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(54) **FUEL COMPOSITIONS**  
**BRENNSTOFFZUSAMMENSETZUNGEN**  
**COMPOSITIONS DE COMBUSTIBLE**

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## Description

[0001] The present invention relates to the use of certain types of additive in fuel compositions containing distillate fuels, for new purposes.

[0002] It is known to include cold flow additives in fuel compositions containing distillate fuels, in particular middle distillate fuels such as diesel fuel compositions, so as to improve their performance at low temperatures. This is done in particular for "winter" fuel compositions which are intended for use in colder climates and/or at colder times of the year. Known cold flow additives include middle distillate flow improvers and wax anti-settling agents.

[0003] It is also common to include detergent additives in such fuel compositions, for the purpose of reducing, removing or slowing the build-up of engine deposits.

[0004] US-A-2005/005507 describes an additive for low sulphur mineral oil distillates having improved cold flowability and paraffin dispersancy, comprising at least one ester of an alkoxyated polyol and at least one polar nitrogen-containing paraffin dispersant.

[0005] EP-A-0885948 describes the use of a co-additive (A) which comprises an oil soluble lubricity additive comprising an ester of a polycarboxylic acid and a polyhydroxyalcohol wherein the acid has from 2 to 50 carbon atoms, the alcohol has one or more carbon atoms and the ester is composed only of carbon, hydrogen and oxygen; said use being in a composition comprising a major proportion of a fuel oil and a minor proportion of component (B) which comprises a cold flow improver additive comprising a copolymeric ethylene flow improver, and being to enhance the cold flow properties of the composition.

[0006] US-A-6086645 describes a fuel composition comprising (A) a middle distillate fuel having a sulphur content of 0.2% by weight or less, (B) a carboxylic acid amide, and (C) a least one member selected from the group consisting of cold flow improvers, ashless dispersants, and mixtures thereof, wherein the carboxylic acid amide comprises the reaction product of a carboxylic acid selected from the group consisting of oleic acid and linoleic acid, and a diethanolamine.

[0007] EP-A-0885947 describes a fuel oil composition comprising a major amount of a fuel oil containing not more than 0.05% by weight of sulphur and having a 95% distillation point of not greater than 350°C, and a minor amount of an additive composition comprising (a) an ashless dispersant comprising an acylated nitrogen compound and (b) a monocarboxylic acid having from 2 to 50 carbon atoms.

[0008] It has been found, however, that the effects of cold flow additives can be detrimentally affected by the inclusion of detergent additives in a fuel composition containing a distillate fuel. A detergent additive can in cases deactivate (at least partially) a cold flow additive, the combination of the two causing impaired cold flow performance compared to that of the fuel composition without the detergent additive.

[0009] It is an aim of the present invention to provide fuel compositions containing distillate fuels, and/or additives for use in such compositions, which can overcome or at least mitigate the above described problems.

[0010] According to a first aspect of the present invention there is provided the use, in a fuel composition containing a distillate fuel, a detergent additive and a cold flow additive, as defined in Claim 1, of a further additive, wherein the further additive is a carboxylic acid or mixture thereof, for the purpose of reducing the effect of the detergent additive on the cold flow performance of the composition.

[0011] A second aspect of the present invention provides the use, in a fuel composition containing a distillate fuel, a detergent additive and a cold flow additive, as defined in Claim 2, of a further additive as defined above, for the purpose of improving the cold flow performance of the composition.

[0012] A third aspect of the present invention provides the use, in a fuel composition containing a distillate fuel, a detergent additive and a cold flow additive, as defined in Claim 3, of a further additive as defined above, for the purpose of increasing the concentration of detergent additive in the composition either without impairing the cold flow performance of the composition or with reduced impairment of the cold flow performance compared to that which would otherwise be caused by the increase in detergent additive concentration.

[0013] In the context of this third aspect of the present invention, the term "increasing" embraces any degree of increase, for instance 1 % or more of the original detergent additive concentration, preferably 2 or 5 or 10 or 20 % or more. The increase may be as compared to the concentration of detergent additive which would otherwise have been incorporated into the fuel composition in order to achieve the properties and performance required and/or desired of it in the context of its intended use. This may for instance be the concentration of detergent additive which was present in the fuel composition prior to the realisation that a further additive could be used in the way provided by the present invention, and/or which was present in an otherwise analogous fuel composition intended (e.g. marketed) for use in an analogous context, prior to adding a further additive to it.

[0014] According to a fourth aspect of the present invention, there is provided a method for formulating a fuel composition, the method comprising (i) blending together a distillate base fuel, a detergent additive and a cold flow additive, as defined in claim 4, optionally with other fuel components, (ii) measuring the cold flow performance of the resultant blend and (iii) incorporating a further additive as defined above, in an amount sufficient to improve the cold flow performance of the blend. This method may also involve measuring the cold flow performance of the base fuel and the cold

flow additive, measuring the change in cold flow performance as a result of incorporating the detergent additive, and incorporating the further additive in an amount sufficient to counter, at least partly and preferably completely, any detrimental effect of the detergent additive on the cold flow performance of the base fuel/cold flow additive blend.

**[0015]** A fifth aspect of the present invention provides the use of a further additive as defined above, in a fuel composition containing a distillate fuel, a detergent additive and a cold flow additive, as defined in claim 7, for the purpose of reducing the amount of cold flow additive in the composition. Since the further additive may be used to counter, at least partly, any detrimental effect of the detergent additive on cold flow performance, it potentially enables lower levels of cold flow additive to be used in order to achieve a desired target level of cold flow performance in the overall composition.

**[0016]** In the context of this fifth aspect of the present invention, the term "reducing" embraces any degree of reduction - for instance 1% or more of the original cold flow additive concentration, preferably 2 or 5 or 10 or 20% or more - although suitably not reduction to zero. The reduction may be as compared to the concentration of cold flow additive which would otherwise have been incorporated into the fuel composition in order to achieve the properties and performance required and/or desired of it in the context of its intended use. This may for instance be the concentration of cold flow additive which was present in the fuel composition prior to the realisation that a further additive could be used in the way provided by the present invention, and/or which was present in an otherwise analogous fuel composition intended (e.g. marketed) for use in an analogous context, prior to adding a further additive to it.

**[0017]** In the case for example of a diesel fuel composition intended for use in an automotive engine, a certain level of cold flow performance may be desirable in order for the composition to meet current fuel specifications, and/or to safeguard engine performance, and/or to satisfy consumer demand, in particular in cold climates or seasons. According to the present invention, such standards may still be achievable even with reduced levels of cold flow additives, due to the further additive reducing the negative impact of any detergent additives present.

**[0018]** In the following description, the term "distillate fuel composition" is used to mean a fuel composition containing a distillate fuel, typically a middle distillate fuel. Such a composition may contain 0.1 %v/v or more of a distillate fuel, suitably 1 or 2 or 5 %v/v or more, preferably 5 or 10 or 25 or 50 %v/v or more, typically 75 or 80 or 90 or 95 %v/v or more, in each case the distillate fuel preferably being a middle distillate fuel. The distillate fuel may itself comprise two or more fuel components. Most preferably, a fuel composition prepared according to the present invention is, overall, a middle distillate fuel.

**[0019]** Middle distillate fuel compositions for which the present invention is used may include for example heating oils, industrial gas oils, automotive diesel fuels, distillate marine fuels or kerosene fuels such as aviation fuels or heating kerosene. Typically the composition will be either an automotive diesel fuel or a heating oil. Preferably, the fuel composition to which the present invention is applied is for use in an internal combustion engine; more preferably, it is an automotive fuel composition, yet more preferably a diesel fuel composition which is suitable for use in an automotive diesel (compression ignition) engine.

**[0020]** The fuel composition may in particular be adapted for, and/or intended for, use in colder climates and/or during colder seasons (for example, it may be a so-called "winter fuel").

**[0021]** In the context of the present invention, a distillate fuel composition will typically contain a major proportion of, or consist essentially or entirely of, a distillate hydrocarbon base fuel. A "major proportion" means typically 80 %v/v or greater, more suitably 90 or 95 %v/v or greater, most preferably 98 or 99 or 99.5% v/v or greater.

**[0022]** Such a base fuel may in particular be a middle distillate base fuel, in particular a diesel base fuel, and in this case it may itself comprise a mixture of middle distillate fuel components (components typically produced by distillation or vacuum distillation of crude oil), or of fuel components which together form a middle distillate blend. Middle distillate fuel components or blends will typically have boiling points within the usual middle distillate range of 125 to 550°C or 150 to 400°C.

**[0023]** A diesel base fuel may be an automotive gas oil (AGO). A diesel base fuel used in the present invention will preferably have a sulphur content of at most 2000 ppmw (parts per million by weight). More preferably, it will have a low or ultra low sulphur content, for instance at most 500 ppmw, preferably no more than 350 ppmw, most preferably no more than 100 or 50 or 10 ppmw, of sulphur.

**[0024]** Typical diesel fuel components comprise liquid hydrocarbon middle distillate fuel oils, for instance petroleum derived gas oils. Such base fuel components may be organically or synthetically derived. They will typically have boiling points within the usual diesel range of 125 or 150 to 400 or 550°C, depending on grade and use. They will typically have densities from 0.75 to 1.0 g/cm<sup>3</sup>, preferably from 0.8 to 0.86 g/cm<sup>3</sup>, at 15°C (IP 365) and measured cetane numbers (ASTM D613) of from 35 to 80, more preferably from 40 to 75 or 70. Their initial boiling points will suitably be in the range 150 to 230°C and their final boiling points in the range 290 to 400°C. Their kinematic viscosity at 40°C (ASTM D445) might suitably be from 1.5 to 4.5 mm<sup>2</sup>/s (centistokes). However, a fuel composition for use according to the present invention may contain fuel components outside of these ranges, since the properties of an overall blend may differ, often significantly, from those of its individual constituents.

**[0025]** Such fuels are generally suitable for use in a compression ignition (diesel) internal combustion engine, of either the indirect or direct injection type.

**[0026]** A diesel fuel composition which results from carrying out the present invention will also preferably fall within these general specifications. Suitably it will comply with applicable current standard specification(s), such as for example EN 590:99 (for Europe) or ASTM D-975-05 (for the USA). By way of example, the fuel composition may have a density from 0.82 to 0.845 g/cm<sup>3</sup> at 15°C; a final boiling point (ASTM D86) of 360°C or less; a cetane number (ASTM D613) of 51 or greater; a kinematic viscosity (ASTM D445) from 2 to 4.5 mm<sup>2</sup>/s (centistokes) at 40°C; a sulphur content (ASTM D2622) of 350 ppmw or less; and/or a total aromatics content (IP 391(mod)) of less than 11 %m. Relevant specifications may, however, differ from country to country and from year to year and may depend on the intended use of the fuel composition.

**[0027]** A petroleum derived gas oil may be obtained from refining and optionally (hydro)processing a crude petroleum source. It may be a single gas oil stream obtained from such a refinery process or a blend of several gas oil fractions obtained in the refinery process via different processing routes. Examples of such gas oil fractions are straight run gas oil, vacuum gas oil, gas oil as obtained in a thermal cracking process, light and heavy cycle oils as obtained in a fluid catalytic cracking unit and gas oil as obtained from a hydrocracker unit. Optionally, a petroleum derived gas oil may comprise some petroleum derived kerosene fraction.

**[0028]** Such gas oils may be processed in a hydrodesulphurisation (HDS) unit so as to reduce their sulphur content to a level suitable for inclusion in a diesel fuel composition.

**[0029]** In the methods of the present invention, a base fuel may be or contain a so-called "biodiesel" fuel component, such as a vegetable oil or vegetable oil derivative (e.g. a fatty acid ester, in particular a fatty acid methyl ester) or another oxygenate such as an acid, ketone or ester. Such components need not necessarily be bio-derived.

**[0030]** A base fuel may be or contain a Fischer-Tropsch derived fuel component, in particular a Fischer-Tropsch derived gas oil. Such fuels are known and in use in diesel fuel compositions. They are, or are prepared from, the synthesis products of a Fischer-Tropsch condensation reaction, as for example the commercially used gas oil obtained from the Shell Middle Distillate Synthesis (Gas-To-Liquid) process operating in Bintulu, Malaysia.

**[0031]** In general, other products of gas-to-liquid processes may be suitable for inclusion in a fuel composition prepared according to the present invention. The gases which are converted into liquid fuel components using such processes can include natural gas (methane), LPG (e.g. propane or butane), "condensates" such as ethane, synthesis gas (CO/hydrogen) and gaseous products derived from coal, biomass and other hydrocarbons.

**[0032]** The detergent additive in the fuel composition is selected from polyolefin substituted succinimides or succinamides of polyamines, for instance polyisobutylene succinimides or polyisobutylene amine succinamides, aliphatic amines, Mannich bases or amines and polyolefin (e.g. polyisobutylene) maleic anhydrides. Succinimide dispersant additives are described for example in GB-A-960493, EP-A-0147240, EP-A-0482253, EP-A-0613938, EP-A-0557516 and WO-A-98/42808. Particularly preferred are polyolefin substituted succinimides such as polyisobutylene succinimides.

**[0033]** The detergent additive may be present in the composition at an active matter concentration of from 50 to 1000 ppmw, suitably from 100 to 500 or from 100 to 300 ppmw.

**[0034]** The cold flow additive in the fuel composition is a middle distillate flow improver (MDFI) or a wax anti-settling agent (WASA) or more typically a mixture thereof. In the context of the present invention, the cold flow additive may in particular be or at least include a wax anti-settling agent.

**[0035]** MDFIs may for example comprise vinyl ester-containing compounds such as vinyl acetate-containing compounds, in particular polymers. Copolymers of alkenes (for instance ethylene, propylene or styrene, more typically ethylene) and unsaturated esters (for instance vinyl carboxylates, typically vinyl acetate) are for instance known for use as MDFIs.

**[0036]** Other known cold flow additives (also referred to as cold flow improvers) include comb polymers (polymers having a plurality of hydrocarbyl group-containing branches pendant from a polymer backbone), polar nitrogen compounds including amides, amines and amine salts, hydrocarbon polymers and linear polyoxyalkylenes. Examples of such compounds are given in WO-A-95/33805, at pages 3 to 16 and in the examples.

**[0037]** Yet further examples of compounds useable as cold flow additives include those described in WO-A-95/23200. These include the comb polymers defined at pages 4 to 7, in particular those consisting of copolymers of vinyl acetate and alkyl-fumarate esters; and the additional low temperature flow improvers described at pages 8 to 19, such as linear oxygen-containing compounds, including alcohol alkoxylates (e.g. ethoxylates, propoxylates or butoxylates) and other esters and ethers; ethylene copolymers of unsaturated esters such as vinyl acetate or vinyl hexanoate; polar nitrogen containing materials such as phthalic acid amide or hydrogenated amines (in particular hydrogenated fatty acid amines); hydrocarbon polymers (in particular ethylene copolymers with other alpha-olefins such as propylene or styrene); sulphur carboxy compounds such as sulphonate salts of long chain amines, amine sulphones or amine carboxamides; and hydrocarbylated aromatics.

**[0038]** Ideally compounds used as cold flow additives will have or be associated with available protons.

**[0039]** Particularly preferred cold flow additives for use in the present invention are those containing nitrogen atoms, preferably in association with protons. Suitable compounds are amines, amine salts and amides, in particular amines and their salts, most particularly protonated amines. Suitably at least one such compound is present in a fuel composition

prepared according to the present invention.

**[0040]** Cold flow additives are conventionally included in middle distillate fuel compositions, such as diesel fuel compositions, so as to improve their performance at lower temperatures, and thus to improve the low temperature operability of systems (typically vehicles) running on the compositions.

**[0041]** The (active matter) concentration of the cold flow additive in a fuel composition prepared according to the present invention may be up to 1000 ppmw, preferably up to 500 ppmw, more preferably up to 400 or 300 ppmw. Its (active matter) concentration will suitably be at least 20 ppmw, preferably at least 30 or 50 ppmw, more preferably at least 100 ppmw.

**[0042]** When practising the present invention, the cold flow additive and the detergent additive are typically such that the cold flow performance of the composition is worse when both additives are present than it would be if only the cold flow additive were present (at the same concentration). In such cases the present invention can provide a beneficial effect in countering the detrimental interaction between the cold flow and detergent additives.

**[0043]** The cold flow performance of a fuel composition can suitably be assessed by measuring its cold filter plugging point (CFPP), preferably using the standard test method IP 309 or an analogous technique. The CFPP of a fuel indicates the temperature at and below which wax in the fuel will cause severe restrictions to flow through a filter screen, and can correlate with vehicle operability at lower temperatures. A reduction in CFPP will correspond to an improvement in cold flow performance, other things being equal. Improved cold flow properties increase the range of climatic conditions or seasons in which a fuel can efficiently be used.

**[0044]** Cold flow performance may be assessed in any other suitable manner, for example using the Aral short sediment test (EN 23015), and/or by assessing the low temperature performance of a diesel engine, vehicle or other system running on the fuel composition. The temperature at which such performance is measured may depend on the climate in which the fuel composition is intended to be used - in Greece, for example, "low temperature performance" may be assessed at -5°C, whereas in Finland low temperature performance may be required at -30°C; in hotter countries where fuels are generally used at higher ambient temperatures, "low temperature" performance may need to be assessed at only 5 to 10 degrees below the ideal ambient temperature. In general, an improvement in cold flow performance may be manifested by a reduction in the minimum temperature at which a system running on the fuel composition can perform to a given standard.

**[0045]** An improvement in cold flow performance may be manifested by a reduction in, ideally suppression of, so-called "hesitation" effects which can occur in a CFPP test at temperatures higher than the CFPP value of a fuel. "Hesitation" may be understood as an at least partial obstruction of the CFPP test filter occurring at a temperature higher than the CFPP. Such an obstruction will be manifested - in a CFPP machine modified to allow such measurements - by an increased filtration time, albeit at a level below 60 seconds. If severe enough, hesitation causes the test to terminate early and the CFPP value to be recorded as the higher temperature - thus when hesitation occurs to a great enough extent, it is not recognised as hesitation but simply as a higher CFPP. References in this specification to CFPP values may generally be taken to include values which take account of - i.e. are raised as a result of - such hesitation effects.

**[0046]** A reduction in hesitation effects may be manifested by complete elimination of a hesitation effect which would be observed when measuring the CFPP of the fuel composition without the further additive present; and/or by a reduction in severity of such a hesitation effect (e.g. severe hesitation becomes only mild hesitation); and/or by a lowering of the temperature at which such a hesitation effect occurs. Since hesitation effects can cause variability in the measured CFPP of a fuel composition, in severe test machines triggering an increase in the recorded value, such a reduction may be beneficial because it can allow the CFPP of the composition to be more reliably and accurately measured, in turn allowing the composition to be more readily tailored to meet, and proven to meet, specifications such as industry or regulatory standards.

**[0047]** References to a "detrimental effect" on cold flow performance may be construed in accordance with the above. Such an effect will typically correspond to an increase in the CFPP of the fuel composition, and/or an increase in hesitation effects when measuring the CFPP of the composition, and/or poorer performance of an engine or vehicle or other system running on the composition, particularly at low temperatures as described above.

**[0048]** In the context of the first aspect of the present invention, "reducing" the effect of the detergent additive on cold flow performance embraces any degree of reduction in the effect (typically a detrimental effect, for instance as manifested by an increased CFPP) of the detergent additive on the cold flow performance of the fuel composition. This can be assessed by measuring the cold flow performance of the composition (including the cold flow additive) both before and after incorporation of the detergent additive. Thus, the further additive may be added for the purpose of reducing deactivation of the cold flow additive by the detergent additive and/or by any other moiety present in the fuel composition. Ideally, the effect of the detergent additive on cold flow performance will be entirely negated by the further additive; in other words, the cold flow performance of the final composition will be no worse than - and in some cases may be better than - that of the composition with the cold flow additive but without the detergent additive.

**[0049]** In the context of the second and fourth aspects of the present invention, "improving" the cold flow performance of the fuel composition embraces any degree of improvement compared to the performance of the composition before

the further additive is incorporated. This may for example involve adjusting the cold flow performance of the composition, by means of the further additive, in order to meet a desired target, for instance a desired target CFPP value.

**[0050]** By using the present invention, the CFPP of the composition may be reduced by at least 1°C compared to its value prior to addition of the further additive, preferably by at least 2°C, more preferably by at least 3°C and most preferably by at least 4 or 5 or in cases 6 or 7 or 8°C.

**[0051]** By using the present invention, the CFPP of the composition may be reduced by at least 0.3% of its value (expressed in degrees Kelvin) prior to addition of the further additive, more preferably by at least 0.5% and most preferably by at least 1 or 1.5 or 2 or even 3 or 4%.

**[0052]** A fuel composition prepared according to the present invention may have a CFPP of -5°C or lower, preferably -10 or -15°C or lower. In a preferred embodiment, it may have a CFPP of -20°C or lower, preferably -25 or -28 or -30°C or lower.

**[0053]** In accordance with the present invention, the "further additive" used in the distillate fuel composition is selected from carboxylic acids and mixtures thereof. A lubricity enhancing additive may itself contain one or more acids; thus a further additive which is a carboxylic acid, and most particularly a fatty acid may be used as a constituent of another fuel additive such as a lubricity enhancing additive.

**[0054]** Carboxylic acids may thus be any organic acid containing a -CO<sub>2</sub>H or -CO<sub>2</sub><sup>-</sup> H<sup>+</sup> group. It may be aliphatic (whether saturated or at least partially unsaturated, and optionally including cyclic moieties) or aromatic, straight or branched chain. It may for instance contain from 1 to 30, preferably from 1 to 20, carbon atoms. It may be substituted with other groups as well as the acid group; for example it may be a hydroxyacid such as lactic or glycolic acid, or a carbonyl substituted acid such as levulinic acid. It may be an unsaturated acid such as acrylic or methacrylic acid, or a derivative thereof in particular an oligomer or polymer.

**[0055]** Particularly preferred carboxylic acids for use in the present invention are fatty acids and mixtures thereof. Such fatty acids may be saturated or unsaturated (which includes polyunsaturated). They may for example contain from 1 or 2 to 30 carbon atoms, suitably from 10 to 22 carbon atoms, preferably from 12 to 22 or from 14 to 20 carbon atoms, more preferably from 16 to 18 carbon atoms and most preferably 18 carbon atoms. Examples include oleic acid, linoleic acid, linolenic acid, linolic acid, stearic acid, palmitic acid and myristic acid. Of these, oleic, linoleic and linolenic acids may be preferred, more preferably oleic and linoleic acids.

**[0056]** Dimers or oligomers of fatty acids may also be useable as further additives.

**[0057]** In one embodiment of the present invention, the further additive is tall oil fatty acid, which is derived from tall oil and contains mostly fatty acids (such as oleic and linoleic) with a small proportion of rosin acids. Tall oil fatty acid is already in use as a lubricity enhancing additive.

**[0058]** In another embodiment of the present invention, the further additive is acetic acid. Other C<sub>1</sub> to C<sub>10</sub> or C<sub>1</sub> to C<sub>8</sub> or C<sub>1</sub> to C<sub>6</sub> or C<sub>1</sub> to C<sub>4</sub> carboxylic acids may also be of use as the further additive.

**[0059]** A mixture, for example containing two or more, preferably three or more, suitably four or more, carboxylic acids (ideally fatty acids) may be preferred for use in the present invention. Such acids may for example be selected from oleic, linoleic, linolenic, stearic and palmitic acids.

**[0060]** An especially preferred mixture may contain from 25 to 85 %w/w (suitably from 35 to 75 or from 40 to 70 or from 50 to 60 %w/w) of oleic acid, and/or from 5 to 50 %w/w (suitably from 10 to 40 or from 10 to 30 or from 15 to 25 %w/w) of linoleic acid, and/or from 1 to 30 %w/w (suitably from 2 to 20 or from 5 to 15 %w/w) of linolenic acid, and/or from 1 to 30 %w/w (suitably from 2 to 20 or from 5 to 15 or from 5 to 10 %w/w) of stearic acid, and/or from 1 to 30 %w/w (suitably from 2 to 20 or from 5 to 15 or from 5 to 10 %w/w) of palmitic acid. Such a mixture preferably contains at least oleic and linoleic acid, more preferably at least oleic, linoleic and linolenic acids, and most preferably oleic, linoleic, linolenic, stearic and palmitic acids.

**[0061]** Another preferred carboxylic acid for use in the present invention is an aromatic compound having at least one carboxyl group attached to the aromatic nucleus, as disclosed in WO-A-98/01516, in particular at page 2, lines 28 to 35, at page 4, line 3 to page 5, line 11 and at page 8, lines 4 to 18. Such aromatic acids can include naphthalene and other diaromatic or polyaromatic acids, as well as benzoic acids. They are preferably substituted with one or more alkyl and/or alkoxy groups. Suitably the acid is an alkyl-substituted salicylic acid having the formula (R)<sub>n</sub>-C<sub>6</sub>H<sub>(4-n)</sub>(OH)CO<sub>2</sub>H, where each R is independently selected from straight and branched chain, optionally substituted (though preferably unsubstituted) alkyl groups having from 6 to 30, preferably from 8 to 22, more preferably from 8 to 18 carbon atoms, and n is an integer from 1 to 4, preferably 1. The further additive may of course be a mixture of two or more such alkyl-substituted aromatic acids.

**[0062]** A lubricity enhancing additive is any additive capable of improving the lubricity of a distillate fuel composition and/or of imparting anti-wear effects when the composition is in use in an engine or other fuel-consuming system.

**[0063]** A lubricity enhancing additive may contain, typically as active constituent(s), one or more carboxylic acids such as those defined above, in particular fatty acids and/or alkylsalicylic acids.

**[0064]** Suitable commercially available lubricity enhancing additives include the fatty acid-based R650 (ex. Infineum).

**[0065]** Preferably, a lubricity enhancing additive contains one or more fatty acids, for instance as defined above.

Commercially available examples of such additives include Infineum's R650 and Lubrizol's Lz 539 series of products.

**[0066]** In accordance with the present invention, more than one further additive may be used in the fuel composition.

**[0067]** According to the present invention, the further additive may be used in the distillate fuel composition at any suitable concentration, for instance up to 3000 ppmw, in cases up to 2000 or 1000 ppmw, preferably up to 700 ppmw, more preferably up to 500 ppmw, or up to 400 or 300 or in cases 200 ppmw. Its concentration may be at least 1 ppmw, preferably at least 5 or 10 ppmw, preferably at least 50 or 100 ppmw. The concentration used may depend on the concentrations of the detergent and cold flow additives present in the composition, and on the cold flow performance desired of it. In certain cases it may be appropriate for the concentration of the further additive to be such as to yield an acidity equivalent to using oleic acid at a concentration within the above defined ranges.

**[0068]** A further additive which is a lubricity enhancing additive may be used in the fuel composition, in accordance with the present invention, at a concentration which is different to (for example higher than) its standard treat rate. Thus, use of a lubricity enhancing additive in accordance with the present invention may involve incorporating it at a concentration other than that which would have been necessary or desirable or usual if it had been incorporated into the composition purely for its lubricity enhancing properties. The use may involve incorporating the additive at a concentration higher than that which would be necessary or desirable or usual in order to impart adequate lubricity properties to the overall fuel composition (e.g. taking account of any other additives present in the composition).

**[0069]** In particular, use of a lubricity enhancing additive in accordance with the present invention may involve incorporating it into a fuel composition which already has (typically because one or more lubricity enhancing additives are already present) adequate lubricity.

**[0070]** In the context of the present invention, "use" of an additive in a fuel composition means incorporating the additive into the composition, typically as a blend (i.e. a physical mixture) with one or more other fuel components. An additive will conveniently be incorporated before the composition is introduced into an internal combustion engine or other system which is to be run on the composition. Instead or in addition the use of an additive may involve running a fuel-consuming system, typically a diesel engine, on a fuel composition containing the additive, typically by introducing the composition into a combustion chamber of an engine.

**[0071]** "Use" of a further additive in the ways described above may also embrace supplying such a further additive together with instructions for its use in a distillate fuel composition to achieve the purpose(s) of any of the first to the fifth aspects of the present invention, for instance to achieve a desired target level of cold flow performance (e.g. a desired target CFPP value) and/or to reduce the concentration of cold flow additive in the composition. The further additive may itself be supplied as a component of a formulation suitable for and/or intended for use as a fuel additive, in which case the further additive may be included in such a formulation for the purpose of influencing its effects on the cold flow performance of a distillate fuel composition.

**[0072]** Thus, the further additive may be incorporated into an additive formulation or package along with one or more other fuel additives, for example the detergent additive itself.

**[0073]** According to the present invention, the distillate fuel composition - in particular when it is a diesel fuel composition - may contain other components in addition to the detergent and cold flow additives and the further additive. Such components will typically be present in fuel additives. Examples are lubricity enhancers; dehazers, e.g. alkoxylated phenol formaldehyde polymers; anti-foaming agents (e.g. polyether-modified polysiloxanes); ignition improvers (cetane improvers) (e.g. 2-ethylhexyl nitrate (EHN), cyclohexyl nitrate, di-tert-butyl peroxide and those disclosed in US-A-4208190 at column 2, line 27 to column 3, line 21); anti-rust agents (e.g. a propane-1,2-diol semi-ester of tetrapropenyl succinic acid, or polyhydric alcohol esters of a succinic acid derivative, the succinic acid derivative having on at least one of its alpha-carbon atoms an unsubstituted or substituted aliphatic hydrocarbon group containing from 20 to 500 carbon atoms, e.g. the pentaerythritol diester of polyisobutylene-substituted succinic acid); corrosion inhibitors; reodorants; anti-wear additives; anti-oxidants (e.g. phenolics such as 2,6-di-tert-butylphenol, or phenylenediamines such as N,N'-di-sec-butyl-p-phenylenediamine); metal deactivators; static dissipator additives; and combustion improvers. Such components may be incorporated with other additives, for example in a detergent additive.

**[0074]** A distillate fuel composition may for example include a lubricity enhancer, in particular when the fuel composition has a low (e.g. 500 ppmw or less) sulphur content. A lubricity enhancer is conveniently used at a concentration of less than 1000 ppmw, preferably from 50 to 1000 or from 100 to 1000 ppmw, more preferably from 50 to 500 ppmw. Suitable examples of lubricity enhancers include those described above in connection with the further additive.

**[0075]** It may also be preferred for the fuel composition to contain an anti-foaming agent, more preferably in combination with an anti-rust agent and/or a corrosion inhibitor and/or a lubricity enhancing additive.

**[0076]** Unless otherwise stated, the concentration of each such additional component in the fuel composition is preferably up to 10000 ppmw, more preferably in the range from 0.1 to 1000 ppmw, advantageously from 0.1 to 300 ppmw, such as from 0.1 to 150 ppmw. (All additive concentrations quoted in this specification refer, unless otherwise stated, to active matter concentrations by mass.)

**[0077]** The concentration of any dehazer in the fuel composition will preferably be in the range from 0.1 to 20 ppmw, more preferably from 1 to 15 ppmw, still more preferably from 1 to 10 ppmw, advantageously from 1 to 5 ppmw. The

concentration of any ignition improver present will preferably be 2600 ppmw or less, more preferably 2000 ppmw or less, conveniently from 300 to 1500 ppmw.

**[0078]** If desired one or more additive components, such as those listed above, may be co-mixed - preferably together with suitable diluent(s) - in an additive concentrate, and the additive concentrate may then be dispersed into the fuel composition in a suitable quantity.

**[0079]** A distillate fuel additive may for example contain a detergent, optionally together with other components as described above, and a distillate fuel-compatible diluent, which in the case of a diesel fuel may be a non-polar hydrocarbon solvent such as toluene, xylene, white spirits and those sold by Shell companies under the trade mark "SHELLSOL", and/or a polar solvent such as an ester or in particular an alcohol, e.g. hexanol, 2-ethylhexanol, decanol, isotridecanol and alcohol mixtures, most preferably 2-ethylhexanol. The further additive may, in accordance with the present invention, be incorporated into such an additive formulation.

**[0080]** The total additive content in the fuel composition may suitably be from 50 to 10000 ppmw, preferably below 5000 ppmw.

**[0081]** Additives may be added at various stages during the production of a fuel composition; those added at the refinery for example might be selected from anti-static agents, pipeline drag reducers, flow improvers, lubricity enhancers, anti-oxidants and wax anti-settling agents. When carrying out the present invention, a base fuel may already contain such refinery additives. Other additives may be added downstream of the refinery.

**[0082]** According to a further aspect of the present disclosure, there is provided a fuel composition containing a distillate base fuel, a detergent additive, a cold flow additive and a further additive selected from:

carboxylic acids, and mixtures thereof.

**[0083]** The further additive may be as defined above in connection with the first to the fifth aspects of the present invention. In particular, it is a carboxylic acid, for example a C<sub>1</sub> to C<sub>10</sub> carboxylic acid such as acetic acid. Again, the distillate base fuel is preferably a middle distillate base fuel.

**[0084]** According to a further aspect of the present disclosure, there is provided a process for the preparation of a fuel composition, such as a composition according to the sixth aspect, which process involves blending a distillate (typically middle distillate) base fuel with a detergent additive, a cold flow additive and a further additive as defined above. The blending is ideally carried out for one or more of the purposes described in connection with the first to the fifth aspects of the present invention, in particular with respect to the cold flow properties of the resultant fuel composition.

**[0085]** The process may form part of a process for, or be implemented using a system for, controlling the blending of a fuel composition, for example in a refinery. Such a system will typically include means for introducing each of the relevant additives and a distillate base fuel into a blending chamber, flow control means for independently controlling the volumetric flow rates of the additives and the base fuel into the chamber, means for calculating the proportions of each of the additives needed to achieve a desired target cold flow property (e.g. a desired target CFPP) input by a user into the system, and means for directing the result of that calculation to the flow control means which is then operable to achieve the desired proportions of additives in the product composition by altering the flow rates of its constituents into the blending chamber.

**[0086]** In order to calculate the required proportions, a process or system of this type will suitably make use of known cold flow properties for the base fuel concerned, and conveniently also a model predicting, and/or data describing, the cold flow properties of fuel compositions containing varying proportions of the relevant additives. The process or system may then for example, according to the present invention, select and produce a cold flow additive concentration lower than that predicted to be necessary if only the cold flow additive and the detergent additive were present.

**[0087]** The present invention may thus conveniently be used to automate, at least partially, the formulation of a distillate fuel composition, preferably providing real-time control over the relative proportions of the additives and base fuel incorporated into the composition, for instance by controlling the relative flow rates or flow durations for the constituents.

**[0088]** There is provided a method of operating a fuel consuming system, which method involves introducing into the system a fuel composition according to the sixth aspect of the present invention, and/or a fuel composition prepared in accordance with any one of the first to the fifth aspects. Again the fuel composition is preferably introduced for one or more of the purposes described above in connection with the first to the fifth aspects of the present invention. Thus, the system is preferably operated with the fuel composition of the present invention for the purpose of improving the low temperature performance of the system.

**[0089]** The system may in particular be an internal combustion engine, and/or a vehicle which is driven by an internal combustion engine, in which case the method involves introducing the relevant fuel composition into a combustion chamber of the engine. The engine is preferably a compression ignition (diesel) engine. Such a diesel engine may be of the direct injection type, for example of the rotary pump, in-line pump, unit pump, electronic unit injector or common rail type, or of the indirect injection type. It may be a heavy or a light duty diesel engine.

**[0090]** Throughout the description and claims of this specification, the words "comprise" and "contain" and variations of the words, for example "comprising" and "comprises", mean "including but not limited to", and are not intended to (and do not) exclude other moieties, additives, components, integers or steps.



**[0091]** Throughout the description and claims of this specification, the singular encompasses the plural unless the context otherwise requires. In particular, where the indefinite article is used, the specification is to be understood as contemplating plurality as well as singularity, unless the context requires otherwise.

**[0092]** Preferred features of the second and subsequent aspects of the present invention may be as described in connection with any of the other aspects.

**[0093]** Other features of the present invention will become apparent from the following examples. Generally speaking, the present invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims and drawings). Thus features, integers, characteristics, compounds, chemical moieties or groups described in conjunction with a particular aspect, embodiment or example of the present invention are to be understood to be applicable to any other aspect, embodiment or example described herein unless incompatible therewith.

**[0094]** Moreover, unless stated otherwise, any feature disclosed herein may be replaced by an alternative feature serving the same or a similar purpose.

**[0095]** The following examples illustrate the properties and performance of fuel compositions prepared in accordance with the present invention, and assess the effects of various additives on the cold flow performance of diesel fuel compositions.

**[0096]** A number of commercially available diesel fuels were sampled, some of which already contained cold flow additives. For others, cold flow additives were blended into the fuels in accordance with the additive supplier's instructions (typically at 45 to 65°C, followed by cooling to an ambient temperature of approximately 20°C) - in these cases the cold flow additives included both a MDFI and a WASA, each typically at a concentration of from 150 to 200 ppmw.

**[0097]** Other additives were blended into the fuels either whilst still warm or at ambient temperature, as convenient.

**[0098]** Cold flow performance was assessed by measuring cold filter plugging points (CFPPs) for the fuel/additive blends, using a 5GS CFPP test machine (ex. ISL) and a method analogous in key respects to the standard test method IP 309.

**[0099]** The following lubricity enhancing additives were used:

- Additive A a commercially available additive containing a mixture of tall oil fatty acids;
- Additive B a commercially available additive containing a mixture of primarily C<sub>16</sub> to C<sub>22</sub> (primarily C<sub>16</sub> to C<sub>18</sub>) fatty acids;
- Additive C a commercially available ester-based additive containing a mixture of glycerol esters of linoleic acid, primarily glycerol mono(linoleate), glycerol di(linoleate) and glycerol tri(linoleate) in an approximate ratio of 4:4:1;
- Additive D a commercially available additive containing a mixture of tall oil fatty acids;
- Additive E a commercially available additive containing a mixture of tall oil fatty acids;
- Additive F an additive containing an alkylsalicylic acid of the type described in WO-A-98/01516 at page 8, lines 4 to 18; and
- Additive G a commercially available amide-based additive containing tall oil fatty acid amides of diethanolamine, of the general formula R-C(O)-N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>.

#### Example 1

**[0100]** A commercially available diesel fuel composition, obtained from Germany, was mixed with standard cold flow additives (150 ppmw of a MDFI and 150 ppmw of a WASA) to obtain a fuel composition falling within the EN 590:99 winter diesel specification for Germany. This composition (fuel F1) was then blended with a detergent additive and with further additives in accordance with the present invention. The cold filter plugging point (CFPP) of each blend was measured as described above. Some measurements were conducted in duplicate or in triplicate, using different test kits, the CFPP measurements for each blend being referred to as #1, #2 and #3.

**[0101]** The fuel composition (prior to addition of the cold flow additives) had the specification shown in Table 1 below.

Table 1

Fuel property	Test method	
Density @ 15°C (g/cm <sup>3</sup> )	IP 365	0.8352
Cloud point (°C)	IP 219	-8
CFPP (°C)	IP 309	-11 (no hesitation)

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(continued)

	Fuel property	Test method	
5	Kinematic viscosity @ 40°C (mm <sup>2</sup> /s) (centistokes)	IP 71	3.284
	Cetane number by IQT	IP 498	53.5
10	Distillation (°C) :	IP 123	
	IBP		165.8
	10% recovered		224.7
	50% recovered		281.7
15	80% recovered		321.9
	90% recovered		342.2
	95% recovered		358.6
	FBP		365.4
20			
	Aromatics (%m)	IP 391	
	Mono		20.3
25	Di		3.4
	Tri		0.4
	Total		24.1
30	Total sulphur (mg/kg)	ASTM D2622	< 5

**[0102]** The detergent additive used in the experiments was OCTIMISE™ D3016 (ex. Octel), containing a polyisobutene succinimide of a polyamine (as a detergent active) and minor amounts of other fuel additives including a silicone antifoam agent and a dehazer. Its nominal treat rate was 1000 ppmw.

**[0103]** The further additives used, in accordance with the present invention, were the commercially available lubricity enhancing additives A, B and C as described above.

**[0104]** The results are shown in Table 2 below. For the compositions containing neither detergent additive nor further additive, the results quoted are a mean of several replicate readings, with the range of the readings shown in brackets. Table 2 also details hesitation effects where observed; these can aid in the interpretation of the CFPP readings.

Table 2

	Detergent additive (ppmw)	Further additive (ppmw)	CFPP #1 (°C)	CFPP #2 (°C)	CFPP #3 (°C)
45	0	0	-26 (-24 to - 28)	-25 (-24 to - 25)	
	1000	0	-25 Severe hesitation at -15/-21	-19	-19
50	1000	Additive A (500)	-26	-24	
	1000	Additive A (300)	-24 Severe hesitation at -21	-21	-26 Mild hesitation at -21
55	1000	Additive B (500)	-26	-26	
	1000	Additive C* (500)	-26 Mild hesitation at -21	-20	-27 Mild hesitation at -21

(continued)

Detergent additive (ppmw)	Further additive (ppmw)	CFPP #1 (°C)	CFPP #2 (°C)	CFPP #3 (°C)
1000	Additive B (150)	-26	-26	
*Not according to the present invention				

Table 2 shows that the CFPP of fuel composition F1 (with the cold flow additives) is around -25 to -26°C. Incorporation of the detergent additive results in a significant rise in CFPP, demonstrating the detrimental interaction between the cold flow additives and the subsequently added detergent.

**[0105]** Addition of the lubricity enhancing additives, however, in accordance with the present invention, results in a surprising decrease in CFPP, thus countering the negative effects of the detergent additive. The severe hesitation observed in the CFPP #1 reading for detergent alone is also reduced, and in most cases eliminated, following addition of the further additive.

**[0106]** Two of the additives are shown to be effective at different treat rates (Additive A at both 500 and 300 ppmw, and Additive B at both 500 and 150 ppmw).

### Example 2

**[0107]** A second commercially available diesel fuel composition F2 (ex. Shell) was obtained from Germany. This contained standard cold flow additives (80 to 120 ppmw of the MDFI R252 and 150 ppmw of the WASA R474 (both ex. Infineum)). F2 was blended with a detergent additive (OCTIMISE™ D3016) and with further additives in accordance with the present invention. For each blend, the CFPP was measured as in Example 1.

**[0108]** The fuel composition F2 (already containing cold flow additives) had the specification shown in Table 3 below.

Table 3

Fuel property	Test method	
Density @ 15°C (g/cm <sup>3</sup> )	IP 365	0.8448
Cloud point (°C)	IP 219	-11
Kinematic viscosity @ 40°C (mm <sup>2</sup> /s) (centistokes)	IP 71	2.999
Cetane number by IQT	IP 498	55.1
Distillation (°C) :	IP 123	
IBP		167.6
10% recovered		227.9
50% recovered		275.4
80% recovered		309.4
90% recovered		328.9
95% recovered		348.5
FBP		356.7
Aromatics (%m)	IP 391	
Mono		25.5
Di		5.6
Tri		0.5
Total		31.6

(continued)

Fuel property	Test method	
Total sulphur (mg/kg)	ASTM D2622	11

**[0109]** The further additives used were (a) acetic acid, (b) the lubricity enhancing additives A, B, D and E as described above and (c) a mixture of fatty acids containing oleic acid (55 %w/w), linoleic acid (19 %w/w), linolenic acid (9 %w/w), stearic acid (8.5 %w/w) and palmitic acid (8.5 %w/w).

**[0110]** The CFPP results are shown in Table 4 below. For the compositions containing neither detergent additive nor further additive, the results quoted are a mean of several replicate readings, with the range of the readings shown in brackets.

Table 4

Detergent additive (ppmw)	Further additive (ppmw)	CFPP #1 (°C)	CFPP #2 (°C)	CFPP #3 (°C)
0	0	-30 (-29 to -31)	-31 (-30 to -31)	-29 (-28 to -30)
1000	0	-20	-19	
1000	Additive A (500)	-29	-30	
1000	Acetic acid (110)	-25	-21	-30
1000	Additive A (300)	-29	-29	
1000	Additive B (500)	-27	-28	
1000	Additive B (150)	-30	-30	
1000	Additive D (500)	-28	-28	-29
1000	Additive E (290)	-30	-31	-32
1000	Mixed acids (500)	-30	-27	-30

**[0111]** Table 4 shows that the CFPP of fuel composition F2 is around -30°C. Incorporation of the detergent additive results in a significant rise in CFPP to -20°C, demonstrating the detrimental interaction between the cold flow additives present in F2 and the subsequently added detergent.

**[0112]** Incorporation of further additives in accordance with the present invention, however, results in decreases in CFPP, thus countering at least partially the negative effects of the detergent additive. In some cases the effect of the detergent on cold flow performance appears to be entirely negated by the further additive.

**[0113]** Particularly effective further additives include the fatty acid mixture, and the fatty acid-based lubricity enhancing additives such as Additives A, B and E.

**[0114]** Two of the additives are shown to be effective at different treat rates (Additive A at both 500 and 300 ppmw, and Additive B at both 500 and 150 ppmw).

### Example 3

**[0115]** Example 1 was repeated but using as the detergent additive a formulation containing a polyisobutylene succinimide (based on polyisobutylene with a number-average molecular weight of about 1000) of tetraethylenepentamine. The standard treat rate for this additive is 636 ppmw. The further additives used, in accordance with the present invention, were (a) acetic and linolenic acids and (b) the lubricity enhancing additives F, C, G and A.

**[0116]** The results are shown in Table 5 below. For the compositions containing neither detergent additive nor further additive, the results quoted are a mean of several replicate readings, with the range of the readings shown in brackets. Table 5 also details hesitation effects where observed.

Table 5

Detergent additive (ppmw)	Further additive (ppmw)	CFPP #1 (°C)	CFPP #2 (°C)	CFPP #3 (°C)
0	0	-26 (-24 to -28)	-25 (-24 to -25)	

(continued)

Detergent additive (ppmw)	Further additive (ppmw)	CFPP #1 (°C)	CFPP #2 (°C)	CFPP #3 (°C)
636	0	-19 Severe hesitation at-17	-19	-17
636	Additive F (225)	-20	-30 Severe hesitation at-21	-30 Mild hesitation at-20
636	Additive F (450)	-26	-24	
636	Acetic acid (110)	-27	-24	-25
636	Additive C* (500)	-25	-24	
636	Additive G* (500)	-24	-24	
636	Additive A (500)	-27	-24	-26
636	Additive C* (1000)	-28	-28	
636	Additive G* (1000)	-25	-27	-25
636	Linolenic acid (500)	-26	-20	-26
*Not according to the present invention				

[0117] These data again show that using a further additive in accordance with the present invention, the cold flow performance of a diesel fuel containing both a cold flow additive and a detergent additive can be improved, countering the apparently detrimental effect of the detergent.

#### Example 4

[0118] Example 2 was repeated but using the same detergent additive as in Example 3. The further additives used, in accordance with the present invention, were (a) acetic acid and (b) the lubricity enhancing additives F and A as described above.

[0119] The results are shown in Table 6 below. For the compositions containing neither detergent additive nor further additive, the results quoted are a mean of several replicate readings, with the range of the readings shown in brackets.

Table 6

Detergent additive (ppmw)	Further additive (ppmw)	CFPP #1 (°C)	CFPP #2 (°C)	CFPP #3 (°C)
0	0	-30 (-29 to -31)	-31 (-30 to -31)	-29 (-28 to -30)
600	0	-18	-19	
636	Additive F (225)	-31	-31	-20
636	Additive F (450)	-29	-30	
636	Acetic acid (110)	-32	-31	-29
636	Additive A (500)	-31	-28	-30

#### Example 5

[0120] Further commercially available diesel fuels F3 to F5, obtained during the winter, were tested in similar manner to Examples 1 to 4 above. All either contained cold flow additives or were blended with cold flow additives prior to addition of any detergent or further additives.

[0121] Fuel composition F3 was based on the same commercially available German diesel fuel as used in Example 1, but mixed with 200 ppmw of a MDFI additive and 150 ppmw of a WASA additive. Its cloud point prior to incorporation of the cold flow additives was -8°C.

[0122] Fuel composition F4 was a Dutch fuel containing 150 ppmw of a MDFI additive and 150 ppmw of a WASA

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additive. Its cloud point prior to incorporation of the cold flow additives was -10°C.

**[0123]** Fuel composition F5 was a German fuel containing standard cold flow additives (including a MDFI and at least 150 ppmw of a WASA). Its cloud point prior to incorporation of cold flow additives was -9°C.

**[0124]** The same detergent additive was used as in Example 1, at its standard treat rate (1000 ppmw). Blends were prepared with various further additives in accordance with the present invention.

**[0125]** The CFPP results are shown in Table 7 below. For the F3 compositions containing neither detergent additive nor further additive, the results quoted are a mean of several replicate readings, with the range of the readings shown in brackets.

Table 7

Fuel	Detergent (ppmw)	Further additive (ppmw)	CFPP #1 (°C)	CFPP #2 (°C)	CFPP #3 (°C)
F3	0	0	-31 (-30 to -31)	-31 (-)	
F3	1000	0	-25	-24	
F3	1000	Additive A (500)	-27	-28	
F3	1000	Additive B (500)	-28	-28	
F4	0	0	-21	-27	-20
F4	1000	0	-15	-17	-15
F4	1000	Additive B (150)	-20	-20	
F5	0	0	-28	-30	
F5	1000	0	-20	-27	-21
F5	1000	Additive B (150)	-30	-28	

**[0126]** Again the inclusion of a lubricity enhancing additive is seen to counter the detrimental effect of the detergent additive on cold flow performance.

### Example 6

**[0127]** The diesel fuel used as the starting material in Example 1 was blended with various additives selected from (i) the detergent additive used in Example 1, (ii) two cold flow additives (a MDFI and a WASA) and (iii) the lubricity enhancing additive A. For each blend, the CFPP was measured as in Example 1.

**[0128]** The CFPP results are shown in Table 8.

Table 8

MDFI additive (ppmw)	WASA additive (ppmw)	Detergent additive (ppmw)	Additive A (ppmw)	CFPP #1 (°C)	CFPP #2 (°C)	CFPP #3 (°C)
150	150	0	0	-27		-25
0	0	0	0	-11	-11	
0	0	0	500	-9	-10	
0	0	1000	500	-9	-10	
150	150	0	500	-28	-28	

**[0129]** The first line of Table 8 shows that the inclusion of standard cold flow additives in the fuel composition results in a CFPP of around -27°C. Without these additives (second line of Table 8), the CFPP of the composition increases to -11°C. Incorporation of a lubricity enhancer alone or a lubricity enhancer together with a detergent does not appear to affect the CFPP a great deal.

**[0130]** Nor does inclusion of the lubricity enhancer with the cold flow additives appear to affect the CFPP significantly, as compared to that for the fuel with cold flow additives alone. This suggests that in order to achieve the beneficial effects of the present invention (as seen in Example 1 to 5, for instance), it is necessary to include cold flow and detergent additives as well as the further additive of the present invention. In other words, an unexpected synergy appears to take

place between the three additives together, reducing the otherwise detrimental interaction between the cold flow and detergent additives alone.

#### Example 7

**[0131]** This example illustrates that a further additive may be incorporated into a fuel composition, in accordance with the present invention, in order to reduce undesirable hesitation effects when detergent and cold flow additives are combined.

**[0132]** Fuel compositions F1 and F4, both containing standard cold flow additives (in each case a combination of MDFI and WASA), were blended with detergent additives and further additives and subjected to CFPP tests as in the previous examples.

**[0133]** Table 9 below shows the results for fuel F1 combined with the OCTIMISE™ D3016 detergent additive used in Example 1. The further additives used, in accordance with the present invention, were (a) stearic acid and (b) the lubricity enhancing Additives B and C. Where hesitation was observed, this is shown with the CFPP figures; all values are quoted in °C.

Table 9

Detergent additive (ppmw)	Further additive (ppmw)	CFPP #1 (°C)	CFPP #2 (°C)	CFPP #3 (°C)
0	0	-25	-25	
1000	0	-25 Severe hesitation at -15/-21	-19	-19
1000	Additive B (150)	-26	-26	
1000	Stearic acid (500)	-21	-20	
1000	Additive C* (500)	-26 Mild hesitation at -21	-20	-27 Mild hesitation at -21
*Not according to the present invention				

**[0134]** It can be seen that incorporation of the detergent additive causes a marked increase in CFPP, and severe hesitation effects in one of the test kits used. In the presence of Additive C, only mild hesitation is observed, and at -21°C rather than at both -15 and -21°C. The hesitation at -15°C is also eliminated in the presence of stearic acid. Inclusion of Additive B results in complete elimination of hesitation effects. Thus, the further additive of the present invention can reduce hesitation effects, leading to a fuel which is likely to be less problematic on CFPP testing.

**[0135]** Table 10 below shows the results for fuel F4 combined with OCTIMISE™ D3016. The further additive used, in accordance with the present invention, was the fatty acid-based lubricity enhancing Additive B. Where hesitation was observed, this is shown with the CFPP figures; all values are quoted in °C.

Table 10

Detergent additive (ppmw)	Further additive (ppmw)	CFPP #1 (°C)	CFPP #2 (°C)	CFPP #3 (°C)
0	0	-21 Mild downphase hesitation at -19	-27 Mild downphase hesitation at -21	-20
1000	0	-15 Severe hesitation at -13	-17 Mild hesitation at -13	-15 Mild hesitation at -13
1000	Additive B (150)	-20	-20	

**[0136]** Here, incorporation of the detergent additive leads to severe hesitation effects in one of the test kits used and

mild hesitation in the other two test kits. Even without the detergent additive, the fuel still appears to suffer from mild hesitation. Incorporation of Additive B removes the hesitation effects completely.

## Claims

1. Use, in a fuel composition containing a distillate fuel, a detergent additive, wherein the detergent additive is selected from a polyolefin substituted succinimide or succinamide of polyamine, an aliphatic amine, Mannich base or amine or polyolefin maleic anhydride; and a cold flow additive, wherein the cold flow additive is selected from a middle distillate flow improver (MDFI) or a wax anti-settling agent (WASA) or a mixture thereof, of a further additive, wherein the further additive is a carboxylic acid or mixture thereof, for the purpose of reducing the effect of the detergent additive on the cold flow performance of the composition.
2. Use, in a fuel composition containing a distillate fuel, a detergent additive, wherein the detergent additive is selected from a polyolefin substituted succinimide or succinamide of polyamine, an aliphatic amine, Mannich base or amine or polyolefin maleic anhydride; and a cold flow additive, wherein the cold flow additive is selected from a middle distillate flow improver (MDFI) or a wax anti-settling agent (WASA) or a mixture thereof, of a further additive, wherein the further additive is a carboxylic acid or mixture thereof, for the purpose of improving the cold flow performance of the composition.
3. Use, in a fuel composition containing a distillate fuel, a detergent additive, wherein the detergent additive is selected from a polyolefin substituted succinimide or succinamide of polyamine, an aliphatic amine, Mannich base or amine or polyolefin maleic anhydride; and a cold flow additive, wherein the cold flow additive is selected from a middle distillate flow improver (MDFI) or a wax anti-settling agent (WASA) or a mixture thereof, of a further additive, wherein the further additive is a carboxylic acid or mixture thereof, for the purpose of increasing the concentration of detergent additive in the composition either without impairing the cold flow performance of the composition or with reduced impairment of the cold flow performance compared to that which would otherwise be caused by the increase in detergent additive concentration.
4. A method for formulating a fuel composition, the method comprising (i) blending together a distillate base fuel, a detergent additive, wherein the detergent additive is selected from a polyolefin substituted succinimide or succinamide of polyamine, an aliphatic amine, Mannich base or amine or polyolefin maleic anhydride; and a cold flow additive, wherein the cold flow additive is selected from a middle distillate flow improver (MDFI) or a wax anti-settling agent (WASA) or a mixture thereof, (ii) measuring the cold flow performance by measuring the cold filter plugging point (CFPP) of the resultant blend and (iii) incorporating a further additive, wherein the further additive is a carboxylic acid or mixture thereof, in an amount sufficient to improve the cold flow performance of the blend.
5. The method of claim 4, wherein the CFPP of the composition is improved by demonstrating a reduction of at least 1° Celsius when compared to a composition that does not include the further additive of (iii).
6. The method of claim 4, wherein the CFPP of the composition is improved by demonstrating a reduction of at least 0.3% of its value, expressed in degrees Kelvin, when compared to a composition that does not include the further additive of (iii).
7. Use of a further additive, wherein the further additive is a carboxylic acid or mixture thereof, in a fuel composition containing a distillate fuel, a detergent additive, wherein the detergent additive is selected from a polyolefin substituted succinimide or succinamide of polyamine, an aliphatic amine, Mannich base or amine or polyolefin maleic anhydride; and a cold flow additive, wherein the cold flow additive is selected from a middle distillate flow improver (MDFI) or a wax anti-settling agent (WASA) or a mixture thereof, for the purpose of reducing the amount of cold flow additive in the composition.
8. Method or use according to any one of the preceding claims, wherein the distillate fuel is a middle distillate fuel.
9. Method or use according to any one of the preceding claims, wherein the fuel composition is a diesel fuel composition.
10. Method or use according to any one of the preceding claims, wherein the further additive is a fatty acid or mixture thereof.



## Patentansprüche

1. Verwendung eines Detergentadditivs in einer Kraftstoffzusammensetzung, die Destillatkraftstoff enthält, wobei das Detergentadditiv aus einem Polyolefin-substituierten Succinimid oder einem Succinimid aus Polyamin, einem aliphatischen Amin, einer Mannich Base oder einem Amin oder Polyolefinmaleinsäureanhydrid und einem Kaltflussadditiv ausgewählt ist, wobei das Kaltflussadditiv aus einem Mitteldestillat-Fließverbesserer (middle distillate flow improver - MDFI) oder einem Wachsantiabsetzmittel (wax anti-settling agent - WASA) oder einem Gemisch daraus, aus einem weiteren Additiv ausgewählt ist, wobei das weitere Additiv eine Karbonsäure oder ein Gemisch daraus ist, zum Zweck eines Verringerns der Wirkung des Detergentadditivs auf die Kaltflussleistung der Zusammensetzung.
2. Verwendung eines Detergentadditivs in einer Kraftstoffzusammensetzung, die Destillatkraftstoff enthält, wobei das Detergentadditiv aus einem Polyolefin-substituierten Succinimid oder einem Succinimid aus Polyamin, einem aliphatischen Amin, einer Mannich Base oder einem Amin oder Polyolefinmaleinsäureanhydrid und einem Kaltflussadditiv ausgewählt ist, wobei das Kaltflussadditiv aus einem Mitteldestillat-Fließverbesserer (middle distillate flow improver - MDFI) oder einem Wachsantiabsetzmittel (wax anti-settling agent - WASA) oder einem Gemisch daraus, aus einem weiteren Additiv ausgewählt ist, wobei das weitere Additiv eine Karbonsäure oder ein Gemisch daraus ist, zum Zweck eines Verbesserns der Kaltflussleistung der Zusammensetzung.
3. Verwendung eines Detergentadditivs in einer Kraftstoffzusammensetzung, die Destillatkraftstoff enthält, wobei das Detergentadditiv aus einem Polyolefin-substituierten Succinimid oder einem Succinimid aus Polyamin, einem aliphatischen Amin, einer Mannich Base oder einem Amin oder Polyolefinmaleinsäureanhydrid und einem Kaltflussadditiv ausgewählt ist, wobei das Kaltflussadditiv aus einem Mitteldestillat-Fließverbesserer (middle distillate flow improver - MDFI) oder einem Wachsantiabsetzmittel (wax anti-settling agent - WASA) oder einem Gemisch daraus, aus einem weiteren Additiv ausgewählt ist, wobei das weitere Additiv eine Karbonsäure oder ein Gemisch daraus ist, zum Zweck eines Erhöhen der Konzentration des Detergentadditivs in der Zusammensetzung, entweder ohne die Kaltflussleistung der Zusammensetzung zu beeinträchtigen oder mit einer verringerten Beeinträchtigung der Kaltflussleistung im Vergleich zu dem, was sonst durch die Erhöhung der Konzentration des Detergentadditivs verursacht werden würde.
4. Verfahren zum Formulieren einer Kraftstoffzusammensetzung, wobei das Verfahren Folgendes umfasst: (i) Mischen eines Destillatbasiskraftstoffs, eines Detergentadditivs, wobei das Detergentadditiv aus einem Polyolefin-substituierten Succinimid oder einem Succinimid aus Polyamin, einem aliphatischen Amin, einer Mannich Base oder einem Amin oder Polyolefinmaleinsäureanhydrid und einem Kaltflussadditiv ausgewählt ist, wobei das Kaltflussadditiv aus einem Mitteldestillat-Fließverbesserer (MDFI) oder einem Wachsantiabsetzmittel (WASA) oder einem Gemisch daraus ausgewählt ist, (ii) Messen der Kaltflussleistung durch Messen des Temperaturgrenzwerts der Filtrierbarkeit (cold filter plugging point - CFPP) der Endproduktmischung und (iii) Einarbeiten eines weiteren Additivs, wobei das weitere Additiv eine Karbonsäure oder ein Gemisch daraus ist, in einer Menge, die ausreicht, um die Kaltflussleistung der Mischung zu verbessern.
5. Verfahren nach Anspruch 4, wobei der CFPP der Zusammensetzung durch Nachweisen einer Verringerung von wenigstens 1° Celsius verglichen mit einer Zusammensetzung, die das weitere Additiv von (iii) nicht beinhaltet, verbessert wird.
6. Verfahren nach Anspruch 4, wobei der CFPP der Zusammensetzung durch Nachweisen einer Verringerung von wenigstens 0,3 % ihres Wertes, ausgedrückt in Grad Kelvin, verglichen mit einer Zusammensetzung, die das weitere Additiv von (iii) nicht beinhaltet, verbessert wird.
7. Verwendung eines weiteren Additivs, wobei das weitere Additiv eine Karbonsäure oder ein Gemisch daraus ist, in einer Kraftstoffzusammensetzung, die einen Destillatkraftstoff, ein Detergentadditiv enthält, wobei das Detergentadditiv aus einem Polyolefin-substituierten Succinimid oder einem Succinimid aus Polyamin, einem aliphatischen Amin, einer Mannich Base oder einem Amin oder Polyolefinmaleinsäureanhydrid und einem Kaltflussadditiv ausgewählt ist, wobei das Kaltflussadditiv aus einem Mitteldestillat-Fließverbesserer (MDFI) oder einem Wachsantiabsetzmittel (WASA) oder einem Gemisch daraus ausgewählt ist, zum Zweck des Verringerns der Menge des Kaltflussadditivs in der Zusammensetzung.
8. Verfahren oder Verwendung nach einem der vorhergehenden Ansprüche, wobei der Destillatkraftstoff ein Mitteldestillatkraftstoff ist.

9. Verfahren oder Verwendung nach einem der vorhergehenden Ansprüche, wobei die Kraftstoffzusammensetzung eine Dieseldieselkraftstoffzusammensetzung ist.
10. Verfahren oder Verwendung nach einem der vorhergehenden Ansprüche, wobei das weitere Additiv eine Fettsäure oder Gemisch daraus ist.

## Revendications

1. Utilisation, dans une composition de carburant contenant un carburant de distillat, un additif détergent, l'additif détergent étant choisi parmi un succinimide substitué par polyoléfine ou un succinamide de polyamine, une amine aliphatique, une base de Mannich ou une amine ou un anhydride maléique polyoléfinique ; et un additif d'écoulement à froid, l'additif d'écoulement à froid étant choisi parmi un agent d'amélioration d'écoulement de distillat moyen (MDFI) ou un anti-sédiment de cire (WASA) ou un mélange de ceux-ci, d'un autre additif, l'autre additif étant un acide carboxylique ou un mélange de celui-ci, dans le but de réduire l'effet de l'additif détergent sur les performances d'écoulement à froid de la composition.
2. Utilisation, dans une composition de carburant contenant un carburant de distillat, un additif détergent, l'additif détergent étant choisi parmi un succinimide substitué par polyoléfine ou un succinamide de polyamine, une amine aliphatique, une base de Mannich ou une amine ou un anhydride maléique polyoléfinique ; et un additif d'écoulement à froid, l'additif d'écoulement à froid étant choisi parmi un agent d'amélioration d'écoulement de distillat moyen (MDFI) ou un anti-sédiment de cire (WASA) ou un mélange de ceux-ci, d'un autre additif, l'autre additif étant un acide carboxylique ou un mélange de celui-ci, dans le but d'améliorer les performances d'écoulement à froid de la composition.
3. Utilisation, dans une composition de carburant contenant un carburant de distillat, un additif détergent, l'additif détergent étant choisi parmi un succinimide substitué par polyoléfine ou un succinamide de polyamine, une amine aliphatique, une base de Mannich ou une amine ou un anhydride maléique polyoléfinique ; et un additif d'écoulement à froid, l'additif d'écoulement à froid étant choisi parmi un agent d'amélioration d'écoulement de distillat moyen (MDFI) ou un anti-sédiment de cire (WASA) ou un mélange de ceux-ci, d'un autre additif, l'autre additif étant un acide carboxylique ou un mélange de celui-ci, dans le but d'augmenter la concentration de l'additif détergent dans la composition, soit sans altérer les performances d'écoulement à froid de la composition, soit en réduisant l'altération des performances d'écoulement à froid par rapport à celles qui seraient autrement causées par l'augmentation de la concentration de l'additif de détergent.
4. Procédé de formulation d'une composition de carburant, le procédé comprenant (i) la combinaison d'un carburant à base de distillat, d'un additif détergent, l'additif détergent étant choisi parmi un succinimide polyoléfinique substitué ou un succinamide de polyamine, une amine aliphatique, une base de Mannich ou une amine ou une polyoléfine anhydride maléique ; et un additif d'écoulement à froid, l'additif d'écoulement à froid étant choisi parmi un agent d'amélioration d'écoulement de distillat moyen (MDFI) ou un anti-sédiment de cire (WASA) ou un mélange de ceux-ci, (ii) la mesure des performances d'écoulement à froid en mesurant la température limite de filtrabilité (CFPP) de la combinaison résultante et (iii) l'incorporation d'un autre additif, l'autre additif étant un acide carboxylique ou un mélange de celui-ci, en une quantité suffisante pour améliorer les performances d'écoulement à froid de la combinaison.
5. Procédé selon la revendication 4, dans lequel la CFPP de la composition est améliorée en démontrant une réduction d'au moins 1 ° Celsius par rapport à une composition qui ne comporte pas l'autre additif de (iii) .
6. Procédé selon la revendication 4, dans lequel la CFPP de la composition est améliorée en démontrant une réduction d'au moins 0,3 % de sa valeur, exprimée en degrés Kelvin, par rapport à une composition qui ne comporte pas l'autre additif de (iii).
7. Utilisation d'un autre additif, l'autre additif étant un acide carboxylique ou un mélange de celui-ci, dans une composition de carburant contenant un carburant de distillat, un additif détergent, l'additif détergent étant choisi parmi un succinimide substitué par polyoléfine ou un succinamide de polyamine, une amine aliphatique, une base de Mannich ou une amine ou un anhydride maléique polyoléfinique ; et un additif d'écoulement à froid, l'additif d'écoulement à froid étant choisi parmi un agent d'amélioration d'écoulement de distillat moyen (MDFI) ou un anti-sédiment de cire (WASA) ou un mélange de ceux-ci, dans le but de réduire la quantité d'écoulement à froid d'additif dans la compo-

sition.

8. Procédé ou utilisation selon l'une quelconque des revendications précédentes, dans lesquels le carburant de distillat est un carburant de distillat moyen.

5 9. Procédé ou utilisation selon l'une quelconque des revendications précédentes, dans lesquels la composition de carburant est une composition de carburant diesel.

10 10. Procédé ou utilisation selon l'une quelconque des revendications précédentes, dans lesquels l'autre additif est un acide gras ou un mélange de celui-ci.

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**REFERENCES CITED IN THE DESCRIPTION**

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