



(51) International Patent Classification:

C10L 1/10 (2006.01)

(21) International Application Number:

PCT/EP2017/062687

(22) International Filing Date:

24 May 2017 (24.05.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

16171534.7 26 May 2016 (26.05.2016) EP

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(54) Title: FUEL COMPOSITIONS

(57) Abstract: Use of 2-ethylhexyl nitrate in combination with one or more detergents in a diesel fuel composition for the purpose of reducing internal diesel injector deposits (IDIDs) in a compression ignition combustion engine.



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FUEL COMPOSITIONS

Field of the Invention

The present invention relates to liquid fuel compositions having improved cleanliness and deposit reduction properties, especially internal diesel injector deposit (IDID) reduction properties, and in particular to the use of 2-ethylhexyl nitrate and one or more detergents in combination in a diesel fuel composition to provide said improvements.

Background of the Invention

Government regulations and market demands continue to emphasize conservation of fossil fuels in the transportation industry. The build-up of deposits arising from fuel combustion in an engine reduces the efficiency of further combustion and leads to inefficient use of fuel over the lifetime of an engine.

A common problem with diesel engines is fouling of the injector, particularly the injector body and the injector nozzle. Injector nozzle fouling occurs when the nozzle becomes blocked with deposits from the diesel fuel. Deposits are also known to occur at the injector tip.

In addition to these "external" injector deposits in the nozzle hole and at the injector tip which lead to reduced flow and power loss, deposits may occur within the injector body causing further problems. These deposits may be referred to as internal diesel injector deposits, or IDIDs. IDIDs include deposits at the needle seat and upstream within the injector, and exclude deposits in the injector nozzle holes. IDIDs occur inside the injector on the critical moving parts. IDIDs

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can hinder the movement of these parts affecting the timing and quantity of fuel injection and also have other undesirable effects. Since modern diesel engines operate under very precise conditions these deposits can have a significant impact on performance.

IDIDs can cause a number of problems, including power loss, engine breakdowns, rough idle and reduced fuel economy due to less than optimal fuel metering and combustion. Initially the user may experience cold start problems and/or rough engine running. Eventually, these deposits can lead to more serious injector sticking. This occurs when the deposits stop parts of the injector from moving and thus the injector stops working. When one or more of the injectors stick the engine may fail completely.

Detergent additives are normally added to diesel fuels in order to reduce, remove or slow the build-up of engine deposits. Detergent additives have thus commonly been used in fuel compositions to try to reduce deposits but there is still a need for better additives to reduce deposit formation, in particular "internal" diesel injector deposits or IDIDs formation.

Any incremental improvement in fuel economy (FE) is also of great importance in the automotive sector. There is therefore also a continuing need for improvements in fuel economy performance of fuel compositions used to fuel an internal combustion engine.

Organic nitrates have been known for some time as ignition accelerants in fuels, and some are also known to increase the cetane number of diesel fuels. Perhaps the most commonly used diesel fuel ignition improver is 2-ethylhexyl nitrate (2-EHN), which is generally understood to operate by shortening the ignition delay of a fuel to

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which it is added.

There are a few proposals in the art of the use of 2-EHN in combination with other diesel fuel components to achieve specific benefits, often in relation to enhancing the cetane number properties of the resulting fuel formulation.

RU2010124844A is one such proposal and relates to diesel fuel containing additives which increase cetane number. Additives consist of premixed cyclohexyl nitrate or 2-EHN and peroxides selected from di-tert-butyl peroxide, dicumyl peroxide and cumyl hydroperoxide. The effect of these additives is high cetane number of diesel fuel and low content of nitrogen oxides in exhaust gas.

It is therefore known from the prior art that use of 2-EHN alone or in combination with certain other components achieves an enhanced cetane number effect.

In the industry, there has been no knowledge hitherto that 2-EHN has any effect on engine cleanliness or deposit formation, in particular internal diesel injector deposit (IDID) formation.

Summary of the Invention

It has now surprisingly been found that through the use of 2-EHN in combination with a detergent, a synergistic effect of enhanced cleanliness of the engine and reduction of engine injector deposits, in particular "internal" diesel injector deposits or IDIDs, can be achieved. Such a boost in cleanliness over and above that which can be achieved by the use of the detergent alone is totally surprising and unexpected.

The combined use of 2-EHN and detergent reduces injector deposits, in particular "internal" diesel injector deposits or IDIDs, boosts engine cleanliness and indirectly leads to an improvement in the fuel economy

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properties of a fuel composition. It also enables the possibility to use a reduced quantity of expensive detergent additive.

Accordingly, in a first aspect of the present invention, there is provided the use of 2-ethylhexyl nitrate and one or more detergents in a diesel fuel composition for the purpose of avoiding or reducing "internal" diesel injector deposits or IDIDs in a compression ignition engine and/or for the purpose of improving fuel economy.

In another aspect of the present invention, there is provided a method of improving the cleanliness and/or the fuel economy performance of an internal combustion engine by fuelling the internal combustion engine with a diesel fuel composition comprising 2-ethylhexyl nitrate and one or more detergents in combination.

Detailed Description of the Invention

The term "fuel economy" as used herein refers to optimized efficiency of an engine consuming fuel, i.e. the same power output can be obtained from the engine while consuming less fuel (and therefore emitting less carbon dioxide).

According to the present invention, there is provided the use of 2-ethylhexyl nitrate and one or more detergents in a diesel fuel composition inter alia for the purpose of improving cleanliness and, as a result, fuel economy. In the context of this aspect of the invention, the term "improving" embraces any degree of improvement. We have found via our cleanliness rating (assessed via deposit reduction) that improvement of between 250 and 300 % is found. The improvement may be of the order of 10% or more, preferably 20% or more, more preferably 50% or more, and especially 100% or more of

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the cleanliness of an analogous fuel formulation, as measured by an increase in the rating score, for example according to the CEC F-110-16 (issue 1) test method, prior to adding both 2-ethylhexyl nitrate and a detergent to it in accordance with the present invention.

In accordance with the present invention, the cleanliness and deposit reduction may be determined in any known manner in the art. In connection with the present invention, it is however preferably assessed via the CEC F-110-16 (issue 1) test method.

In accordance with the present invention, fuel economy of a fuel composition may also be determined in any known manner, for instance using the standard test procedure according to *EEC Directive 90/C81/01* using the New European Drive Cycle (NEDC) for a vehicle on a chassis dynamometer or a bench engine. This provides a so-called "measured" fuel consumption number obtained under engine running conditions. In some embodiments, the methods/uses encompass adding 2-EHN and one or more detergents to a fuel composition so as to adjust the fuel economy performance or to achieve or reach a desired target fuel economy value. In the context of the invention, to "reach" a target fuel economy value can also embrace exceeding that number. Thus, the target fuel economy number may be a target minimum fuel economy value.

Detergent additives are added to diesel fuels at levels intended to reduce, remove or slow the build-up of engine deposits. By the findings of the present invention this normal action is synergistically boosted or enhanced by the use of 2-EHN. The (active matter) concentration of one or more detergents in the diesel fuel composition is conventionally in the range from 5 to

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1500 ppmw, suitably from 10 to 750 ppmw, more suitably from 10 to 600 ppmw. In one embodiment of the present invention, the (active matter) concentration of one or more detergents in the diesel fuel composition is in the range of from 10 to 500 ppmw. It is an advantage of the present invention that by virtue of the synergistic effect of using 2-EHN alongside the detergent, the amount of expensive detergent additive can then be reduced.

The 2-EHN is preferably present in the fuel composition at a level in the range from 10 to 1500 ppmw, more preferably from 50 to 1000 ppmw, even more preferably from 100 to 800 ppmw and especially from 200 to 700 ppmw. The levels of 2-EHN provided here refer to 2-EHN which is added to the base fuel over and above any 2-EHN which may already be present in the base fuel. 2-EHN may already be present in the base fuel, for example, in order for the base fuel to comply with standard diesel fuel specifications such as EN590 or ASTM D975. Up to 1500 ppmw, or more, of 2-EHN may already be present in the base fuel, by weight of the total base fuel.

The composition contains one or more detergents. In one embodiment of the present invention the composition contains only one detergent.

Examples of detergents suitable for use for the present purpose include 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

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succinimides such as polyisobutylene succinimides, and especially PIBSI-TEPA (polyisobutylene succinimides generated using polyamine technical mixtures which contain a high proportion of tetraethylene pentamine).

5 Other detergents suitable for use in diesel fuel additives for the present purpose include quaternary ammonium salts such as those disclosed in US2012/0102826, US2012/0010112, WO2011/149799, WO2011/110860 and WO2006/135881.

10 The diesel fuel additive mixture may contain other components in addition to the detergent and 2-EHN. Examples are lubricity enhancers; dehazers, e.g. alkoxyated phenol formaldehyde polymers; anti-foaming agents (e.g. polyether-modified polysiloxanes);
15 additional ignition improvers (cetane improvers) such as 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
20 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
25 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
30 deactivators; combustion improvers; static dissipator additives; cold flow improvers; and wax anti-settling agents.

Unless otherwise stated, the (active matter)

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concentration of each such optional additional additive component in the additivated diesel 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.

Hereinafter other additives are discussed in more detail.

The diesel fuel additive mixture may contain a lubricity enhancer, especially when the diesel fuel composition has a low (e.g. 500 ppmw or less) sulphur content. In the additivated diesel fuel composition, the lubricity enhancer is conveniently present at a concentration of less than 1000 ppmw, preferably between 50 and 1000 ppmw, more preferably between 70 and 1000 ppmw. Suitable commercially available lubricity enhancers include ester- and acid-based additives. Other lubricity enhancers are described in the patent literature, in particular in connection with their use in low sulphur content diesel fuels, for example in:

- the paper by Danping Wei and H.A. 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;
- US-A-5490864 - 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.

In addition to 2-EHN, the fuel composition herein may comprise one or more other cetane number enhancers. Cetane number enhancers are known and commercially

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available, and may also be known (in the context of diesel fuels) as "cetane (number) improvers", "combustion improvers" and "ignition improvers" etc. as previously described.

5 Cetane enhancers are often added to diesel fuels, at additive levels (typically 10 to 2000 ppm w/w).

They function to reduce the ignition delay, i.e. the period between the time of injection of the fuel and the start of combustion (ignition).

10 The cetane number (CN) of a fuel is defined by reference to the ignition properties of standard mixtures of n-hexadecane (cetane, CN = 100) and 2,2,4,4,6,8,8-hepta-methylnonane (CN = 15). A fuel with a high CN has a short ignition delay. Typically, molecules with high
15 octane numbers, which confer a resistance to spontaneous ignition in gasoline spark ignition engines, have low cetane numbers. The addition of small amounts of cetane enhancers to a diesel fuel may, therefore, result in improved fuel properties based on the shorter ignition
20 delay.

Known cetane number enhancers include, but are not limited to certain organic nitrates other than 2-EHN (e.g. isopropyl nitrate, cyclohexyl nitrate, and methoxyethyl nitrate) and organic peracids and peresters.

25 It may also be preferred for the diesel 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.

30 The (active matter) concentration of any dehazer in the diesel 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, and

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especially from 1 to 5 ppmw. Alternatively, higher levels of a dehazer compound may be used.

The (active matter) concentration of any additional ignition improver present will preferably be 2600 ppmw or less, more preferably 2000 ppmw or less, even more preferably 300 to 1500 ppmw.

A conventional fuel additive mixture for a diesel fuel composition will typically contain a diesel fuel-compatible diluent. Such a diluent may be a mineral oil, a solvent such as those sold by Shell companies under the trade mark "SHELLSOL", a polar solvent such as an ester and, in particular, an alcohol, e.g. hexanol, 2-ethylhexanol, decanol, isotridecanol and alcohol mixtures such as those sold by Shell companies under the trade mark "LINEVOL", especially LINEVOL 79 alcohol which is a mixture of C₇₋₉ primary alcohols, or a C₁₂₋₁₄ alcohol mixture which is commercially available. A fuel additive mixture for achieving the use of the present invention, may contain the one or more detergents, the 2-EHN and diluent as described above. A fuel additive mixture for achieving the use of the present invention may alternatively contain the one or more detergents and diluent as described above without the 2-EHN. In such case, the 2-EHN is present in the base fuel already or is added to the base fuel separately. In another embodiment, the 2-EHN may be present both in a fuel additive mixture and in the base fuel.

In use, the 2-EHN and the one or more detergents may thus be pre-dissolved in a suitable solvent, for example an oil such as a mineral oil or Fischer-Tropsch derived hydrocarbon mixture; a fuel component (which again may be either mineral or Fischer-Tropsch derived) compatible with the diesel fuel composition in which the additive is

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to be used (for example a middle distillate fuel component such as a gas oil or kerosene); a poly alpha olefin; a so-called biofuel such as a fatty acid alkyl ester (FAAE), a Fischer-Tropsch derived biomass-to-liquid synthesis product, a hydrogenated vegetable oil, a waste or algae oil or an alcohol such as ethanol; an aromatic solvent; any other hydrocarbon or organic solvent; or a mixture thereof. Preferred solvents for use in this context are mineral oil based diesel fuel components and solvents, including heavy aromatic naphtha, and Fischer-Tropsch derived components such as the "XtL" components referred to below. Biofuel solvents may also be preferred in certain cases. Typically, the 2-EHN and the one or more detergents will be part of an additive (performance) package additionally containing other additives such as anti-foaming agents, corrosion inhibitors, dehazers etc. Alternatively, the 2-EHN and the one or more detergents may be blended directly with the base fuel.

The total content of the optional additional additives in the diesel fuel composition may be suitably between 0 and 10000 ppmw and preferably below 5000 ppmw.

In the above, amounts (concentrations, % vol, ppmw, % wt) of components are of active matter, i.e. exclusive of volatile solvents/diluent materials.

The liquid fuel composition of the present invention may be produced by admixing the fuel additive combination with a diesel base fuel suitable for use in an internal combustion engine.

The remainder of the composition will typically consist of one or more automotive base fuels optionally together with one or more other fuel additives, for instance as described above.

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The engine in which the fuel composition of the invention is used may be any appropriate engine. Thus, where the fuel is a diesel, including a biodiesel, fuel composition, the engine is a diesel or compression
5 ignition engine. Likewise, any type of diesel engine may be used, such as a turbo charged diesel engine, provided the same or equivalent engine is used to measure fuel economy with and without the fuel economy increasing components. Generally, the fuel economy improvers of the
10 invention are suitable for use over a wide range of engine working conditions.

A diesel fuel composition prepared in accordance with the present invention may in general be any type of diesel fuel composition suitable for use in a compression
15 ignition (diesel) engine; and it may itself comprise a mixture of diesel fuel components.

Thus, in addition to the 2-EHN and one or more detergents, a diesel fuel composition prepared according to the present invention may comprise one or more diesel
20 fuel components of conventional type. It may, for example, include a major proportion of a diesel base fuel, for instance of the type described below. In this context, a "major proportion" means at least 50% w/w, and typically at least 85% w/w based on the overall
25 composition. More suitably, at least 90% w/w or at least 95% w/w. In some cases at least 98% w/w or at least 99% w/w of the fuel composition consists of the diesel base fuel. Accordingly, in some embodiments, the base fuel may itself comprise a mixture of two or more diesel fuel
30 components of the types described below.

Typical diesel fuel components comprise liquid hydrocarbon middle distillate fuel oils, for instance petroleum derived gas oils. Such base fuel components may

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be organically or synthetically derived, and are suitably obtained by distillation of a desired range of fractions from a crude oil. They will typically have boiling points within the usual diesel range of 150 to 410°C or 170 to 370°C, depending on grade and use. They will typically have densities from 0.75 to 0.9 g/cm³, such as from 0.8 to 0.86 g/cm³, at 15°C (IP 365) and measured cetane numbers (ASTM D613) of from 35 to 80, more preferably from 40 to 75. 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 centistokes. Such fuels are generally suitable for use in compression ignition (diesel) internal combustion engines, of either the indirect or direct injection type.

An automotive diesel fuel composition which results from carrying out the present invention will also suitably fall within these general specifications. Accordingly, it will generally comply with applicable current standard specification(s) such as for example EN 590 (for Europe) or ASTM D975 (for the USA). By way of example, the fuel composition may have a density from 0.82 to 0.845 g/cm³ at 15°C; a T₉₅ boiling point (ASTM D86) of 360°C or less; a cetane number (ASTM D613) of 45 or greater; a kinematic viscosity (ASTM D445) from 2 to 4.5 mm²/s at 40°C; a sulphur content (ASTM D2622) of 50 mg/kg or less; and/or a polycyclic aromatic hydrocarbons (PAH) content (IP391 (mod)) of less than 11% w/w. 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. In particular, its measured cetane number will preferably be from 40 to 70,

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to 75 or to 80, more preferably from 50 to 65, or at least greater than 50, greater than 55, greater than 60, or greater than 65.

5 A petroleum derived gas oil, e.g. obtained from refining and optionally (hydro) processing a crude petroleum source, may be incorporated into a diesel fuel composition. 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
10 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
15 hydrocracker unit. Optionally a petroleum derived gas oil may comprise some petroleum derived kerosene fraction. Such gas oils may be processed in a hydro-desulphurisation (HDS) unit so as to reduce their sulphur content to a level suitable for inclusion in a diesel
20 fuel composition. This also tends to reduce the content of other polar species such as oxygen- or nitrogen-containing species. In some cases, the fuel composition will include one or more cracked products obtained by splitting heavy hydrocarbons.

25 In some embodiments of the present invention, the base fuel may be or contain another so-called "biodiesel" fuel component, such as a vegetable oil, hydrogenated vegetable oil or vegetable oil derivative (e.g. a fatty acid ester, in particular a fatty acid methyl ester, FAME), or another oxygenate such as an acid, ketone or
30 ester. Such components need not necessarily be bio-derived. Where the fuel composition contains a biodiesel component, the biodiesel component may be present in

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quantities up to 100%, such as between 1% and 99% w/w, between 2% and 80% w/w, between 2% and 50% w/w, between 3% and 40% w/w, between 4% and 30% w/w, or between 5% and 20% w/w. In one embodiment the biodiesel component may be FAME.

A diesel base fuel may consist of or comprise a Fischer-Tropsch derived diesel fuel component, typically a Fischer-Tropsch derived gas oil. As used herein, the term "Fischer-Tropsch derived" means that a material is, or is obtained from, a synthesis product of a Fischer-Tropsch condensation process. A Fischer-Tropsch derived fuel or fuel component will therefore be a hydrocarbon stream in which a substantial portion, except for added hydrogen, is derived directly or indirectly from a Fischer-Tropsch condensation process.

Fischer-Tropsch fuels may be derived by converting gas, biomass or coal to liquid (XtL), specifically by gas to liquid conversion (GtL), or from biomass to liquid conversion (BtL). Any form of Fischer-Tropsch derived fuel component may be used as a base fuel in accordance with the invention.

The base fuel suitably has a low sulphur content, for example at most 2000 mg/kg (2000 parts per million by weight/ppmw). More suitably it will have a low or ultra low sulphur content, for instance at most 500 mg/kg (500 ppmw), such as no more than 350 mg/kg (350 ppmw), and still more suitably no more than 100 or 50 or 10 or even 5 mg/kg (5 ppmw) of sulphur. It may be a so-called "zero-sulphur" fuel; although in some cases it may be desired that the base fuel is not a sulphur free ("zero sulphur") fuel. Ideally a fuel composition which results from carrying out the present invention will also have a sulphur content falling within these limits.

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An automotive diesel fuel composition prepared according to the present invention will suitably comply with applicable current standard specification(s) such as, for example, EN 590 (for Europe) or ASTM D-975 (for the USA). By way of example, the overall fuel composition may have a density from 820 to 845 kg/m³ at 15°C (ASTM D-4052 or EN ISO 3675); a T₉₅ boiling point (ASTM D-86 or EN ISO 3405) of 360°C or less; a measured cetane number (ASTM D-613) of 40 or greater; a V_{k40} (ASTM D-445 or EN ISO 3104) from 2 to 4.5 mm²/s; a sulphur content (ASTM D-2622 or EN ISO 20846) of 50 mg/kg or less; and/or a polycyclic aromatic hydrocarbons (PAH) content (IP 391 (mod)) of less than 8% w/w. 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.

It will be appreciated, however, that a diesel fuel composition prepared according to the present invention may contain fuel components with properties outside of these ranges, since the properties of an overall blend may differ, often significantly, from those of its individual constituents.

In accordance with one aspect of the invention, there is provided the use of 2-EHN and one or more detergents for improving the deposit reducing or cleanliness performance of a fuel composition, and/or improving the fuel economy performance of a fuel composition. In the context of the present invention, "use" of 2-EHN and one or more detergents in a fuel composition means incorporating the 2-EHN and/or the one or more detergents into the composition, typically as a blend (i.e. a physical mixture) with one or more fuel components (typically diesel base fuels) and optionally

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with one or more additional fuel additives, being other than 2-EHN and detergent(s).

5 The 2-EHN and the one or more detergents are preferably incorporated into the fuel composition before the composition is introduced into an engine which is to be run on the composition. Accordingly, the 2-EHN and the one or more detergents may be dosed directly into (e.g. blended with) one or more components of the fuel composition or the base fuel at the refinery. For 10 instance, they may be pre-diluted in a suitable fuel component, which subsequently forms part of the overall automotive fuel composition. Alternatively, they may be added to a diesel fuel composition downstream of the refinery. For example, they may be added as part of an 15 additive package containing one or more other fuel additives. This can be particularly advantageous because in some circumstances it can be inconvenient or undesirable to modify the fuel composition at the refinery. For example, the blending of base fuel 20 components may not be feasible at all locations, whereas the introduction of fuel additives, at relatively low concentrations, can more readily be achieved at fuel depots or at other filling points such as road tanker, barge or train filling points, dispensers, customer tanks and vehicles. 25

Accordingly, the "use" of the invention may also encompass the supply of 2-EHN and/or one or more detergents together with instructions for their use in a diesel fuel composition to achieve one of the benefits of 30 the present invention. The 2-EHN and/or one or more detergents may therefore be supplied as a component of a formulation which is suitable for and/or intended for use as a fuel additive, in particular a diesel fuel additive.

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By way of example, the 2-EHN and/or one or more detergents may be incorporated into an additive formulation or package along with one or more other fuel additives. As described above, the one or more fuel
5 additives may be selected from any useful additive, such as anti-corrosion additives, dehazers, anti-foaming agents, esters, poly-alpha olefins, long chain organic acids, components containing amine or amide active centres, and mixtures thereof, as is known to the person
10 of skill in the art.

According to another aspect of the invention, there is provided a process for the preparation of an automotive fuel composition, which process involves
15 blending a diesel base fuel (or base fuel mixture) with 2-EHN and one or more detergents. The blending may be carried out for one or more of the purposes described herein.

In some cases the 2-EHN and/or the one or more detergents may not be suitable for pre-mixing with other
20 fuel additives and may, therefore, be dosed directly into the fuel composition from a concentrated (100%) or pre-diluted stock.

While the amount of the 2-EHN and the one or more detergents for use in accordance with the invention may
25 vary depending on fuel type and/or engine working conditions to be used, a further benefit of the invention is that under some engine conditions the amount particularly of the one or more detergents needed to observe the benefit of the invention may be surprisingly
30 low and lower than the normal detergent additive concentration required to provide the same cleaning/deposit reduction effect. This in turn can reduce the cost and complexity of the fuel preparation

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process.

Moreover, an additive which is to be used at a relatively low concentration can naturally be transported, stored and introduced into a fuel composition more cost effectively than can a fuel component which needs to be used at concentrations of the order of tens of percent by weight.

Another aspect of the invention provides a method of operating an internal combustion engine and/or a vehicle powered by such an engine, which comprises introducing into a combustion chamber of the engine a fuel composition prepared in accordance with the invention. The fuel composition is advantageously introduced for one or more of the purposes described in connection with this invention. Thus, the engine is preferably operated with the fuel composition for the purpose of improving cleanliness and deposit reduction, and /or fuel economy, during use of the engine and, for example, associated benefits such as reduced engine emissions, etc. The engine is in particular a diesel engine, and may be a turbo charged diesel engine. The 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. For example, it may be an electronic unit direct injection (EUDI) engine.

Where relevant to a particular assessment, emission levels may be measured using standard testing procedures such as the European R49, ESC, OICA or ETC (for heavy-duty engines) or ECE+EUDC or MVEG (for light-duty engines) test cycles. Ideally emissions performance is measured on a diesel engine built to comply with the Euro

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II standard emissions limits (1996) or with the Euro III (2000), IV (2005) or even V (2008) standard limits.

Throughout the description and claims of this specification, the singular encompasses the plural unless
5 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.

Thus features, integers, characteristics, compounds,
10 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. Thus, features of the
15 "uses" of the invention are directly applicable to the "methods" of the invention. Moreover, unless stated otherwise, any feature disclosed herein may be replaced by an alternative feature serving the same or a similar purpose.

20 The invention will now be further illustrated by way of the following non-limiting examples.

Examples

Example 1

An additive package containing detergent and 2-EHN
25 in amounts sufficient to achieve a level of 160ppmw of detergent in the final fuel formulation and a level of 600ppmw of 2-EHN in the final fuel formulation was blended into a standard low sulphur diesel base fuel compliant with EN590. The additive package contained
30 some other minor components in addition. Pro-foulant in the form of low molecular weight PIB succinimide was blended into the diesel base fuel at a level of 10ppmw by weight of the final composition. The specification of

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the base fuel is shown in Table 1 below.

Table 1

Density at 15°C	IP365	835.1 kg/m ³
Kinematic Viscosity at 40°C	IP71	3.217 mm ² /s
Initial boiling point	IP123	205°C
Cold Filter Plugging Point	IP309	-22°C
Cloud Point	IP219	n/a
Lubricity (HFRR wear scar diameter)	ISO 12156	338 micron
Sulphur	ISO 20846	<1 mg/kg
Total aromatics	IP391	22.6 %wt

Example 2

An additive package containing detergent but no 2-EHN was blended into the same standard low sulphur diesel base fuel as used in Example 1 above. The type and level of detergent and minor additive components used in Example 2 were the same as those used in Example 1. Pro-foulant in the form of low molecular weight PIB succinimide was included in the diesel fuel formulations at a level of 10ppmw by weight of the final composition.

The fuel blends to be tested were subjected to the CEC F-110-16 (issue 1) test method. For the avoidance of doubt, sodium and dodecenylsuccinic acid (DDSA) mentioned in CEC F-110-16 (issue 1) were not blended into either of the fuels in Example 1 or Example 2. As noted above, pro-foulant in the form of low molecular weight PIB succinimide was used instead at a level of 10 ppmw by weight of the final composition.

The results from the fuel blend containing detergent and 2-EHN in combination (Example 1), plus from the base fuel alone and the same fuel with just the same level of detergent added (Example 2), are given in Table 2.

Table 2

Additive Package	Completed Main Runs	Rating
Detergent + 2-EHN (Example 1)	5	5.5

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Detergent alone (Example 2)	2	2.0
None	1	2.0

Discussion

5 The results shown in Table 2 demonstrate a significant reduction in deposits by the use of 2-EHN in combination with a detergent package compared to the reference fuel containing the same detergent package alone (without 2-EHN).

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C L A I M S

1. Use of 2-ethylhexyl nitrate and one or more detergents in a diesel fuel composition for the purpose of reducing internal injector deposits in a compression ignition combustion engine.
- 5 2. Use according to Claim 1 for the additional purpose of improving the fuel economy of a compression ignition combustion engine.
3. Use according to claim 1 or claim 2 , wherein the concentration of 2-ethylhexyl nitrate in the diesel fuel composition is in the range of from 10 to 1500 ppmw,
10 based on the weight of the total diesel fuel composition.
4. Use according to any of claims 1 to 3, wherein the concentration of the one or more detergents in the diesel fuel composition is in the range of from 5 ppmw to 1500
15 ppmw, based on the weight of the total diesel fuel composition.
5. Use according to any one of claims 1 to 4, wherein said detergent is a polyisobutylene succinimide of poly(ethyleneamines).
- 20 6. Use according to any one of claims 1 to 5, wherein the diesel fuel composition additionally comprises one or more fuel additives other than a detergent and other than 2-EHN.
7. Use according to any of Claim 1 to 6 wherein the reduction in internal diesel injector deposits is
25 measured according to the CEC F-110-16 test method.
8. Method for reducing internal injector deposits in an internal combustion engine by fuelling the internal combustion engine with a diesel fuel composition

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comprising 2-ethylhexyl nitrate and one or more detergents.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2017/062687

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10L1/10

ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10L

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

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

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 247 706 A2 (ETHYL CORP [US]) 2 December 1987 (1987-12-02) page 2, line 40 - page 3, line 23; claims 1,2,3,10 page 5, line 6 - line 49	1,3,4,6, 8
X	EP 0 968 259 A1 (INFINEUM HOLDINGS BV [NL]) 5 January 2000 (2000-01-05) paragraphs [0001], [0006], [0025], [0026], [0041], [0047], [0065] - paragraph [0085]; table 2	1-8



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"&" document member of the same patent family

Date of the actual completion of the international search

3 July 2017

Date of mailing of the international search report

25/07/2017

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2017/062687

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