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# DESCRIPTION

## Field of the Invention

[0001] This invention relates to the use of certain compounds in diesel fuel formulations, and in diesel fuel additive compositions, for new purposes.

## Background to the Invention

[0002] Hydrocarbon fuels are prone to degradation through oxidation, especially at high temperatures. This degradation manifests itself as changes in the colour and acidity of the fuel, and in extreme cases in the formation of deposits, such as gums and particulates, which can cause operational problems in fuel storage and distribution systems and in engines and other systems in which the fuel is used. Stability of hydrocarbon fuels is a balance between the natural propensity of the hydrocarbon to oxidize versus the level of natural antioxidancy present. In the case of synthetic paraffinic fuels, paraffin molecules are inherently highly stable towards oxidation, but there is a low level of natural antioxidant. Provided there are no factors to promote oxidation, such fuels have excellent stability.

[0003] Operating conditions in internal combustion engines and other fuel-consuming systems are becoming increasingly severe, in particular the operating temperatures and pressures to which the fuel is exposed. This means that oxidative stability will be more of an issue for fuel formulators in the future.

[0004] It is known to include antioxidant additives in fuel formulations to mitigate the above described problems. Many such additives are known and commercially available; examples include hindered phenols and aromatic amines.

[0005] It can be desirable to improve the performance of such antioxidant additives, and/or to provide alternative antioxidant additives with comparable or ideally superior performance, so as in turn to improve the oxidative stability of vulnerable fuel formulations.

[0006] It may also be desirable to reduce the concentrations of antioxidant additives in fuel formulations. This may be driven by consumer preferences and/or by technical or economic considerations. Reductions in additive concentrations can be achieved through improvements in additive performance, and/or through the provision of better-performing alternatives.

[0007] US2012/124896 relates to a diesel composition which comprises a base diesel and an additive composition, characterized in that said base diesel comprises biodiesel and said additive composition comprises (a) an arylamine-type antioxidant and (b) one or more polyamines or derivatives thereof. The diesel composition is said to have a superior oxidation

stability.

**[0008]** US2012/103290 relates to a fuel composition comprising a C1-4 alkyl fatty acid ester (biodiesel), a nitrogen containing detergent and a hindered phenolic antioxidant to improved oxidation stability.

**[0009]** US2008/0256846 discloses a fuel composition for diesel engines and teaches that by blending GTL with a light oil composition the amount of antioxidant required to prevent oxidation at high temperature can be reduced.

### **Statements of the Invention**

**[0010]** According to a first aspect of the present invention there is provided the use of a species selected from:

1. (i) detergents; and
2. (ii) mixtures containing both a lubricity improver and a conductivity improver;

in a diesel fuel formulation containing 60 to 99% v/v of paraffinic hydrocarbons and an antioxidant, for the purpose of increasing the oxidative stability of the formulation, as measured according to ASTM D7545-09, wherein the antioxidant is selected from phenolic antioxidants, amines and mixtures thereof, wherein the species (i) comprises a polyisobutenyl (PIB) succinimide detergent, wherein the species (ii) comprises a fatty acid ester lubricity improver, wherein the species (ii) comprises a sulphonic acid conductivity improver, and wherein the diesel fuel formulation contains 75% v/v or greater of a Fischer-Tropsch derived diesel fuel component or mixture thereof. The increase in stability may be measured relative to that achieved using the antioxidant alone (ie in the absence of species (i) or (ii)), at the same concentration.

**[0011]** It has surprisingly been found that when species (i) or (ii) is combined with an antioxidant, in a relatively high paraffin content diesel fuel formulation, the oxidative stability of the formulation is increased compared to that achieved using the antioxidant alone. This synergy appears possible even where the species (i) or (ii) is not itself active as an antioxidant. Indeed, species (i) and (ii) would not be expected to contribute significant antioxidant activity to a fuel formulation.

**[0012]** The combination of species (i) or (ii) with an antioxidant, in a relatively high paraffin content diesel fuel formulation, also appears to lead to an overall antioxidant effect which is greater than might be predicted from the sums of the antioxidant effects of the relevant individual additive components. Thus, in accordance with the invention, species (i) or (ii) may be used in the diesel fuel formulation for the purpose of increasing the oxidative stability of the formulation by an amount which is greater than the sum of the increases in oxidative stability caused by species (i) or (ii) and the antioxidant individually.

**[0013]** In effect, therefore, species (i) or (ii) may be used to increase the effectiveness of the antioxidant, and its presence may allow the use of a lower concentration of the antioxidant than would otherwise have been necessary or desirable. Instead or in addition, its presence may allow the use of an alternative antioxidant, for example one which gives a smaller antioxidant effect than would otherwise have been necessary or desirable.

**[0014]** These effects can offer greater flexibility for the fuel formulator, in terms of types and concentrations of additives which can be used to achieve a desired level of oxidative stability in a diesel fuel formulation.

**[0015]** In the present context, an antioxidant is a substance which is capable of reducing the rate of oxidation of a fuel formulation to which it is added, or of a component of such a formulation. It is therefore capable of increasing the oxidative stability of such a fuel formulation or component. Typically, antioxidants inhibit the oxidation of other molecules by removing free radical intermediates, a process which involves their own oxidation: they are therefore usually reducing agents.

**[0016]** According to the invention, the antioxidant is selected from phenolic antioxidants, in particular hindered phenols such as butylated hydroxytoluene; quinones; hydroquinones; amines, in particular aromatic amines; and mixtures thereof.

**[0017]** In an embodiment, the antioxidant is a phenolic antioxidant, in particular a hindered phenol. It may for example be selected from 2,6-di-*t*-butyl-4-methylphenol (also known as 2,6-di-*t*-butyl-*p*-cresol, 3,5-di-*t*-butyl-4-hydroxytoluene or butylated hydroxytoluene (BHT)); 2,4-dimethyl-6-*t*-butylphenol; 2,6-di-*t*-butylphenol; and mixtures of *t*-butylphenols. The antioxidant may in particular be BHT.

**[0018]** Such phenolic antioxidants may in particular be used (a) when the diesel fuel formulation comprises a Fischer-Tropsch derived diesel fuel component (as described below), or a mixture of a hydrogenated vegetable oil (HVO) and a Fischer-Tropsch derived diesel fuel component, and a detergent (i) is used to increase the oxidative stability of the formulation; or (b) when the diesel fuel formulation comprises a Fischer-Tropsch derived diesel fuel component, or a combination of a HVO and a Fischer-Tropsch derived diesel fuel component, and a mixture (ii) is used to increase oxidative stability.

**[0019]** In an embodiment, the antioxidant is an amine. It may be an aromatic amine, in particular a phenylene diamine containing one or more alkyl and/or aryl groups. It may for example be selected from *N,N'*-di-2-butyl-1,4-phenylenediamine; *N*-isopropyl-*N'*-phenyl-*p*-phenylene diamine; *N*-(1,3-dimethyl butyl)-*N'*-phenyl-*p*-phenylene diamine; *N*-(1-methylheptyl)-*N'*-phenyl-*p*-phenylene diamine; *N*-cyclohexyl-*N'*-phenyl-*p*-phenylene diamine; *N,N'*-di-sec-butyl-*p*-phenylene diamine; *N,N'*-diisopropyl-*p*-phenylene diamine; *N,N'*-diphenyl-*p*-phenylene diamine; *N,N'*-ditolyl-*p*-phenylene diamine; *N*-tolyl-*N'*-xylenyl-*p*-phenylene diamine; and mixtures thereof. In an embodiment, it is *N,N'*-di-*t*-butyl-1,4-phenylenediamine.

**[0020]** Such amine antioxidants may be used when a mixture (ii) is used to increase the oxidative stability of the fuel formulation. They may in particular be used when the fuel formulation comprises a Fischer-Tropsch derived diesel fuel component or a mixture of a HVO and a Fischer-Tropsch derived diesel fuel component, more particularly a Fischer-Tropsch derived diesel fuel component.

**[0021]** Such amine antioxidants may be used (a) when the diesel fuel formulation comprises a Fischer-Tropsch derived diesel fuel component or a combination of a Fischer-Tropsch derived diesel fuel component and a HVO, and a detergent (i) is used to increase the oxidative stability of the formulation; or (b) when the diesel fuel formulation comprises a Fischer-Tropsch derived diesel fuel component or a mixture of a HVO and a Fischer-Tropsch derived diesel fuel component, and a mixture (ii) is used to increase oxidative stability.

**[0022]** In an embodiment, the antioxidant is selected from BHT; N,N'-di-t-butyl-1,4-phenylenediamine; and mixtures thereof.

**[0023]** According to the invention, the diesel fuel formulation may contain a mixture of two or more antioxidants.

**[0024]** The antioxidant may for example be used in the diesel fuel formulation at an (active matter) concentration of up to 1,000 ppmw or up to 750 or 500 ppmw. It may for example be used at a concentration of 10 ppmw or greater, or 50 or 100 or 200 or 250 ppmw or greater, for example from 10 to 1,000 ppmw or from 50 to 500 ppmw. It may be used at a concentration below its normal treat rate, due to the additional stabilising effect of the species (i) or (ii).

**[0025]** The diesel fuel formulation in which species (i), or (ii) is used contains an antioxidant and also 60 to 99% v/v or more of paraffinic hydrocarbons. In other respects it may be any type of diesel fuel formulation, typically in liquid form, suitable and/or adapted for use as a combustible fuel in a compression ignition fuel-consuming system. It is hydrocarbon-based, ie comprising a major proportion (for example 80% v/v or more, or 85 or 90 or 95% v/v or more) of hydrocarbon fuel components such as alkanes, cycloalkanes, alkenes and aromatic hydrocarbons. The hydrocarbon fuel components may be mineral-derived, or derived from a biological source, or synthetic. Such a formulation may contain one or more fuel components in addition to its hydrocarbon fuel components, for example selected from oxygenates and fuel additives.

**[0026]** A diesel fuel formulation may be suitable and/or adapted for use in a diesel fuel-consuming system such as an engine (in particular an internal combustion engine) or a heating appliance. It may be selected from automotive diesel fuel formulations, marine diesel fuel formulations, industrial gas oil formulations, and heating oil formulations. In an embodiment, it is an automotive diesel fuel formulation.

**[0027]** The diesel fuel formulation suitably comprises a diesel base fuel. A diesel base fuel is

any fuel component, or mixture thereof, which is suitable and/or adapted for combustion within a compression ignition fuel-consuming system. It may be a liquid hydrocarbon middle distillate fuel, for example, a gas oil. It may contain a petroleum-derived (ie mineral) component. It may contain a kerosene fuel component. It is or contains a product of a Fischer-Tropsch condensation process as described below. It may contain a fuel component derived from a biological source. It may contain an oxygenate such as a fatty acid alkyl ester, in particular a fatty acid methyl ester (FAME) such as rapeseed methyl ester (RME) or palm oil methyl ester (POME).

**[0028]** A diesel base fuel will typically boil in the range from 150 or 180 to 370°C (ASTM D86 or EN ISO 3405). It will suitably have a measured cetane number (ASTM D613) of from 40 to 70 or from 40 to 65 or from 51 to 65 or 70.

**[0029]** A diesel fuel formulation prepared or used according to the invention comprises a diesel base fuel at a concentration of 60 or 70 or 80% v/v or greater, or 85 or 90 or 95 or 98% v/v or greater. The base fuel concentration may be up to 99.99% v/v, or up to 99.95% v/v, or up to 99.9 or 99.8 or 99.5% v/v. It may be up to 99% v/v, for example up to 98 or 95 or 90% v/v, or in cases up to 85 or 80% v/v.

**[0030]** Where the diesel fuel formulation comprises an oxygenate and/or a biologically derived component such as a FAME, its concentration may be 1% v/v or greater, or 2 or 5% v/v or greater, based on the overall formulation, or in cases 7 or 10% v/v or greater. The FAME concentration may be up to 25 or 20% v/v. Oxidative stability can be more of an issue in fuel formulations containing oxygenates, and the present invention may therefore be of particular use in such cases. The FAME concentration may be between 1 and 5% v/v, or between 5 and 10% v/v, or between 10 and 20% v/v.

**[0031]** A diesel fuel formulation prepared or used according to the invention will suitably comply with applicable current standard diesel fuel specification(s) such as for example EN 590 (for Europe) or ASTM D975 (for the USA). By way of example, the overall formulation may have a density from 820 to 845 kg/m<sup>3</sup> at 15°C (ASTM D4052 or EN ISO 3675); a T95 boiling point (ASTM D86 or EN ISO 3405) of 360°C or less; a measured cetane number (ASTM D613) of 40 or greater, ideally of 51 or greater; a kinematic viscosity at 40°C (VK40) (ASTM D445 or EN ISO 3104) from 2 to 4.5 centistokes (mm<sup>2</sup>/s); a flash point (ASTM D93 or EN ISO 2719) of 55°C or greater; a sulphur content (ASTM D2622 or EN ISO 20846) of 50 mg/kg or less, preferably 10 mg/kg or less; a cloud point (IP 219) of less than -10°C; and/or a polycyclic aromatic hydrocarbons (PAH) content (EN 12916) of less than 8% w/w. Relevant specifications may however differ from country to country, from season to season and from year to year, and may depend on the intended use of the formulation. Moreover a formulation prepared or used according to the invention may contain individual fuel components with properties outside of these ranges.

**[0032]** A diesel fuel formulation prepared or used according to the invention may comprise, in addition to the antioxidant and species (i) or (ii), one or more fuel or refinery additives. Many

such additives are known and commercially available and may be present in a base fuel, or may be added to the formulation at any point during its preparation. Non-limiting examples of additives which can be included in a diesel base fuel or diesel fuel formulation include cetane improvers, antistatic additives, lubricity additives, cold flow additives, detergents, and combinations thereof, as well as solvents, diluents and carriers therefor. Such additives may be included in the fuel formulation at a concentration of up to 4,000 ppmw (parts per million by weight), or up to 3,000 or 2,000 or 1,000 or 500 or 300 ppmw, for example from 50 to 4,000 ppmw or from 50 to 1,500 ppmw or from 50 to 1,000 ppmw or from 50 to 500 ppmw or from 50 to 300 ppmw.

**[0033]** The diesel fuel formulation contains a Fischer-Tropsch derived diesel fuel component or mixture thereof. It contains from 75% v/v or greater of a Fischer-Tropsch derived diesel fuel component or mixture thereof. In an embodiment, the diesel fuel formulation consists essentially of one or more Fischer-Tropsch derived diesel fuel components, ie in addition to the antioxidant, the species (i) or (ii) and any optional diesel fuel additives, it contains only Fischer-Tropsch derived diesel fuel components.

**[0034]** By "Fischer-Tropsch derived diesel fuel component" is meant a hydrocarbon mixture that is, or derives from, a synthesis product of a Fischer-Tropsch condensation process. The Fischer-Tropsch reaction converts carbon monoxide and hydrogen into longer chain, usually paraffinic, hydrocarbons:  $n (\text{CO} + 2\text{H}_2) = (-\text{CH}_2)_n + n\text{H}_2\text{O} + \text{heat}$ , in the presence of an appropriate catalyst and typically at elevated temperatures (e.g., 125 to 300°C, preferably 175 to 250°C) and/or pressures (e.g., 5 to 100 bar, preferably 12 to 50 bar). Ratios of hydrogen to carbon monoxide other than 2:1 may be employed if desired.

**[0035]** The carbon monoxide and hydrogen may themselves be derived from organic or inorganic, natural or synthetic sources, typically either from natural gas or from organically derived methane.

**[0036]** A middle distillate fuel product may be obtained directly from the Fischer-Tropsch reaction, or indirectly for instance by fractionation of a Fischer-Tropsch synthesis product or from a hydrotreated Fischer-Tropsch synthesis product. Hydrotreatment can involve hydrocracking to adjust the boiling range of the product (see, e. g. GB2077289 and EP0147873) and/or hydroisomerisation which can improve cold flow properties by increasing the proportion of branched paraffins. EP0583836 describes a two-step hydrotreatment process in which a Fischer-Tropsch synthesis product is firstly subjected to hydroconversion under conditions such that it undergoes substantially no isomerisation or hydrocracking (this hydrogenates the olefinic and oxygen-containing components), and then at least part of the resultant product is hydroconverted under conditions such that hydrocracking and isomerisation occur to yield a substantially paraffinic hydrocarbon fuel. The desired middle distillate fuel fraction(s) may subsequently be isolated for instance by distillation.

**[0037]** Typical catalysts for the Fischer-Tropsch synthesis of paraffinic hydrocarbons comprise, as the catalytically active component, a Group VIII metal, in particular ruthenium, iron, cobalt or

nickel. Suitable catalysts are described for instance in EP0583836.

**[0038]** An example of a Fischer-Tropsch based process is the SMDS (Shell Middle Distillate Synthesis) described in "The Shell Middle Distillate Synthesis Process", van der Burgt et al (vide supra). This process produces middle distillate range products by conversion of a natural gas (primarily methane) derived synthesis gas into a heavy long-chain hydrocarbon (paraffin) wax which can then be hydroconverted and fractionated to produce liquid transport fuels such as the gas oils useable in diesel fuel compositions. Versions of the SMDS process, utilising fixed-bed reactors for the catalytic conversion step, are currently in use in Bintulu, Malaysia, and in Pearl GTL, Ras Laffan, Qatar. Middle distillate fuels prepared by the SMDS process are commercially available for instance from the Royal Dutch/Shell Group of Companies. Such Fischer-Tropsch middle distillate fuels are described in Technical Specification CEN TS 15940.

**[0039]** A Fischer-Tropsch derived diesel fuel component may suitably have a cetane number (ISO 5165) of 70 or greater; a density at 15°C (ISO 3675) of from 770 to 800 kg/m<sup>3</sup>; a sulphur content (ISO 14596) of 3.0 mg/kg or less; a total aromatics content (EN 12916) of 0.5% w/w or less; a polycyclic aromatics content (EN 12916) of 0.1% w/w or less; a total olefin content (ASTM D1159) of 0.1% w/w or less; a paraffin content of 97% w/w or more; a kinematic viscosity at 40°C (ISO 3104) of from 2.0 to 4.5 mm<sup>2</sup>/s; a flash point (EN 2719) of 68°C or greater; and/or a cold filter plugging point (EN 116) of -9°C or lower or (in particular for use in or as a winter grade fuel) of - 20°C or lower. Such a component may suitably have a distillation curve (ISO 3405) such that the recovery at 250°C is 65% v/v or less; the recovery at 350°C is 85% v/v or greater; and/or 95% v/v recovery is achieved at 360°C or less.

**[0040]** A diesel fuel formulation prepared or used according to the invention may comprise a mixture of (a) one or more Fischer-Tropsch derived diesel fuel components and (b) one or more other diesel fuel components, for example petroleum-derived, optionally with one or more diesel fuel additives.

**[0041]** In an embodiment, the diesel fuel formulation contains 0.5% v/v or greater, or 1 or 5% v/v or greater, of non-Fischer-Tropsch paraffinic diesel components such as hydrotreated vegetable oils or fats or a mixture thereof (hereafter referred to as HVO). HVO is also known as "Hydrogenation-Derived Renewable Diesel" (HDRD) and, in the context of the U.S. Renewable Fuel Standard, as "Non-ester renewable diesel" (ref. 40CFR Part 80: Subpart M in the Code of Federal Regulations).

**[0042]** In this context, the HVO component or mixture should be suitable and/or adapted for use as a diesel fuel component. Such products are commercially available, for example the NExBTL renewable diesel products ex Neste Oil. They may be used in the form of a blend containing two or more HVOs selected for example from soybean, palm, canola and rapeseed oils; animal tallow; vegetable oil waste and brown trap grease; and mixtures thereof.

**[0043]** The HVO component or mixture will, in certain embodiments, have a paraffin content of at least 97% by weight, a cetane number of at least 70, a density at 15°C of between 770 and

790 kg/m<sup>3</sup>, an aromatics content of not greater than 1% by weight, a polyaromatics content of not greater than 0.1% by weight, a sulfur content of not greater than 5 ppm, and a flash point of at least 59°C.

**[0044]** The diesel fuel formulation may comprise a mixture of (a) one or more HVO diesel fuel components and (b) one or more other diesel fuel components, for example petroleum-derived, optionally with one or more diesel fuel additives. In such a mixture, the volume ratio of the HVO diesel fuel component(s) to the other diesel fuel component(s) may for example be from 1:200 to 3:1, or from 1:20 to 2:1, or from 1:20 to 1:1, such as about 1:1. In an embodiment, the diesel fuel formulation comprises a 1:1 v/v mixture of (a) one or more HVO diesel fuel components and (b) one or more other diesel fuel components, for example petroleum-derived diesel fuel components.

**[0045]** In an embodiment, the diesel fuel formulation comprises a mixture of (a) one or more Fischer-Tropsch derived diesel fuel components and (b) one or more HVO diesel fuel components, optionally with one or more diesel fuel additives.

**[0046]** Thus in an embodiment of the invention, the diesel fuel formulation is selected from (1) a formulation consisting essentially of one or more Fischer-Tropsch derived diesel fuel components; (2) a mixture of one or more Fischer-Tropsch derived diesel fuel components and one or more HVO diesel fuel components; and (3) a mixture of one or more Fischer-Tropsch derived diesel fuel components and one or more petroleum-derived diesel fuel components. It may be selected from (1) a formulation consisting essentially of one or more Fischer-Tropsch derived diesel fuel components; and (2) a mixture of one or more Fischer-Tropsch derived diesel fuel components and one or more HVO diesel fuel components.

**[0047]** Even in embodiments where the diesel fuel formulation includes a mixture of two or more diesel fuel components, the overall formulation shall contain 60% v/v or more of paraffinic hydrocarbons. A paraffinic hydrocarbon is a saturated hydrocarbon (alkane); it may be a straight chain (normal) paraffin or a branched chain (iso) paraffin. The diesel fuel formulation suitably comprises a mixture of normal and isoparaffins, since such mixtures can provide a suitable balance between low freezing point (isoparaffins) and good ignition quality (normal paraffins). Typically the weight ratio of isoparaffins to normal paraffins in a paraffinic hydrocarbon mixture employed in a diesel fuel formulation will be from 0.5 to 10, preferably from 1 to 9. A paraffinic hydrocarbon will typically contain from 5 to 40 carbon atoms, for example from 9 to 30 carbon atoms.

**[0048]** The diesel fuel formulation contains 60% v/v or more of paraffinic hydrocarbons. It contains up to 99% v/v of paraffinic hydrocarbons, or up to 90 or 80 or 75% v/v, such as from 20 to 99% v/v or from 30 or 50 or 60 to 99% v/v. In an embodiment, it consists essentially of paraffinic hydrocarbons, ie it contains at least 99% v/v of paraffinic hydrocarbons, together with relatively small concentrations of the antioxidant and other optional diesel fuel additives.

**[0049]** In certain cases, it may be preferred for the diesel fuel formulations that include the

species (i) or (ii) that such formulations do not to contain a petroleum-derived fuel components, or to contain less than 50% v/v of such components, or less than 40 or 30 or 20% v/v, or that such formulations contain between 10 and 20% v/v, or between 20 and 30% v/v.

**[0050]** According to the invention, a species (i) or (ii) may be used in the diesel fuel formulation to enhance its oxidative stability beyond what is achieved by the already-present antioxidant. Each of species (i) and (ii) should be suitable and/or adapted for use as an additive in a diesel fuel formulation, in particular an automotive diesel fuel formulation.

**[0051]** The species (i) is a detergent, by which is meant an agent (suitably a surfactant) which, when added to a fuel formulation, can act to remove, and/or to prevent the accumulation of, deposits such as combustion-related deposits within a fuel-consuming system in which the formulation is used, in particular within a fuel injection system such as in or on the fuel injector nozzles. Many such materials are known and commercially available for use as diesel fuel additives.

**[0052]** The detergent (i) is a polyisobutenyl (PIB) succinimide.

**[0053]** According to the invention, a mixture of two or more detergents (i), for example of the types defined above, may be used in the diesel fuel formulation.

**[0054]** The detergent (i) may for example be used in the diesel fuel formulation at an (active matter) concentration of up to 1,500 ppmw or up to 1,000 or 500 ppmw. It may for example be used at a concentration of 250 ppmw or greater, or 500 or 1,000 ppmw or greater, for example from 250 to 1,500 ppmw or from 250 to 1,000 ppmw.

**[0055]** According to the invention, a mixture (ii) of a lubricity improver and a conductivity improver may be used in the diesel fuel formulation to enhance its oxidative stability. By "lubricity improver" is meant an agent which is capable of improving the lubricity of a diesel fuel formulation to which it is added, and/or imparting anti-wear effects when such a formulation is used in an engine or other fuel-consuming system. Many such compounds are known and commercially available for use as diesel fuel additives, for example the "R" series of additives ex Infineum (trade mark) or the Hitec (trade mark) additives ex Afton.

**[0056]** Known lubricity improvers include acid-based, ester-based and amide-based agents. They can be available in the form of lubricity additives, which may contain one or more additional active ingredients as well as the lubricity improver, for example dehazers, anti-rust agents, conductivity improvers, and combinations thereof.

**[0057]** An acid-based lubricity improver comprises an acid, typically a mono-acid, more typically an organic acid, as a lubricity-enhancing active ingredient. The acid may for example be a carboxylic acid, such as a fatty acid or aromatic acid, in particular the former. Such fatty acids may be saturated or unsaturated (which includes polyunsaturated). They may contain from 1 or 2 to 30 carbon atoms, or from 10 to 22 carbon atoms, or from 12 to 22 or from 14 to

20 carbon atoms, or from 16 to 20 or 16 to 18 carbon atoms, such as 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 used, in particular oleic and linoleic acids.

**[0058]** Examples of acid-based lubricity additives are known and commercially available, for example as R650 (trade mark), ex Infineum; products in the Lz 539 (trade mark) series, ex Lubrizol; and ADX4101B™ (ex Adibis).

**[0059]** An ester-based lubricity improver comprises, as a lubricity-enhancing active ingredient, an ester such as a carboxylic acid ester, in particular an ester of a fatty acid. Such fatty acids may be as described above in connection with acid-based lubricity improvers. Ester-based lubricity improvers may alternatively be based on ester-functionalised oligomers or polymers (eg olefin oligomers). Such esters may be mono-alcohol esters such as methyl esters, or more suitably may be polyol esters such as glycerol esters. In an embodiment of the invention, an ester-based lubricity improver contains a mono-, di- or tri-glyceride of a fatty acid, or a mixture of two or more such species.

**[0060]** An amide-based lubricity improver may for example comprise, as a lubricity-enhancing active ingredient, a fatty acid amide. The fatty acid element of such an ingredient may be as described above in connection with acid-based lubricity improvers. The ingredient may for example be a fatty acid amide of a mono- or in particular di-alkanolamine such as diethanolamine.

**[0061]** Other lubricity improvers are described for example in:

- the paper by Danping Wei and HA Spikes, "The Lubricity of Diesel Fuels", *Wear*, III (1986) 217-235;
- WO-A-95/33805 - cold flow improvers to enhance lubricity of low sulphur fuels;
- WO-A-94/17160 - certain esters of a carboxylic acid and an alcohol wherein the acid has from 2 to 50 carbon atoms and the alcohol has 1 or more carbon atoms, particularly glycerol monooleate and di-isodecyl adipate, as fuel additives for wear reduction in a diesel engine injection system;
- US Pat. No. 5,490,864 - certain dithiophosphoric diester-dialcohols as anti-wear lubricity additives for low sulphur diesel fuels; and
- WO-A-98/01516 - certain alkyl aromatic compounds having at least one carboxyl group attached to their aromatic nuclei, to confer anti-wear lubricity effects particularly in low sulphur diesel fuels.

**[0062]** The lubricity improver used in the mixture (ii) is an ester-based lubricity improver. In an embodiment, it is used in the form of the lubricity-enhancing additive R662 (trade mark), ex Infineum, which is described by the supplier as a combination of ester chemistry lubricity improver and conductivity additives.

**[0063]** According to the invention, a mixture of two or more lubricity improvers may be used in the diesel fuel formulation.

**[0064]** The lubricity improver may for example be used in the diesel fuel formulation at a concentration of up to 1,000 ppmw or up to 750 or 500 ppmw. It may for example be used at a concentration of 50 ppmw or greater, or 100 or 150 or 250 ppmw or greater, for example from 50 to 1,000 ppmw or from 50 to 500 ppmw.

**[0065]** By "conductivity improver" is meant an agent which is capable of increasing the electrical conductivity of a diesel fuel formulation to which it is added. Also referred to as "static dissipaters" or "antistatic additives", they reduce the risk of electrostatic charge accumulation, which can occur for example during pumping of a fuel and can increase fire and explosion hazards during subsequent fuel handling.

**[0066]** Fuels with an inherently lower conductivity generally require higher levels of conductivity improvers. Low conductivity fuels include in particular those which are low in polar fuel components such as aromatics and sulphur- or nitrogen-containing compounds: Fischer-Tropsch derived fuels can fall into this category. As pressure to reduce sulphur levels in fuels, in particular automotive fuels, increases, this in turn increases the need for conductivity improvers.

**[0067]** A conductivity improver may for example comprise an active ingredient selected from organic acids, in particular (benzene)sulphonic acids; amines, in particular polyamines; sulphones, in particular polysulphones; and other hydrocarbon-soluble (co)polymers such as vinyl (co)polymers, in particular those containing cationic monomer units.

**[0068]** Examples of conductivity improvers include those having components selected from aliphatic amines-fluorinated polyolefins (US 3,652,238); chromium salts and amine phosphates (US 3,758,283); alpha-olefin-sulphone copolymer class-polysulphone and quaternary ammonium salt (US 3,811,848); polysulphone and quaternary ammonium salt amine/epichlorhydrin adducts; dinonylnaphthylsulphonic acid (US 3,917,466); copolymers of alkyl vinyl monomers and cationic vinyl monomers (US 5,672,183); alpha-olefin-maleic anhydride copolymer class (US 3,677,725 and US 4,416,668); methyl vinyl ether-maleic anhydride copolymers and amines (US 3,578,421); alpha-olefin-acrylonitriles (US 4,333,741 and US 4,388,452); alpha-olefin-acrylonitrile copolymers and polymeric polyamines (US 4,259,087); copolymers of an alkylvinyl monomer, a cationic vinyl monomer and a polysulphone (US 6,391,070); ethoxylated quaternary ammonium compounds (US 5,863,466); hydrocarbyl monoamines or hydrocarbyl-substituted poly(alkyleneamine (US 6,793,695); acrylic-type ester-acrylonitrile copolymers and polymeric polyamines (US 4,537,601 and US 4,491,651); and diamine succinamides reacted with adducts of a ketone and SO<sub>2</sub> ( $\beta$ -sulphone chemistry) (US 4,252,542).

**[0069]** Commercially available static dissipaters, for use as fuel additives, include Stadis (trade

mark) 450 and Stadis 425 (both ex Innospec), Tolad (trade mark) 3514 (ex Baker-Petrolite) and HiTEC (trade mark) 4545 (ex Afton Chemical). Stadis 450 for example contains dinonylnaphthyl sulphonic acid as an active ingredient; it is typically used in distillate fuels, solvents, commercial jet fuels and certain military fuels. Stadis 425 contains similar active(s) to Stadis 450 and is typically used in distillate fuels and solvents. Tolad 3514 contains a hydrocarbon-soluble copolymer of an alkylvinyl monomer and a cationic vinyl monomer.

**[0070]** A conductivity improver may be included in a diesel fuel additive package in combination with one or more additional active ingredients, such as a lubricity improver.

**[0071]** In the present invention, the conductivity improver used in the mixture (ii) is a sulphonic acid, in particular a naphthyl sulphonic acid, more particularly an alkylnaphthyl sulphonic acid such as dinonylnaphthyl sulphonic acid. In an embodiment, it is used in the form of the combined lubricity-enhancing and conductivity-improving additive R662 (trade mark), ex Infineum.

**[0072]** According to the invention, a mixture of two or more conductivity improvers may be used in the diesel fuel formulation.

**[0073]** The conductivity improver may for example be used in the diesel fuel formulation at a concentration of up to 10 ppmw or up to 5 or 3 or 2 or 1 ppmw. It may for example be used at a concentration of 0.1 ppmw or greater, or 0.5 ppmw or greater, for example from 0.1 to 5 ppmw or from 0.1 to 3 ppmw.

**[0074]** A mixture (ii) of a lubricity improver and a conductivity improver is used in the present invention. The two components may be added to the diesel fuel formulation together (for example as part of a multi-functional additive package) or separately. In an embodiment, they are added together. They may be added in the form of an additive composition which contains one or more other fuel additives in addition to the lubricity improver and the conductivity improver.

**[0075]** In the present invention, the mixture (ii) is a mixture of an ester-based lubricity improver and a sulphonic acid (in particular a naphthyl sulphonic acid) conductivity improver. In particular, it may be the commercially available combined lubricity-enhancing and conductivity-improving additive R662.

**[0076]** In the mixture (ii), the weight ratio of the lubricity improver to the conductivity improver may for example be up to 2,500, or up to 1,000, or up to 500 or 250. The ratio may for example be 20 or greater, or 50 or 75 or 100 or greater, such as from 100 to 250. Moreover, the species (i) and (ii) may be used in the diesel fuel formulation at concentrations as described above. However, due to their combined effect on antioxidant activity, it may be possible to use a lower concentration of either of the individual species (i) and (ii) .

**[0077]** In an embodiment of the invention, a detergent (i) is used to increase the oxidative

stability of the diesel fuel formulation. In an embodiment, a mixture (ii) of a lubricity improver and a conductivity improver is used to increase the oxidative stability of the diesel fuel formulation.

**[0078]** In embodiments of the invention, the weight ratio, in the diesel fuel formulation, of the antioxidant to the species (i) or (ii) may for example be up to 0.02, or up to 0.1, or up to 0.4, or up to 0.6, or up to 0.8 or up to 1. The ratio may for example be less than 1, or less than 0.8, or less than 0.6, or less than 0.4, or less than 0.2, or less than 0.1, or less than 0.05. In certain embodiments, the ratio may be between 0.02 and 1, alternatively between 0.02 and 0.1, or between 0.1 and 0.2, or between 0.2 and 0.4, or between 0.4 and 0.6, or between 0.6 and 0.8, or between 0.8 and 1.

**[0079]** According to the present invention, the species (i) or (ii) may be used to achieve any degree of improvement in the oxidative stability of the diesel fuel formulation, and/or to achieve or exceed a desired target level of oxidative stability.

**[0080]** Oxidative stability is determined herein using ASTM D7545-09 "Standard test method for oxidation stability of middle distillate fuels: Rapid small-scale oxidation test (RSSOT)", as in the examples below. Another test method is EN 16091:2011 "Liquid petroleum products - Middle distillates and fatty acid methyl ester (FAME) fuels and blends - Determination of oxidation stability by rapid small scale oxidation method", available from the European Committee for Standardisation (CEN), which involves subjecting a test fuel to accelerated oxidation conditions, and measuring the induction period to breakpoint in a pressure bomb apparatus, to provide a measure of the oxidation stability of the fuel. As for ASTM D7545-09, a longer measured induction period indicates that a more oxidation resistant test fuel. Another test method is the standard test method ASTM D2274-03, which measures residues of oxidation products generated in a test fuel under specified conditions, a lower residue indicating a higher oxidative stability. D2274-03 is equivalent to IP 388 (Energy Institute, London) and EN ISO 12205:1996 (CEN).

**[0081]** In general terms, the oxidative stability of a fuel formulation may be assessed with reference to the generation of an oxidation product, such as a carboxylic acid or peroxide, in the formulation. For a fuel formulation containing a biodiesel component such as a FAME, for example, CEN Test Method EN 15751:2009 "Fatty acid methyl ester (FAME) fuel and blends with diesel fuel - Determination of oxidation stability by accelerated oxidation method" (also known as a "Modified Rancimat" test method) may be used to assess oxidative stability.

**[0082]** The invention may additionally or alternatively be used to adjust any property of the diesel fuel formulation which is equivalent to or associated with oxidative stability. For example, improved oxidative stability may be associated with reduced deposit formation, with improved combustion and energy efficiency for a system running on the fuel formulation, with improved storage stability and/or with overall better retention of fuel properties.

**[0083]** In accordance with the invention, species (i) or (ii) may be added to the diesel fuel

formulation at any suitable time and location. It may be premixed with the antioxidant and the resultant premix then added to the fuel formulation, or alternatively species (i) or (ii) may be added separately, to a diesel fuel formulation which already contains, and/or is subsequently to be mixed with, an antioxidant. A premixed additive composition comprising species (i) or (ii) and an antioxidant may constitute an essential element for the carrying out of the present invention. Such an additive composition may comprise one or more appropriate solvents or carriers, as described below in connection with a second aspect. It may contain one or more additional diesel fuel additives.

**[0084]** According to a second aspect, there is described herein the use of a species selected from (i) or (ii) as defined above, in a diesel fuel additive composition containing an antioxidant, for the purpose of increasing the antioxidant activity of the composition.

**[0085]** A diesel fuel additive composition is a composition which contains a diesel fuel additive and which is suitable and/or adapted and/or intended, in particular suitable and/or adapted, for use in a diesel fuel formulation, for instance a diesel fuel formulation of the type described above in connection with the first aspect of the invention. In particular, a diesel fuel additive composition prepared or used according to the second aspect described herein may be suitable and/or adapted and/or intended, in particular suitable and/or adapted, for use in a diesel fuel formulation containing 10% v/v or more of paraffinic hydrocarbons.

**[0086]** An increase in the antioxidant activity of the additive composition means that the composition causes a greater increase in the oxidative stability of a diesel fuel formulation to which it is added. The increase may be measured relative to that achieved using the antioxidant alone (ie in the absence of species (i) or (ii)), at the same concentration.

**[0087]** An additive composition prepared or used according to the second aspect described herein may comprise a solvent or other carrier, or mixture thereof, for the additives present in it. Suitable such solvents are well known and commercially available. They may in particular be liquid carriers. They may conveniently be of low polarity, and/or hydrophobic, and/or non-aqueous, to render them suitable for use in diesel fuel formulations.

**[0088]** Commonly used additive solvents include hydrocarbon solvents such as alkanes, alkenes and aromatic hydrocarbons; mixtures of hydrocarbons such as in distillate fractions; and more polar solvents such as alcohols and ethers. The nature of the carrier or carrier mixture used in the additive composition (in particular its polarity) may be chosen to suit the natures and polarities of the additives present, as well as of a diesel fuel formulation in which the additive composition is to be used, so as to optimise the stability and efficacy of the composition during use.

**[0089]** A detergent (i) may be used in the additive composition at a concentration sufficient to provide a level of detergent in the finished fuel of 100 ppmw or greater, or 250 ppmw or greater, or 500 ppmw or greater, or 1000 ppmw or greater. It may be used at a concentration of up to 250 ppmw, or up to 500 ppmw, or up to 1000 ppmw, or up to 2000 ppmw, for example

from 100 to 2000 ppmw, or between 100 and 250 ppmw, or between 250 and 500 ppmw, or between 500 and 1000 ppmw, or between 1000 and 2000 ppmw.

**[0090]** A mixture (ii) of a lubricity improver and a conductivity improver may be used in the additive composition at a concentration sufficient to provide a level of (ii) in the finished fuel of 25 ppmw or greater, or of 50 ppmw or greater, or 100 ppmw or greater, or 200 ppmw or greater, or 300 ppmw or greater. It may be used at a concentration of up to 50 ppmw, or up to 100 ppmw, or up to 200 ppmw, or up to 300 ppmw, or up to 500 ppmw, for example from 25 to 500 ppmw, or from 25-100 ppmw, or from 100 to 200 ppmw, or from 200 to 300 ppmw, or from 300 to 500 ppmw.

**[0091]** The antioxidant may be used in the additive composition at a concentration sufficient to provide a level in the finished fuel of 20 ppmw or greater, or 50 ppmw or greater, or 100 ppmw or greater, or 250 ppmw or greater. It may be used at a concentration of up to 50 ppmw, or up to 100 ppmw, or up to 250 ppmw, or up to 500 ppmw, for example from 10 to 500 ppmw, or from 20 to 250 ppmw, or from 20 to 100 ppmw.

**[0092]** An additive composition prepared or used according to the second aspect described herein may for example be included in a diesel fuel formulation at a concentration of 100 ppmw or greater, or 250 ppmw or greater, or 500 ppmw or greater, or 750 ppmw or greater, or 1000 ppmw or greater. Its concentration may for example be up to 250 ppmw, or up to 500 ppmw, or up to 750 ppmw, or up to 1000 ppmw, or up to 2000 ppmw, such as from 100 to 2000 ppmw, or from 500 to 1000 ppmw, or from 750 to 1250 ppmw, or from 1000 to 2000 ppmw.

**[0093]** Other preferred features of the second aspect described herein, for example the natures of the species (i) and (ii) and the antioxidant; the purpose(s) for which, and the concentrations at which, these additives are used; and the nature of the diesel fuel formulation in which they are suitable to be used, may be as described above in connection with the first aspect of the invention.

**[0094]** According to a third aspect, the invention provides a method for preparing a diesel fuel formulation, which contains 60 to 99% v/v of paraffinic hydrocarbons, the method comprising (a) providing a diesel fuel component (for example a diesel base fuel) or mixture thereof, which contains 10% v/v or greater of paraffinic hydrocarbons and also an antioxidant selected from phenolic antioxidants, amines and mixtures thereof; (b) optionally assessing the oxidative stability of the component or mixture; (c) adding to the component or mixture species (i) or (ii) as defined above, and (d) assessing the oxidative stability of the resultant formulation, wherein the diesel fuel formulation contains 75% v/v or greater of a Fischer-Tropsch derived diesel fuel component or mixture thereof. Step (d) may be carried out in order to assess the effect of species (i) or (ii) on the oxidative stability of the diesel fuel formulation and/or on the activity of the antioxidant.

**[0095]** In an embodiment of the third aspect of the invention, species (i) or (ii) is added to the diesel fuel component, or mixture thereof, in the form of an additive composition prepared

according to the second aspect described herein. One or more additional diesel fuel additives may also be added to the fuel component or mixture, either with or separately to species (i) or (ii). Preferred features of the antioxidant, of species (i) or (ii) and of the diesel fuel component(s) and additive(s) with which they are mixed, may be as described above in connection with the first of the invention and second aspect described herein, as may the ways in which oxidative stability is assessed.

**[0096]** Because species (i) or (ii) can act to improve the activity of an antioxidant present in a diesel fuel formulation containing 60 to 99% v/v of paraffinic hydrocarbons, it can make possible the use of lower concentrations of the, or other, antioxidant additives in the formulation or in an additive composition for use in the formulation, without or without undue reduction in the oxidative stability of the formulation. This can in turn reduce the cost and complexity of preparing the formulation or composition, and/or can provide greater versatility in diesel fuel or additive formulation practices.

**[0097]** Thus, according to a fourth aspect, the invention provides the use of species (i) or (ii) as defined above, in a diesel fuel additive composition or in a diesel fuel formulation containing 60 to 99% v/v of paraffinic hydrocarbons, in combination with an antioxidant selected from phenolic antioxidants, amines and mixtures thereof, for the purpose of reducing the concentration of the or an antioxidant present in the composition or formulation, wherein the diesel fuel formulation contains 75% v/v or greater of a Fischer-Tropsch derived diesel fuel component or mixture thereof.

**[0098]** In the context of the fourth aspect of the invention, the term "reducing" embraces any degree of reduction, including reduction to zero. The reduction may for instance be 10% or more of the original concentration of the antioxidant, or 25 or 50 or 75 or 90% or more. The reduction may for instance be 2 ppmw or more, or 5 or 10 ppmw or more, or in cases 25 or 50 or 75 ppmw or more. The reduction may be as compared to the concentration of the antioxidant which would otherwise have been incorporated into the composition or formulation in order to achieve the properties and performance required and/or desired of it in the context of its intended use. This may be the concentration of the antioxidant which was present in the composition or formulation prior to the realisation that species (i) or (ii) could be used in the way provided by the present invention, and/or which was present in an otherwise analogous additive composition or diesel fuel formulation which was intended (eg marketed) for use in an analogous context, prior to adding species (i) or (ii) to it in accordance with the invention.

**[0099]** The reduction in concentration of the antioxidant may be as compared to the concentration of the antioxidant which would be predicted to be necessary to achieve a desired property or performance (for instance a desired level of oxidative stability) for the composition or formulation in the absence of species (i) or (ii). It may be as compared to the "standard treat rate" of the antioxidant in the relevant type of diesel fuel formulation.

**[0100]** In accordance with a fifth aspect, there is described herein a method of operating a diesel fuel-consuming system, and/or apparatus (for example a vehicle, or a heating

appliance) which is driven by such a system, the method comprising introducing into the system a diesel fuel formulation prepared according to the first, third or fourth aspect of the invention, or an additive composition prepared according to the second or the fourth aspect. This method may comprise introducing the formulation or the additive composition into a combustion chamber of a fuel-consuming system. The system may for example be an internal combustion engine.

**[0101]** A method according to the fifth aspect described herein may be carried out with the intention of increasing the oxidative stability of the diesel fuel formulation, or of a diesel fuel formulation containing the additive composition, following its introduction into the diesel fuel-consuming system.

**[0102]** In the context of the present invention, "use" of species (i) or (ii) as defined above in a diesel fuel formulation means incorporating the relevant species into the formulation, typically as a blend (ie a physical mixture) with one or more diesel fuel components, for example diesel base fuels, and optionally in combination with one or more additional diesel fuel additives.

**[0103]** Species (i) or (ii) will conveniently, although not necessarily, be incorporated before the formulation is introduced into a fuel-consuming system. Instead or in addition, the use of species (i) or (ii) may involve running a diesel fuel-consuming system on a diesel fuel formulation containing the relevant species, typically by introducing the formulation into a combustion region of the system. It may involve running a vehicle or other apparatus which is driven by a diesel fuel-consuming system, on a diesel fuel formulation containing the relevant species.

**[0104]** "Use" of species (i) or (ii) in the ways described above may also embrace supplying the relevant species together with instructions for its use in a diesel fuel formulation for one or more of the purposes described above in connection with the first to the fifth aspects. The species (i) or (ii) may itself be supplied as part of a composition which is suitable and/or adapted for use as a diesel fuel additive, in particular an additive composition prepared according to the second aspect. In this case, species (i) or (ii) may be included in such a composition for any one or more of the purposes described above in connection with the first to the fifth aspects of the invention.

**[0105]** Thus species (i) or (ii) may be used, in a diesel fuel formulation, in the form of an additive composition which has been prepared according to the second aspect, ie in which species (i) or (ii) is used to enhance the activity of an antioxidant additive. "Use" of species (i) or (ii) may therefore comprise use of such an additive composition.

**[0106]** "Use" of species (i) or (ii) in an additive composition means incorporating the relevant species into the composition, typically as a blend (ie a physical mixture) with one or more solvent carriers and optionally in combination with one or more additional diesel fuel additives. Species (i) or (ii) will conveniently, although not necessarily, be incorporated before the composition is introduced into a diesel fuel formulation or into a diesel fuel-consuming system.

Instead or in addition, the use of species (i) or (ii) may involve running a diesel fuel-consuming system on a diesel fuel formulation containing the relevant species in the additive composition, typically by introducing the formulation into a combustion region of the system. It may involve running a vehicle or other apparatus which is driven by a diesel fuel-consuming system, on a diesel fuel formulation containing species (i) or (ii) in the additive composition.

**[0107]** "Use" of species (i) or (ii) in the ways described above may also embrace supplying the relevant species together with instructions for its use in an additive composition for one or more of the purposes described above in connection with the first to the fifth aspects.

**[0108]** In general, references to "adding" a component to, or "incorporating" a component in, an additive composition or a diesel fuel formulation may be taken to embrace addition or incorporation at any point during the production of the composition or formulation or at any time prior to its use.

**[0109]** In certain embodiments, the present invention may be used to produce at least 1,000 litres of an additive composition or diesel fuel formulation containing a species (i) or (ii), or at least 5,000 or 10,000 or 20,000 or 50,000 litres.

**[0110]** A diesel fuel formulation which is prepared or used according to the invention may be marketed with an indication that it benefits from an improvement due to the inclusion of species (i) or (ii), for example increased oxidative stability and/or a lower concentration of an antioxidant in the formulation. The marketing of such a formulation may comprise an activity selected from: (a) providing the formulation in a container that comprises the relevant indication; (b) supplying the formulation with product literature that comprises the indication; (c) providing the indication in a publication or sign (for example at the point of sale) that describes the formulation; and (d) providing the indication in a commercial which is aired for instance on the radio, television or internet. The improvement may be attributed, in such an indication, at least partly to the presence of species (i) or (ii). The invention may involve assessing the relevant property of the formulation during or after its preparation. It may involve assessing the relevant property both before and after incorporation of species (i) or (ii), for example so as to confirm that the species contributes to the relevant improvement in the formulation.

**[0111]** A diesel fuel additive composition prepared or used according to the invention may be marketed with an indication that it benefits from an improvement due to the inclusion of species (i) or (ii), for example increased oxidative stability in a diesel fuel formulation in which the composition is used, and/or a lower concentration of an antioxidant in the composition. The marketing of such a composition may comprise an activity selected from: (a) providing the composition in a container that comprises the relevant indication; (b) supplying the composition with product literature that comprises the indication; (c) providing the indication in a publication or sign (for example at the point of sale) that describes the composition; and (d) providing the indication in a commercial which is aired for instance on the radio, television or internet. The improvement may be attributed, in such an indication, at least partly to the presence of species (i), (ii) or (iii). The invention may involve assessing the relevant property of the composition

during or after its preparation. It may involve assessing the relevant property both before and after incorporation of the species (i), (ii) or (iii), for example so as to confirm that the species contributes to the relevant improvement in the composition.

**[0112]** Throughout the description and claims of this specification, the words "comprise", "include" and "contain" and variations of these words, for example "comprising" and "comprises", mean "including but not limited to", and do not exclude other moieties, additives, components, integers or steps. Moreover 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.

**[0113]** Preferred features of each aspect of the invention may be as described in connection with any of the other aspects. Other features of the invention will become apparent from the following examples. Generally, the 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 invention are to be understood to be applicable to any other aspect, embodiment or example described herein unless incompatible therewith. For example, for the avoidance of doubt, optional and preferred features (including concentrations) of the antioxidant, the species (i) to (ii), any additional additive(s) and the diesel fuel formulation can apply to all aspects of the invention in which the antioxidant, the species (i) or (ii), the additional additive(s) or the fuel formulation are mentioned.

**[0114]** Unless stated otherwise, any feature disclosed herein may be replaced by an alternative feature serving the same or a similar purpose.

**[0115]** Where upper and lower limits are quoted for a property, for example, concentration of an additive or fuel component, then a range of values defined by a combination of any of the upper limits with any of the lower limits may also be implied.

**[0116]** In this specification, references to physical properties such as antioxidant, detergent, lubricity improver, conductivity improver, additive, fuel and fuel component properties are, unless stated otherwise, to properties measured under ambient conditions, ie at atmospheric pressure and at a temperature from 16 to 22 or 25°C, or from 18 to 22 or 25°C, for example about 20°C.

**[0117]** The present invention will now be further described with reference to the following non-limiting examples.

### **General**

**[0118]** Fuel formulations were prepared, in accordance with the invention, by incorporating antioxidants into diesel base fuels, together with (i) a detergent, (ii) a mixture of a lubricity improver and a conductivity improver, and (iii) a combination of (i) and (ii). For comparison purposes, further formulations were prepared by incorporating antioxidants into the base fuels in the absence of the components (i) to (iii).

**[0119]** The oxidative stability of each fuel formulation was assessed using the standard test method ASTM D7545-09 and a Petrospec (trade mark) "PetroOxy" test apparatus. A 5 ml sample of the test formulation was introduced into a pressure chamber which was then charged with oxygen at 700 kPa and ambient temperature. The test was initiated by switching on a heater and heating the chamber to 140°C. The pressure inside the chamber was recorded continuously until a breakpoint was reached, this being the point at which the pressure had fallen by 10% from the maximum pressure attained in the chamber. The "induction period" was defined as the time between the start of the test and the breakpoint. This provided an indication of the resistance of the test formulation to oxidation.

**[0120]** In the event that no breakpoint was reached within a specified time period T, the result was recorded as "greater than T".

**[0121]** Induction periods recorded in these examples are averages of two measurements.

**[0122]** Two antioxidants were used in the tests, designated AO1 and AO2. AO1 was butylated hydroxytoluene (BHT), obtained as Baynox (trade mark), a 20 g/l solution in biodiesel, ex Lanxess. BHT is employed in fuel formulations to reduce autoxidation rates by reacting with peroxy radicals, converting them to more stable hydroperoxides and non-radical products, thereby terminating the chain reactions that might otherwise occur. It is typically used in distillate fuels at treat rates from 10 to 200 ppmw; in these tests it was included at a concentration of 100 ppmw.

**[0123]** AO2 was N,N'-di-2-butyl-1,4-phenylenediamine, available from Octel Starreon (trade mark) as AO-22. It was included in the formulations at a concentration of 20 ppmw.

**[0124]** Other additives used in the tests were as follows. Neither was expected to cause a large, if any, increase in oxidative stability of a fuel to which it was added.

**[0125]** D1 - a multi-functional diesel performance additive package suitable for use in automotive diesel fuels, ex Innospec (trade mark). This contained as its main (detergent) active ingredient a polyisobutenyl (PIB) succinimide of a polyamine. It also contained minor amounts of other fuel additives, including a silicone antifoaming agent and a dehazer. It was used in the test formulations at a treat rate of 500 ppmw.

**[0126]** LC1 - a commercially available performance additive package suitable for use in automotive distillate fuels, ex Infineum (trade mark). This contained both a fatty ester-based lubricity improver and a conductivity improver. It was used at a treat rate of 250 ppmw.

**Example 1 - Base Fuel 1**

[0127] This example used a Fischer-Tropsch derived diesel base fuel BF1. This was a paraffinic gas oil made from natural gas via a Fischer-Tropsch synthesis, sourced from Qatar Shell GTL. It was free of additives, such as detergents, lubricity improvers and conductivity improvers. Its properties are summarised in Table 1 below.

Table 1

Property	Units	Test method	BF1
Density at 15°C	kg/m <sup>3</sup>	ASTM D4052	778.9
Kinematic viscosity at 40°C	mm <sup>2</sup> /s	EN ISO 3104	2.334
Distillation:		ASTM D86	
Initial boiling point			174.1
50%			255.6
90%	°C		320.1
95%			333.9
Final boiling point			343.9
Cetane number		ASTM D613	>75
Paraffin content	% w/w	Two-dimensional gas chromatography	>99

[0128] The results of the oxidative stability tests for BF1 and for test formulations containing BF1 blended with one or more of the additives AO1, AO2, D1 and LC1 are shown in Table 2 below. The third column shows the increase in induction period relative to that of BF1 alone.

[0129] For formulations containing two or more different additives, the fourth column shows the predicted increase in induction period relative to that of BF1 alone. These predictions assumed that the effects of a combination of additives on oxidative stability would be additive, eg that a combination of additives A and B would give an overall increase in stability equal to the sum of the increases which the two additives caused when used alone at the same concentrations. Thus, numerically, the predicted induction period ( $IP_{mixture}$ ) for a fuel formulation containing a mixture of additives A, B and C is defined by the formula:

$$\text{Predicted } IP_{mixture} = IP_{none} * [1+(\% \text{ increase due to A}$$

+ % increase due to B + % increase due to C)]

where  $IP_{none}$  is the induction period for the same formulation but without any of the three additives.

[0130] The fifth column in Table 2 shows the percentage benefit provided by the invention, ie the difference between the measured increase in induction period and the predicted increase, as a percentage of the predicted increase for the formulations containing two or more additives. A deficit (when the measured increase was smaller than predicted) is shown as a negative number. Synergistic combinations (positive benefit compared to predicted results) are indicated by positive numbers.

Table 2

Test formulation	Measured induction period (hours)	Induction period increase (hours)	Predicted increase (hours)	% benefit/deficit
*BF1	1.419	0.00		
*BF1 + D1	1.933	0.51		
*BF1 + AO1	2.224	0.80		
*BF1 + AO2	3.908	2.49		
*BF1 + LC1	1.468	0.05		
BF1 + D1 + AO1	2.976	1.56	1.319	18
BF1 + D1 + AO2	4.847	3.43	3.002	14
*BF1 + D1 + LC1	1.858	0.44	0.563	-22
BF1 + AO1 + LC1	2.434	1.01	0.853	19
BF1 + AO2 + LC1	4.774	3.35	2.537	32
*BF1 + D1 + AO1 + LC1	2.909	1.49	1.367	9
*BF1 + D1 + AO2 + LC1	3.974	2.55	3.051	-16
*Not according to the present invention				

[0131] It can be seen from Table 2 that antioxidants AO1 and AO2 both increased the oxidative stability (and hence the induction period) of the Fischer-Tropsch derived base fuel alone, as did the detergent D1 to a much smaller extent. The lubricity improver/conductivity improver mixture LC1 did not cause any significant increase in oxidative stability, and the combination of D1 and LC1 caused a significant reduction in stability.

[0132] Surprisingly, when detergent D1 was used together with the antioxidants, the combined effect on oxidative stability was greater than would have been predicted from their individual effects, indicating some form of synergistic interaction between them. The detergent appeared to enhance the activity of the antioxidants. Similar synergies were observed when LC1 was

used with the antioxidants. The combination of D1 and LC1 also appeared to enhance the antioxidant activity of the phenolic antioxidant AO1.

[0133] In the case of this Fischer-Tropsch derived base fuel, unexpectedly good results were observed for binary additive combinations containing an antioxidant with either a detergent or a lubricity improver/conductivity improver mixture, especially the combination of the amine antioxidant AO2 and the lubricity improver/conductivity improver mixture.

**Example 2 - Base Fuel 2 (Not according to the present invention)**

[0134] Example 1 was repeated using a hydrogenated vegetable oil (HVO) blend BF2 as a base fuel. BF2, ex Neste Oil, was a biodiesel fuel produced by hydrotreating vegetable oils and other biologically derived lipids. Its chemical composition was similar to that of Fischer-Tropsch derived base fuels, being paraffinic with essentially no aromatic components or sulphur, although with a relatively narrow carbon chain length distribution. Its properties are summarised in Table 3 below.

Table 3

Property	Units	Test method	BF2
Density at 15°C	kg/m <sup>3</sup>	ASTM D4052	776.2
Kinematic viscosity at 40°C	mm <sup>2</sup> /s	EN ISO 3104	2.57
Distillation:		ASTM D86	
Initial boiling point	°C		161.7
50%			273.9
90%			287.7
95%			291.4
Final boiling point			298.2
Cetane number (CID)		ASTM D7668	79.4
Paraffin content	% w/w	Two-dimensional gas chromatography	99.5

[0135] As indicated in Table 3, analysis revealed that BF2 comprised 99.5% w/w paraffins. More than 90% of the paraffins content of BF2 was represented by carbon chain lengths of C12 to C18. The results of the oxidative stability tests are shown in Table 4 below, for BF2 and for test formulations containing BF2 blended with one or more of the additives AO1, AO2, D1 and LC1. The third, fourth and fifth columns correspond to those in Table 2.

Table 4

Test formulation	Measured induction period (hour s)	Induction period increase (hours)	Predicted increase (hours)	% benefit/ deficit
BF2	1.284	0.00		
BF2 + D1	1.737	0.45		
BF2 + AO1	3.022	1.74		
BF2 + AO2	4.097	2.81		
BF2 + LC1	1.316	0.03		
BF2 + D1 + AO1	3.642	2.36	2.191	8
BF2 + D1 + AO2	4.209	2.93	3.266	-10
BF2 + D1 + LC1	1.686	0.40	0.485	-17
BF2 + AO1 + LC1	2.367	1.08	1.771	-39
BF2 + AO2 + LC1	5.174	3.89	2.845	37
BF2 + D1 + AO1 + LC1	3.395	2.11	2.223	-5
BF2 + D1 + AO2 + LC1	5.057	3.77	3.298	14

[0136] Table 4 shows that both antioxidants increased the oxidative stability of the HVO base fuel alone, as did detergent D1 to a much smaller extent. The lubricity improver/conductivity improver mixture LC1 did not cause any significant increase in oxidative stability, and the combination of D1 and LC1 caused a significant reduction.

[0137] Surprisingly, when detergent D1 was used with the phenolic antioxidant AO1, the combined effect on oxidative stability was unexpectedly greater than would have been predicted from their individual effects, indicating some form of synergistic interaction as the detergent appeared to enhance the activity of the antioxidant. An even more marked synergy was observed when LC1 was used with the amine antioxidant AO2, and when a combination of D1 and LC1 was used in combination with the amine antioxidant.

[0138] In the case of this HVO base fuel, particularly good results were thus seen for the formulations containing an amine antioxidant and a lubricity improver/conductivity improver mixture, both with and without the detergent additive D1.

### Comparative Example 3 - Base Fuel 3

[0139] Example 1 was repeated using a petroleum-derived diesel base fuel BF3. This was a commercially available, EN 590-compliant ultra low sulphur diesel base fuel, ex Shell, formulated without fatty acid methyl esters (FAMES). Its properties are summarised in Table 5 below.

Table 5

Property	Units	Test method	BF3
Density at 15°C	kg/m <sup>3</sup>	ASTM D4052	832.8
Kinematic viscosity at 40°C	mm <sup>2</sup> /s	EN ISO 3104	2.839
Distillation:		ASTM D86	
Initial boiling point	°C		172.9
50%			269.5
90%			337.0
95%			351.6
Final boiling point			363.4
Cetane number		ASTM D613	54.8
Aromatics content	% w/w	EN 12916 (HPLC)	22.5

[0140] The results of the oxidative stability tests for BF3-containing formulations are shown in Table 6 below. The third, fourth and fifth columns correspond to those in Table 2.

Table 6

Test formulation	Measured induction period (hours)	Induction period increase (hours)	Predicted increase (hours)	% benefit/deficit
BF3	0.733	0.00		
BF3 + D1	1.540	0.81		
BF3 + AO1	1.365	0.63		
BF3 + AO2	3.096	2.36		
BF3 + LC1	0.940	0.21		
BF3 + D1 + AO1	1.842	1.11	1.440	-23
BF3 + D1 + AO2	4.377	3.64	3.171	15
BF3 + D1 + LC1	1.495	0.76	1.016	-25
BF3 + AO1 + LC1	1.440	0.71	0.840	-16

Test formulation	Measured induction period (hour s)	Induction period increase (hours)	Predicted increase (hours)	% benefit/deficit
BF3 + AO2 + LC1	1.935	1.20	2.571	-53
BF3 + D1 + AO1 + LC1	1.930	1.20	1.648	-27
BF3 + D1 + AO2 + LC1	4.248	3.52	3.378	4

[0141] Table 6 shows that the surprising effects of the present invention were not generally observed in the case of the petroleum-derived base fuel BF3, which had a relatively low paraffin content. Although antioxidants AO1 and AO2 increased the oxidative stability of the base fuel, the detergent additive D1 only enhanced that stability for the amine antioxidant AO2. The lubricity improver/conductivity improver combination LC1 was detrimental to the antioxidant activities of AO1 and AO2, and when combined with D1 reduced the antioxidant activity of the phenolic antioxidant AO1.

[0142] Thus, with petroleum-derived diesel base fuels, improvements in oxidative stability were achieved only with the amine antioxidant AO2, and only in the presence of the detergent additive.

#### **Example 4 - Base Fuel 4 (not according to the present invention)**

[0143] Example 1 was repeated using a base fuel BF4, which was a 1:1 v/v blend of BF1 and BF2 having an overall paraffinic hydrocarbon content of greater than 99% v/v.

[0144] The results of the oxidative stability tests are shown in Table 7 below. The third, fourth and fifth columns correspond to those in Table 2.

Table 7

Test formulation	Measured induction period (hour s)	Induction period increase (hours)	Predicted increase (hours)	% benefit/deficit
BF4	1.359	0.00		
BF4 + D1	1.711	0.35		
BF4 + AO1	2.418	1.06		
BF4 + AO2	4.210	2.85		
BF4 + LC1	1.361	0.00		
BF4 + D1 + AO1	2.899	1.54	1.411	9

Test formulation	Measured induction period (hour s)	Induction period increase (hours)	Predicted increase (hours)	% benefit/deficit
BF4 + D1 + AO2	4.848	3.49	3.203	9
BF4 + D1 + LC1	1.647	0.29	0.354	-19
BF4 + AO1 + LC1	2.493	1.13	1.061	7
BF4 + AO2 + LC1	4.670	3.31	2.853	16
BF4 + D1 + AO1 + LC1	2.821	1.46	1.413	3
BF4 + D1 + AO2 + LC1	5.534	4.18	3.205	30

[0145] Table 7 shows antioxidants AO1 and AO2 greatly increased oxidative stability of the Fischer-Tropsch fuel/HVO blend BF4. Detergent D1 did so to a smaller extent. The lubricity improver/conductivity improver mixture LC1 did not cause any significant increase in oxidative stability, and the combination of D1 and LC1 caused a significant reduction in stability.

[0146] Surprisingly, when the detergent D1 was used with the antioxidants, the combined effect on oxidative stability was greater than would have been predicted from their individual effects, indicating a synergistic interaction between them. Similar synergies were observed when LC1 was used with antioxidants, and also when D1 and LC1 were used to enhance antioxidant activity (despite the fact that a D1/LC1 mixture on its own caused a large reduction in the oxidative stability of BF4).

[0147] In this case, the Fischer-Tropsch derived and HVO base fuels blend provided particularly good results for formulations containing both the amine antioxidant AO2 and the lubricity improver/conductivity improver mixture LC1.

#### **Example 5 - Base Fuel 5 (not according to the present invention)**

[0148] Example 1 was repeated using a base fuel BF5, which was a 1:1 v/v blend of BF1 and BF3, having a synthetic paraffinic hydrocarbon content of 50% v/v.

[0149] The results of the oxidative stability tests are shown in Table 8 below. The third, fourth and fifth columns correspond to those in Table 2.

Table 8

Test formulation	Measured induction period (hour s)	Induction period increase (hours)	Predicted increase (hours)	% benefit/ deficit
BF5	1.444	0.00		
BF5 + D1	1.800	0.36		
BF5 + AO1	1.928	0.48		
BF5 + AO2	2.858	1.41		
BF5 + LC1	1.551	0.11		
BF5 + D1 + AO1	1.932	0.49	0.840	-42
BF5 + D1 + AO2	4.990	3.55	1.770	100
BF5 + D1 + LC1	1.779	0.34	0.463	-28
BF5 + AO1 + LC1	1.755	0.31	0.591	-47
BF5 + AO2 + LC1	2.962	1.52	1.521	0
BF5 + D1 + AO1 + LC1	2.293	0.85	0.947	-10
BF5 + D1 + AO2 + LC1	5.565	4.12	1.877	120

**[0150]** Table 8 shows that antioxidants AO1 and AO2 increased the oxidative stability of the Fischer-Tropsch fuel/mineral fuel blend, as did detergent D1. The lubricity improver/conductivity improver mixture LC1 did not cause any sizeable increase in oxidative stability, and the combination of D1 and LC1 caused a significant reduction.

**[0151]** Surprisingly, when detergent D1 was used together with amine antioxidant AO2, the combined effect on oxidative stability was far greater than would have been predicted from their individual effects, indicating a synergistic interaction between them. A similarly high level of synergy was observed when a combination of D1 and LC1 was used with the amine antioxidant.

**[0152]** In the case of this blend of Fischer-Tropsch derived and mineral base fuels, particularly good results were achieved using an amine antioxidant and a detergent. This pattern reflected that observed for the mineral base fuel alone (BF3), although the addition of Fischer-Tropsch derived fuel components and the resultant increase in paraffin content appeared to enhance the synergistic interaction between the antioxidant and the detergent.

**[0153]** It can be seen from the above examples that species (i) or (ii), as defined above, can

be used to enhance the antioxidant activity in a relatively high paraffin content diesel fuel formulation. It can be used to improve the oxidative stability of such formulations, which are likely to be more prone to oxidation because of the paraffinic hydrocarbons they contain. A species (i) or (ii) can similarly be used to reduce the concentration of an antioxidant which is needed in such a diesel fuel formulation, without or without undue detriment to the oxidative stability of the formulation. The present invention thus provides more options for the diesel fuel formulator.

**[0154]** Moreover, these results can be achieved through the use of conventional diesel fuel additives (detergents, lubricity improvers and conductivity improvers) which can be of value in a diesel fuel formulation for other purposes as well as their effects on oxidative stability. Species (i) to (ii) are able to interact synergistically with antioxidants in higher paraffin content diesel fuel formulations. This unexpected effect can allow new uses for fuel additives which are not normally regarded as antioxidants.

**[0155]** Thus, in recognising that the species (i) to (ii) may be used for such novel purposes, the invention allows the formulator to achieve more than one aim through the use of a particular additive. This can allow a reduction in overall additive concentrations, with its associated processing benefits, yet without undue loss of fuel stability.

## REFERENCES CITED IN THE DESCRIPTION

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**Patentkrav**

1. Anvendelse af en form valgt blandt:

- 5 (i) detergenter; og  
(ii) blandinger, der både indeholder en smøreevneforbedrer og en ledningsevneforbedrer; i en dieselbrændstofformulering, der indeholder 60 til 99 volumen-% paraffiniske carbonhydrider og en antioxidant, med det formål at øge den oxidative stabilitet af formuleringen målt i henhold til ASTM D7545-09, hvor antioxidanten er valgt blandt  
10 phenoliske antioxidanter, aminer og blandinger deraf, hvor formen (i) omfatter et polyisobutenyl (PIB)-succinimiddetergent, hvor formen (ii) omfatter en fedtsyreester-smøreevneforbedrer, hvor formen (ii) omfatter en sulfonsyre-ledningsevneforbedrer, og hvor dieselbrændstofformuleringen indeholder 75 volumen-% eller mere af en Fischer-Tropsch-afledt dieselbrændstofbestanddel eller en blanding deraf.

- 15 2. Anvendelse ifølge krav 1, hvor antioxidanten er valgt blandt phenoliske antioxidanter, især hindrede phenoler; og blandinger deraf.

- 20 3. Anvendelse ifølge krav 1, hvor antioxidanten er valgt blandt aminer, især aromatiske aminer, og blandinger deraf.

4. Anvendelse ifølge et hvilket som helst af ovennævnte krav, hvor formen (ii) omfatter en naphthylsulphonsyre-ledningsevneforbedrer.

- 25 5. Fremgangsmåde til fremstilling af en dieselbrændstofformulering, der indeholder 60 til 99 volumen-% paraffiniske carbonhydrider, hvilken fremgangsmåde omfatter (a) tilvejebringelse af en dieselbrændstofbestanddel eller en blanding deraf, der indeholder 10 volumen-% eller mere af paraffiniske carbonhydrider og endvidere en antioxidant valgt blandt phenoliske antioxidanter, aminer og blandinger deraf; (b) eventuelt vurdering af den  
30 oxidative stabilitet af bestanddelen eller blandingen; (c) tilsætning til bestanddelen eller blandingen af en form (i) eller (ii) ifølge et hvilket som helst af kravene 1 til 4 og (d) vurdering af den oxidative stabilitet af den resulterende formulering, hvor

dieselbrændstoffformuleringen indeholder 75 volumen-% eller mere af en Fischer-Tropsch-afledt dieselbrændstofbestanddel eller en blanding deraf.

5 6. Anvendelse af en form (i) eller (ii) ifølge et hvilket som helst af kravene 1 til 4 i en dieselbrændstofadditivsammensætning eller i en dieselbrændstofformulering, der indeholder 60 til 99 volumen-% paraffiniske carbonhydrider, i kombination med en antioxidant valgt blandt phenoliske antioxidanter, aminer og blandinger deraf til formålet reducering af koncentrationen af antioxidanten, der er til stede i sammensætningen eller formuleringen, hvor dieselbrændstofformuleringen indeholder 75 volumen-% eller mere of 10 en Fischer-Tropsch-afledt dieselbrændstofbestanddel eller en blanding deraf.