan-1-ol. Likewise suitable as comb polymers are poly(alkyl acrylates), poly(alkyl methacrylates) and poly(alkyl vinyl ethers) which derive from alcohols having 10 to 20 and especially 12 to 18 carbon atoms, and poly(vinyl esters) which derive from fatty acids having 10 to 20 and especially 12 to 18 carbon atoms.

## 5. Oil-soluble polyoxyalkylene compounds

Additionally suitable as flow improvers are oil-soluble polyoxyalkylene compounds for example esters, ethers and ether/esters of polyols, which bear at least one alkyl radical having 12 to 30 carbon atoms. In a preferred embodiment, the oil-soluble polyoxyalkylene compounds possess at least 2, for example 3, 4 or 5, aliphatic hydrocarbon radicals. These radicals preferably independently possess 16 to 26 carbon atoms, for example 17 to 24 carbon atoms. These radicals of the oil-soluble polyoxyalkylene compounds are preferably linear. Additionally preferably, they are very substantially saturated, and are especially alkyl radicals. Esters are particularly preferred.

Polyols which are particularly suitable in accordance with the invention are polyethylene glycols, polypropylene glycols, polybutylene glycols and copolymers thereof with a molecular weight of approx. 100 to approx. 5000 g/mol, preferably 200 to 2000 g/mol. In a particularly preferred embodiment, the oil-soluble polyoxyalkylene compounds derive from polyols having 3 or more OH groups, preferably from polyols having 3 to about 50 OH groups, for example 4 to 10 OH groups, especially from neopentyl glycol, glycerol, trimethylolethane, trimethylolpropane, sorbitan, pentaerythritol, and the oligomers which are obtainable therefrom by condensation and have 2 to 10 monomer units, for example polyglycerol. Also suitable as polyols are higher polyols, for example sorbitol, sucrose, glucose, fructose and oligomers thereof, for example cyclodextrin, provided that the esterified or etherified alkoxylates thereof are oil-soluble at least in application-relevant amounts. Preferred polyoxyalkylene compounds thus have a branched polyoxyalkylene core to which a plurality of alkyl radicals which impart oil solubility are bonded.

Particularly preferred polyoxyalkylene compounds derive from polyols having 3, 4 and 5 OH groups, which bear about 5 to 10 mol of structural units derived from ethylene oxide per hydroxyl group of the polyol and are very substantially completely esterified with very substantially saturated C17-C24 fatty acids. Further particularly preferred polyoxyalkylene compounds are polyethylene glycols which have been esterified with very substantially saturated C17-C24 fatty acids and have molecular weights of about 350 to 1000 g/mol. Examples of particularly suitable polyoxyalkylene compounds are polyethylene glycols which have been esterified with stearic acid and especially behenic acid and have molecular weights between 350 and 800 g/mol; neopentyl glycol 14-ethylene oxide distearate (neopentyl glycol which has been alkoxylated with 14 mol of ethylene oxide and then esterified with 2 mol of stearic acid) and especially neopentyl glycol 14-ethylene oxide dibehenate; glycerol 20-ethylene oxide tristearate, glycerol 20-ethylene oxide dibehenate and especially glycerol 20-ethylene oxide tribehenate; trimethylolpropane 22-ethylene oxide tribehenate; sorbitan 25-ethylene oxide tristearate, sorbitan 25-ethylene oxide tetrastearate, sorbitan 25-ethylene oxide



tribehenate and especially sorbitan 25-ethylene oxide tetrabenhenate; pentaerythritol 30-ethylene oxide tribehenate, pentaerythritol 30-ethylene oxide tetrastearate and especially pentaerythritol 30-ethylene oxide tetrabenhenate and pentaerythritol 20-ethylene oxide 10-propylene oxide tetrabenhenate.

5

## 6. Hydrogenated polymers of alkenes

Additionally suitable as flow improvers are certain hydrogenated polymers of alkenes. The alkenes may suitably be conjugated diene compounds. Hydrogenated polymers of butadiene are especially preferred.

10

Cold flow improvers of the present invention (the first component) preferably comprise copolymers of ethylene and olefinically unsaturated compounds as described above. In some preferred embodiments, the first component additionally comprises one or more of oil soluble polar nitrogen compounds; alkylphenol aldehyde resins; comb polymers; oil soluble polyoxyalkylene compounds; and hydrogenated polymers of alkenes; as described above.

15

Preferably the first component does not comprise a combination of ethylene vinyl propionate copolymers with nitrilotriacetic acid triamides.

20

### Second component

Drag reducing agents are well known in the prior art and are typically high molecular weight, noncrystalline, hydrocarbon soluble polymers.

Preferably the drag reducing agent is selected from polymers (including homopolymers and copolymers) of olefins, in particular very high molecular weight, hydrocarbon soluble polymers of C<sub>4</sub>-C<sub>30</sub>- $\alpha$ -olefins

25

Generally, highly favourable results are observed when the drag reducing polymers are prepared from alpha-monoolefins having 6 to about 20 carbon atoms, in the case of homopolymer preparation, and 4 to about 20 carbon atoms, in the case of copolymer preparation. Such monomers often are preferred since they are easily polymerized to high molecular weight polymers under liquid state polymerization conditions. For the preparation of homopolymers the most preferred monomers are those containing 6 to 16 carbon atoms. For the preparation of copolymers the process may suitably be practiced using butene-1 and at least one other alpha-monoolefin having 5 to 16 carbon atoms.

30

35

Typical molecular weights are > 1million, more typically >5 million. In the prior art, inherent viscosity is sometimes used to characterise the molecular weight of the polymers with typical values being >10 dL/g or as high as 25 dL/g

- 5 Drag reducing agents tend to have very high viscosity and be very difficult to handle. Polymers may be prepared by many methods for example bulk polymerisation, solution polymerisation, emulsion polymerisation. In some cases, the polymerisation is terminated at relatively low conversion for example < 20% to achieve high molecular weight. The drag  
10 reducing agent may be supplied as a solution, or a gel, but more commonly as a suspension of the high molecular weight polymer in a suitable dispersion medium. Much prior art exists on the preparation of drag reducing agents exists for example US6399676, US6172151, US5449732, US4845178, US4433123, US4584244, US4720397; US4826728, US4837249 and EP1335941, the entire teachings of which are incorporated herein by reference.

15 Third component

- Suitable compounds for use as a third component are selected from: copolymers of one or more alkenes and sulphur dioxide; copolymers of one or more alkenes with acrylonitrile; copolymers of alkyl vinyl monomers and cationic monomers; conductivity improvers (which may include compounds defined above, and may embrace further compounds); and mixtures  
20 thereof.

A preferred compound for use as a third component comprises a copolymer of one or more alkenes and sulphur dioxide, referred to as a polysulphone.

- 25 A polysulphone used in this invention can be prepared by the methods known in the art (see for example, Encyclopaedia of Polymer Science and Technology Vol. 9, Interscience Publishers, page 460 et seq.) or by known processes such as those described in US 3917466, US 4416668 and US 2010/072427.

- 30 A polysulphone used in this invention is suitably of the structure  $-R-SO_2-R-SO_2-R-SO_2-R-$  where R represents an alkene-derived moiety.

- Preferred alkenes are one or more linear or branched 1-alkenes having from 2 to 36 carbon atoms. Typically, the copolymers (polysulphones) are alternating 1:1 copolymers in which one  
35 sulphone unit generally follows one alkene unit; it is also possible for sequences of two or more alkene units to occur in small amounts. Some of the alkene monomers may be replaced by ethylenically unsaturated carboxylic acids (e.g. acrylic acid, methacrylic acid or vinylacetic acid) or ethylenically unsaturated dicarboxylic acids (e.g. maleic acid or fumaric acid) or derivatives thereof (e.g. maleic anhydride), so that the copolymer of component (A) is formed

especially from 50 mol % of sulphur dioxide or sulphone units, from 40 to 50 mol % of alkene units and from 0 to 10 mol % of units from said ethylenically unsaturated carboxylic acids, ethylenically unsaturated dicarboxylic acids or derivatives thereof.

- 5 Useful branched and especially linear 1-alkenes having from 2 to 36 carbon atoms include, for example, ethene, propene, 1-butene, 2-butene, isobutene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 1-heneicosene, 1-docosene, 1-tricosene, 1-tetracosene or mixtures thereof. Particular  
10 preference is given to linear 1-alkenes having from 6 to 16 carbon atoms, especially having from 8 to 14 carbon atoms, or linear 1-alkenes having from 12 to 22 carbon atoms, especially from 14 to 20 carbon atoms, and also mixtures thereof, for example a mixture of 1-dodecene and 1-tetradecene. It may also be advantageous to use mixtures of low molecular weight and high molecular weight 1-alkenes, i.e. 1-alkene mixtures with a bimodal distribution, for example  
15 mixtures of 1-alkenes having from 6 to 13 carbon atoms and 1-alkenes having from 14 to 20 carbon atoms, or mixtures of 1-alkenes having from 6 to 10 carbon atoms and 1-alkenes having from 11 to 15 carbon atoms, or mixtures of 1-alkenes having from 2 to 24 carbon atoms and a single 1-alkene having from 4 to 10 carbon atoms. A particularly preferred alkene is 1-decene.

20

In one preferred embodiment, the weight average molecular weight of the polysulphone is preferably in the range from about 1,000 to 1,500,000, with the preferred range being from about 10,000 to 990,000, and the most preferred molecular weights being in the range from about 100,000 to 500,000.

25

In another preferred embodiment, the number average molecular weight of the polysulphone is preferably in the range from 2,000 to 1,000,000, especially from 4,000 to 100,000, in particular from 6,000 to 25,000.

- 30 The molecular weight of a polysulphone used herein may be determined by any suitable method, for example by light scattering or by determination of the inherent viscosity as described in US 3917466 or by gel permeation chromatography.

- In another embodiment, a preferred compound for use as a third component comprises a  
35 copolymer of one or more alkenes and acrylonitrile. In such an embodiment the preferred alkenes are as described for polysulphones. The copolymer may be prepared by a variety of known methods such as those described by Gaylord et al, *Macromolecules*, Vol. 2, page 442, et seq. 1969, and Ikegami et al., *Journal of Polymer Science, Part A-5*, Vol. 8, pages 195-208 (1970).

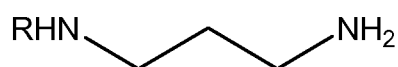
In another embodiment, a preferred compound for use as a third component comprises a copolymer of alkyl vinyl monomers and cationic monomers. Such copolymers are as described in US5672183. Preferred alkyl vinyl monomers are vinyl esters, acrylic esters, methacrylic esters and alkyl vinyl ethers such as alkyl (meth)acrylates having C1-C30 preferably C4-C16 alkyl groups. Preferred cationic monomers are quaternary ammonium compounds such as quaternary ammonium substituted alkyl (meth)acrylates, such as quaternised dimethyl amino alkyl meth(acrylates).

In certain preferred embodiments the compound for use as a third component comprises a polyamine compound.

In certain preferred embodiments the compound for use as a third component is a composition comprising both a polyamine component and a polysulphone component.

A polyamine component in a composition in the present invention is preferably the reaction product of epichlorohydrin with an aliphatic primary monoamine or N-aliphatic hydrocarbyl alkylene diamine.

Preferred diamines are alkyl or alkenyl diamines of the general formula:



wherein R is preferably selected from an alkyl or alkenyl straight chain group of mainly C<sub>8</sub> to C<sub>18</sub> (coco propylene diamine); a straight chain alkyl group of mainly C<sub>16</sub> to C<sub>22</sub> (C<sub>16</sub> – C<sub>22</sub> alkylpropylene diamine); a straight chain alkyl group of mainly C<sub>16</sub> to C<sub>18</sub> (tallow propylene diamine). Most preferably R represents an alkyl or alkenyl straight chain of mainly C<sub>18</sub> and the amine is oleyl (vegetable oil) propylene diamine.

In some embodiments, a polysulphone-polyamine composition for use as a compound for use as a third component in the present invention may comprise further components, for example a soluble sulphonic acid, a viscosity modifier or a solvent. A preferred solvent is an aromatic solvent, for example benzene optionally substituted by from 1 to 3 C(1-4) alkyl groups.

A preferred compound for use as a third component in the present invention further comprises a strong acid, preferably an oil-soluble sulphonic acid. Preferred sulphonic acids include dodecyl benzene sulphonic acid and dinonylnaphthalene sulphonic acid.

In some preferred embodiments, a polysulphone-polyamine composition used in the present invention further comprises a quaternary ammonium compound, as described in US3811848

By "conductivity improvers" we mean to include additives previously known for their utility as conductivity improvers. Preferred additives in this class include: aliphatic amines-fluorinated polyolefins (U.S. Pat. No. 3,652,238); polysulphone and quaternary ammonium salt (U.S. Pat. No. 3,811,848); polysulphone and quaternary ammonium salt amine/epichlorhydrin adduct  
 5 sulphonic acid (U.S. Pat. No. 3,917,466); copolymer of an alkyl vinyl monomer and a cationic vinyl monomer (U.S. Pat. No. 5,672,183); methyl vinyl ether-maleic anhydride copolymers and amines (U.S. Pat. No. 3,578,421); alpha -olefin-acrylonitrile (U.S. Pat. Nos. 4,333,741 & 4,388,452); alpha-olefin-acrylonitrile copolymers and polymeric polyamines (U.S. Pat. No. 4,259,087); copolymer of an alkylvinyl monomer and a cationic vinyl monomer and  
 10 polysulphone (U.S. Pat. No. 6,391,070); an ethoxylated quaternary ammonium compound (U.S. Pat. No. 5,863,466); hydrocarbyl monoamine or hydrocarbyl-substituted polyalkyleneamine (U.S. Pat. No. 6,793,695); acrylic-type ester-acrylonitrile copolymer and polymeric polyamine (U.S. Pat. Nos. 4,537,601 & 4,491,651); and diamine succinamide reacted with an adduct of a ketone and SO<sub>2</sub> (β-sultone chemistry) (U.S. Pat. No. 4,252,542).  
 15 The entire teachings of these patents are incorporated herein by reference.

Preferably the third component does not comprise a chromium acyl amino benzoate compound, and preferably does not comprise any chromium compounds.

20 A preferred compound for use as a third component comprises an olefin- sulphur dioxide copolymer, preferably in combination with: a polymeric polyamine; or an oil soluble sulphonic acid; or with a polymeric polyamine and an oil soluble sulphonic acid.

#### Fuel

25 A base fuel used in the present invention may comprise or consist of a petroleum-based fuel oil, especially a middle distillate fuel oil. Such distillate fuel oils generally boil within the range of from 110°C to 500°C, e.g. 150°C to 400°C. The diesel fuel 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  
 30 hydro-cracked distillates.

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).

35

The fuel composition may comprise 1st generation biodiesel. First generation biodiesel contains esters of, for example, vegetable oils, animal fats and used cooking fats. This form of biodiesel may be obtained by transesterification of oils, for example rapeseed oil, soybean oil, safflower oil, palm 25 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.

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

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

The fuel composition of the present invention may comprise a renewable fuel such as a biofuel composition or biodiesel composition.  
20

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 diesel fuel comprising bio-diesel, and a second fuel. In such blends the bio-diesel may be present in  
25 an amount of from 0.1%, preferably from 0.4% (wt/wt). In such blends the bio-diesel may be present in an amount of, for example up to 0.5%, up to 1%, up to 2%, up to 3%, up to 4%, up to 5%, up to 10%, up to 20%, up to 30%, up to 40%, up to 50%, up to 60%, up to 70%, up to 80%, up to 90%, up to 95% or up to 99% (wt/wt). The second fuel may be a petroleum-based fuel oil, especially a middle distillate fuel oil, or a non-renewable Fischer-Tropsch fuel, or a  
30 blend of both.

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

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

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.

5 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.

#### Other Additives

10 The fuel composition of the present invention 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, dispersants, detergents, cetane improvers, dehazers, stabilisers, demulsifiers, antifoams, corrosion inhibitors, lubricity improvers, dyes, markers, combustion improvers and odour masks.

15 However the presence or absence of other additives is not of central importance to the present invention, which relates to the presence of the first, second and third components in a fuel, and concerns the interactions, negative and positive, between them.

20 The invention will now be described, by way of example, with reference to the following examples. CFPP values stated are believed to be  $\pm 1^{\circ}\text{C}$ .

#### **Additive A**

Additive A was a conductivity improver comprising a polysulphone and a polyamine, the preparation of which is described in U.S. Pat. No. 3,917,466. Additive A is believed to contain approximately 20% w/w of active conductivity improving compounds.

#### **CFI(1)**

25 CFI(1) was a cold flow improver additive having approximately 40% solvent comprising aromatic hydrocarbons, aliphatic hydrocarbons and alcohols and approximately 60% of an ethylene vinyl acetate copolymer having approximately 29% vinyl acetate content; and up to 30 1% of an alkyl methacrylate copolymer.

#### **Additive B**

Additive B was a 50:1 mixture of CFI(1) and Additive A

#### **DRA(1)**

35 DRA(1) was a Drag Reducing Agent comprising a high molecular weight poly alpha olefin as a suspension in vegetable oil.

**Example 1**

Fuel 1 was a middle distillate fuel sourced from Taiwan, having 11 ppm sulphur, a base CFPP of -9°C and distillation characteristics as below:

Distillation, °C

IBP	189.2
5%	221.9
10%	231.2
20%	242.3
50%	270.0
90%	329.1
FBP	364.0

5

CFPP tests were performed on Fuel 1 with several additive combinations as shown below.

Result	CFI(1) ppm w/w	DRA(1) ppm w/w	Additive A ppm w/w	Additive B ppm w/w	CFPP °C
1	-	-	-	-	-9
2	500	-	-	-	-19
3	500	30	-	-	-11
4	500	30	100	-	-19
5	500	30	50	-	-19
6	500	30	10	-	-19
7	-	-	-	510	-19
8*	-	30	-	510	-20
9**	-	30	-	510	-19

\* in this test, the fuel was first dosed with DRA and then dosed with Additive B

10 \*\* in this test, the fuel was first dosed with Additive B and then dosed with DRA.

In the above, Result 2 shows the expected result of the cold flow improver additive. Result 3 shows the detrimental effect of the DRA additive on the CFPP performance. Results 4-6 show that Additive A was effective in combating the detrimental effect of the DRA.

15

Result 7 shows that the combination of CFI(1) and Additive A gave the same performance as CFI(1) alone. The addition of Additive A to CFI(1) had no beneficial or detrimental effect on the performance of CFI(1).



Results 8 and 9 show that the Additive B was effective in combating the detrimental effect of the DRA whether added to the fuel before or after the DRA had been added.

### Example 2

- 5 Fuel 2 was a middle distillate fuel sourced from Taiwan, having 434 ppm sulphur, a base CFPP of -1°C and distillation characteristics as below:

Distillation, °C

IBP	205.2
5%	230.8
10%	236.9
20%	248.4
50%	279.0
90%	350.8
FBP	383.9

CFPP tests were performed on Fuel 2 with several additive combinations as shown below.

10

Result	CFI(1) ppm w/w	DRA(1) ppm w/w	Additive A ppm w/w	CFPP °C
10	-	-	-	-1
11	500	-	-	-7
12	500	30	-	+9
14	500	30	10	-6

### Example 3

Fuel 3 was a middle distillate fuel sourced from Singapore, having 521 ppm sulphur, a base

- 15 CFPP of 7°C and distillation characteristics as below:

Distillation, °C

IBP	164.7
5%	200.7
10%	214.1
20%	236.5
50%	278.5
90%	346.0
FBP	373.4

CFPP tests were performed on Fuel 3 with several additive combinations as shown below.

Result	CFI(1) ppm w/w	DRA(1) ppm w/w	Additive A ppm w/w	CFPP °C
15	-	-	-	+7
16	500	-	-	-3
17	500	30	-	+11
18	500	30	100	-2

#### Example 4

- 5 Fuel 4 was a middle distillate fuel sourced from Korea having <16 ppm Sulphur. This fuel was already treated with a commercially available cold flow improver additive. As the fuel was obtained as a finished fuel, the nature of the cold flow improver additive is unknown. From the measured cloud point of -6°C and CFPP of -14°C, it is apparent that the fuel contained flow improver. Distillation characteristics were as below:

10

Distillation, °C

IBP	158.1
5%	184.8
10%	194.8
20%	218.6
50%	272.2
90%	330.8
FBP	357.4

CFPP tests were performed on Fuel 4 with several additive combinations as shown below.

Result	DRA(1) ppm w/w	Additive A ppm w/w	CFPP °C
19	-	-	-14
20	30	-	-9
21	30	10	-13

15

**CLAIMS**

1. A method of combating antagonism between a first component, namely a cold flow improver, and a second component, namely a drag reducing agent, in a liquid fuel composition, the antagonism being a reduction in the low temperature benefit achieved by the first component;  
by including in the fuel composition a third component, namely a compound selected from: a copolymer of one or more alkenes and sulphur dioxide; a copolymer of one or more alkenes with acrylonitrile; a copolymer of alkyl vinyl monomers and cationic monomers; a conductivity improver; and mixtures thereof.
2. A method as claimed in claim 1, wherein
- there is an improvement in low temperature properties of the fuel composition comprising the first, second and third components compared to the fuel composition absent the third component and
  - the improvement is greater than the improvement in low temperature properties of a fuel composition comprising the first and third components and absent the second component compared to the fuel composition comprising the first component and absent the second and third components.
3. A method as claimed in claim 1 or 2, wherein in the absence of the second component, the third component has substantially no effect or only a small effect on the low temperature benefit provided by the first component.
4. A liquid fuel composition comprising a base fuel, a first component, namely a cold flow improver, a second component, namely a drag reducing agent, and a third component, namely a compound selected from: a copolymer of one or more alkenes and sulphur dioxide; a copolymer of one or more alkenes with acrylonitrile; a copolymer of alkyl vinyl monomers and cationic monomers; a conductivity improver; and mixtures thereof;
- wherein the cold temperature properties of a first reference fuel composition which comprises the base fuel and the first component are better than those of the base fuel;
- wherein the cold temperature properties of a second reference fuel composition which comprises the base fuel, the first component and the second component are worse than those of the first reference composition;
- wherein the cold temperature properties of said liquid fuel composition which comprises the base fuel, the first component, the second component and the third component are better than those of the second reference composition.

5. A liquid fuel composition as claimed in claim 4, wherein the cold temperature properties of a third reference fuel composition comprising the base fuel, the first component and the third component but without the second component are substantially the same as the cold temperature properties of the first reference fuel composition.

5

6. A liquid fuel composition referred to as claimed in claim 4 or 5 or as provided for in claim 1, 2 or 3, having the following characteristics:

- the base fuel alone, without the first component, the second component and the third component, has a first CFPP;
- 10 - a first reference fuel composition comprising the base fuel and the first component, but without the second component and the third component, has a second CFPP, which is lower than the first CFPP;
- a second reference fuel composition comprising the base fuel, the first component, and the second component, but without the third component, has a third CFPP, which is
- 15 higher than the second CFPP;
- said liquid fuel composition comprising the base fuel, the first component, the second component, and the third component, has a fourth CFPP, which is lower than the third CFPP.

20 7. A composition according to claim 5 wherein

- a third reference fuel composition comprising the base fuel, the first component, and the third component, but without the second component, has a fifth CFPP; and
- the difference between the fourth CFPP and the third CFPP is greater than the difference between the fifth CFPP and the second CFPP.

25

8. A combination of fuel composition components, comprising a liquid base fuel which has a first CFPP; a first component which is a cold flow improver; a second component which is a drag reducing agent; and a third component which is a third component, namely a compound selected from: a copolymer of one or more alkenes and sulphur dioxide; a copolymer of one or

30 more alkenes with acrylonitrile; a copolymer of alkyl vinyl monomers and cationic monomers; a conductivity improver; and mixtures thereof;

wherein:

the base fuel has a first CFPP;

a first reference fuel composition provided by addition of the first component to the base fuel

35 has a second CFPP, lower than the first CFPP;

a second reference fuel composition provided by addition of the second component to the first reference fuel composition has a second CFPP, higher than the third CFPP, higher than the second CFPP;

a target fuel composition provided by addition of the third component to the second reference fuel composition has a fourth CFPP, lower than the third CFPP.

9. Use, to reduce the CFPP of a fuel composition which contains a first component which is a cold flow improver and a second component which is a drag reducing agent, of a third component, namely a compound selected from: a copolymer of one or more alkenes and sulphur dioxide; a copolymer of one or more alkenes with acrylonitrile; a copolymer of alkyl vinyl monomers and cationic monomers; a conductivity improver; and mixtures thereof.
10. Use, to reduce the CFPP of a fuel composition which contains a first component, namely a cold flow improver, and a second component, namely a drag reducing agent, and whose CFPP has been raised by the presence of the second component, of a third component, namely a compound selected from: a copolymer of one or more alkenes and sulphur dioxide; a copolymer of one or more alkenes with acrylonitrile; a copolymer of alkyl vinyl monomers and cationic monomers; a conductivity improver; and mixtures thereof.
11. A method of reducing the CFPP of a fuel composition containing a first component, namely a cold flow improver, and a second component, namely a drag reducing agent, by addition of a third component, namely a compound selected from: a copolymer of one or more alkenes and sulphur dioxide; a copolymer of one or more alkenes with acrylonitrile; a copolymer of alkyl vinyl monomers and cationic monomers; a conductivity improver; and mixtures thereof.
12. A method or use of composition as claimed in any preceding claim, wherein the first component is selected from:
- polymer of ethylene and an olefinically unsaturated compound
  - an oil-soluble polar nitrogen compound
  - an alkylphenol-aldehyde resin
  - a comb polymer
  - an oil-soluble polyoxyalkylene compound, and mixtures thereof.
13. A method or use or composition as claimed in any preceding claim, wherein:
- the concentration of the first component in the fuel is at least 10 ppm, up to 10,000 ppm, and/or
  - the concentration of the second component in the fuel is at least 0.1 ppm, up to 1,000 ppm,

- and/or the concentration of the third component in the fuel is at least 0.1 ppm, up to up to 400 ppm.

14. A method or use of composition as claimed in any preceding claim, wherein the second  
5 component is selected from: polymers (including homopolymers and copolymers) of olefins, in particular very high molecular weight, hydrocarbon soluble polymers of C<sub>4</sub>-C<sub>30</sub>- $\alpha$ -olefins.
15. A method or use of composition as claimed in any preceding claim, wherein the third  
10 component is selected from: an olefin- sulphur dioxide copolymer; a polymeric polyamine; an oil soluble sulphonic acids; and any mixture thereof.

# INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2012/051611

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C10L1/14 C10L10/14  
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"&" document member of the same patent family

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12 September 2012

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## INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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International application No

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