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(54) Title: USE OF FUEL COMPOSITION

(57) Abstract: Use of a fuel composition comprising a major amount of a fuel suitable for use in a compression-ignition engine, which fuel comprises one or more hydrocarbon components boiling within the diesel boiling range, at least one of which hydrocarbon component has been treated with a metal adsorbing or absorbing material in a different physical phase from the hydrocarbon component(s), preferably to reduce the level of at least one metal, more preferably the level of at least one heavier metal, most preferably the level of copper and/or iron and/or zinc, in said at least one hydrocarbon component, said treatment including physical separation of the hydrocarbon component from the metal adsorbing or absorbing phase, for the purpose of reducing subsequent formation of deposits, preferably combustion related deposits, during engine operation in a compression-ignition engine into which the fuel composition is introduced and/or of removing from the engine previously incurred deposits. Preferably the level of deposits in the engine after engine operation with said fuel composition in the engine is lower than the level of deposits in the engine after engine operation with an alternative fuel composition in the engine, said alternative fuel composition having essentially the same characteristics as said fuel composition but the hydrocarbon components of which have not been treated with said metal adsorbing or absorbing material.

WO 2006/108854 A1

USE OF A FUEL COMPOSITION

The present invention relates to the use of fuel compositions, particularly in the operation of compression-ignition engines.

5 It is known to treat hydrocarbons by passing them through filtering or adsorbing material such as Fuller's Earth or charcoal, e.g. as disclosed in US-A-2090007, US-A-2338142 or GB-A-614636.

10 GB-A-437023 discloses a process for refining cracked hydrocarbons of substantially gasoline boiling range by the treatment with a solid active adsorbent such as Fuller's Earth, clay or other suitable adsorptive catalysts, under conditions of elevated temperature and superatmospheric pressure adequate to maintain said hydrocarbons in substantially liquid phase, which
15 comprises first removing from said hydrocarbons relatively unstable low boiling constituents, namely dissolved gases, propane, part or all of the butanes and their corresponding unsaturates, and reducing the vapour pressure of said hydrocarbons by submitting them to a
20 stabilising fractionation and thereupon subjecting the stabilised hydrocarbons, whilst still hot, to said refining treatment.

25 US-A-3529944 discloses a method for clarifying and stabilising hydrocarbon liquids which are subject to oxidative deterioration, particularly jet fuels, which includes adding to the fuel a material which accelerates the oxidative deterioration of the fuel, such as a polyphenyl substituted lower alkane or lower alkylene, an alkanol ester of citric acid or acetoxy ethyl
30 monobutylether; passing the hydrocarbon liquid through a solid, particulate, adsorbent media to remove

microimpurities and the products of oxidative deterioration; and thereafter adding additional amounts of a stabilising material to stabilise the hydrocarbon liquid against further oxidative deterioration. Suitable adsorbent materials (column 5, lines 22 to 25) include various types of natural or synthetic clays, either treated or untreated, Fuller's Earth, attapulgite, silica gel and adsorbent catalysts. In the examples, jet fuels are treated by filtration through attapulgite clay.

10 In US-A-4225319, in order to suppress carburettor deposit formation, adsorbent-treated cat cracked gasoline is blended into a fuel composition for use in an internal combustion engine. In column 2, lines 57 to 62, it is stated that adsorbents which are useful "for treating the cat cracked gasoline include many of the well known adsorbents such as silica, alumina, silica-alumina, charcoal, carbon black, magnesium silicate, aluminium silicate, zeolites, clay, fuller's earth, magnesia, and the like". In the examples, the adsorbent used is silica-gel.

20 US-A-5951851 relates to a process for removing elemental sulphur from fluids, particularly fuels such as gasoline, jet fuel, diesel, kerosene and fuel additives such as ethers. The process involves contacting the sulphur contaminated fluid with layered double hydroxide (or hydrotalcite) $Mg_2AlNO_3;mH_2O$ or $Mg_3AlNO_3;mH_2O$, where m is the number of waters of hydration. In Example 1, it is shown that Attapulgus clay, molecular sieve 5 Å, silica gel, alumina, bayerite, tetraphenylphosphonium-montmorillonite, Kao-EG.9.4 Å, Kao-tetraethylene glycol, Al₁₃ pillared montmorillonite, tetramethylammonium-montmorillonite, palygorskite-PF1-s, Kaolinite KGa-1, Kao-cellosolve and Iron (III) montmorillonite are ineffective in removing elemental sulphur, whilst the

hydrotalcites Al_2LiCl , Mg_2AlNO_3 , Mg_2FeNO_3 , Mg_3FeNO_3 and Mg_3AlNO_3 are particularly effective in removing elemental sulphur.

5 The New Encyclopaedia Britannica, Macropaedia, Volume 4, 15th Edition, 1984, ISBN 0-85229-413-1, pages 700 to 706 classifies clay minerals on the basis of variations of atomic structure and chemical composition into 9 groups, viz (1) allophane, (2) kaolinite, (3) halloysite, (4) smectite, (5) illite, (6) chlorite, (7) vermiculite, 10 (8) sepiolite, attapulgite and palygorskite and (9) mixed layer clay minerals.

Group (8), sepiolite, attapulgite and palygorskite, are described as fibrous clay minerals, and these have, as an important structural element, the amphibole double 15 silica chain which is orientated parallel to the c axis.

It is known that diesel fuels can contain a number of trace metals. The content of such metals depends on a number of factors, including the source(s) of crude oil from which the fuel is derived, the types of refinery 20 processes employed, and the handling, storage and distribution history of the fuel.

Compression-ignition (diesel) engines running on diesel fuels can suffer from the formation of deposits during engine operation in their fuel injection systems, in particular in the injector nozzles. This fouling can 25 impair engine performance. To reduce fouling, a detergent-containing additive may be included in the fuel.

However, when at least one hydrocarbon component of 30 a diesel fuel composition has been treated with a metal adsorbing or absorbing material in a different physical phase from the hydrocarbon component(s), which material may for example be in liquid form which is immiscible (including having minimal or low solubility) with the

hydrocarbon component, or a solid, preferably a solid, to reduce the levels of trace metal contaminants, more preferably the level of heavier metals, most preferably the level of copper and/or iron and/or zinc, in said component(s), the fuel composition can itself contribute to a reduction in, and/or reversal of, injector fouling. Said treatment includes physical separation of the hydrocarbon component and the metal adsorbing or absorbing phase, for example by one or more of decanting of immiscible liquid, filtration, vortexing, centrifuging and gravity separation. A fuel composition which has been so treated can therefore be used to help maintain engine cleanliness and/or improve such cleanliness and/or reduce the rate of deterioration of such cleanliness.

For the purpose of this disclosure, "heavier metals" are defined as metals with atomic numbers of 20 or greater.

In accordance with the present invention there is provided use of a fuel composition comprising a major amount of a fuel suitable for use in a compression-ignition engine, which fuel comprises one or more hydrocarbon components boiling within the diesel boiling range, at least one of which hydrocarbon components has been treated with a metal adsorbing or absorbing material in a different physical phase from the hydrocarbon component(s), preferably to reduce the level of at least one metal, more preferably the level of at least one heavier metal, most preferably the level of copper and/or iron and/or zinc, in said at least one hydrocarbon component, said treatment including physical separation of the hydrocarbon component from the metal adsorbing or absorbing phase, for the purpose of reducing subsequent formation of deposits, preferably combustion related deposits, during engine operation in a

compression-ignition engine into which the fuel composition is introduced and/or of removing from the engine previously incurred deposits, preferably wherein the level of deposits in the engine after engine operation with said fuel composition in the engine is lower than the level of deposits in the engine after engine operation with an alternative fuel composition in the engine, said alternative fuel composition having essentially the same characteristics as said fuel composition but the hydrocarbon components of which have not been treated with said metal adsorbing or absorbing material.

Preferably, in the use according to the present invention, reducing subsequent formation of deposits in the compression-ignition engine and/or removing from the engine previously incurred deposits has the effect of reducing any power loss in the engine or improving the power generated by the engine, preferably wherein the power loss in the engine is lower or the power generated in the engine is greater during engine operation with said fuel composition in said engine, as compared to the power loss or power generated respectively during engine operation with said alternative fuel composition in the engine.

In accordance with the present invention there is also provided a method of operating a compression-ignition engine, and/or a vehicle which is driven by a compression-ignition engine, which method involves introducing into a combustion chamber of the engine a fuel composition comprising a major amount of a fuel suitable for use in a compression-ignition engine, which fuel comprises one or more hydrocarbon components boiling within the diesel boiling range, at least one of which hydrocarbon components has been treated with a metal

adsorbing or absorbing material in a different physical phase from the hydrocarbon component(s), preferably to reduce the level of at least one metal, more preferably the level of at least one heavier metal, most preferably the level of copper and/or iron and/or zinc, in said at least one hydrocarbon component, said treatment including physical separation of the hydrocarbon component from the metal adsorbing or absorbing phase, for the purpose of reducing subsequent formation of deposits, preferably combustion related deposits, during engine operation in the compression-ignition engine and/or of removing from the engine previously incurred deposits, preferably wherein the level of deposits in the engine after engine operation with said fuel composition in the engine is lower than the level of deposits in the engine after engine operation with an alternative fuel composition in the engine, said alternative fuel composition having essentially the same characteristics as said fuel composition but the hydrocarbon components of which have not been treated with said metal adsorbing or absorbing material.

In accordance with the present invention there is further provided a method of reducing subsequent formation of deposits, preferably combustion related deposits, during engine operation in a compression-ignition engine into which a fuel composition is introduced and/or of removing from the engine previously incurred deposits, which method comprises bringing into the combustion chambers of such engine a fuel composition comprising a major amount of a fuel suitable for use in a compression-ignition engine, which fuel comprises one or more hydrocarbon components boiling within the diesel boiling range, at least one of which hydrocarbon components has been treated with a metal adsorbing or

absorbing material in a different physical phase from the hydrocarbon component(s), preferably to reduce the level of at least one metal, more preferably the level of at least one heavier metal, most preferably the level of copper and/or iron and/or zinc, in said at least one hydrocarbon component, said treatment including physical separation of the hydrocarbon component from the metal adsorbing or absorbing phase, preferably wherein the level of deposits in the engine after engine operation with said fuel composition in the engine is lower than the level of deposits in the engine after engine operation with an alternative fuel composition in the engine, said alternative fuel composition having essentially the same characteristics as said fuel composition but the hydrocarbon components of which have not been treated with said metal adsorbing or absorbing material.

In accordance with the present invention there is still further provided a method of reducing subsequent formation of deposits, preferably combustion related deposits, during engine operation in a compression-ignition engine into which a fuel composition is introduced and/or of removing from the engine previously incurred deposits, which comprises replacing a fuel composition in said engine by another fuel composition comprising a major amount of a fuel suitable for use in a compression-ignition engine, which fuel comprises one or more hydrocarbon components boiling within the diesel boiling range, at least one of which hydrocarbon components has been treated with a metal adsorbing or absorbing material in a different physical phase from the hydrocarbon component(s), preferably to reduce the level of at least one metal, more preferably the level of at least one heavier metal, most preferably the level of

copper and/or iron and/or zinc, in said at least one hydrocarbon component, said treatment including physical separation of the hydrocarbon component from the metal adsorbing or absorbing phase, preferably wherein the
5 level of deposits in the engine after engine operation with said fuel composition in the engine is lower than the level of deposits in the engine after engine operation with said replaced fuel composition in the engine, said replaced fuel composition having essentially
10 the same characteristics as said fuel composition but the hydrocarbon components of which have not been treated with said metal adsorbing or absorbing material.

Preferably, in the methods according to the present invention, reducing subsequent formation of deposits in
15 the compression-ignition engine and/or removing from the engine previously incurred deposits has the effect of reducing any power loss in the engine or improving the power generated by the engine, preferably wherein the power loss in the engine is lower or the power generated
20 in the engine is greater during engine operation with said fuel composition in said engine, as compared to the power loss or power generated respectively during engine operation with said replaced fuel composition in the engine.

Preferably, the level of deposits in the engine after engine operation with the fuel composition one or more of said hydrocarbons of which have been treated with said metal adsorbing or absorbing material is lower by an amount of at least 10%, preferably at least 20%, more
25 preferably at least 25%.

The term "essentially the same characteristics" relates in particular, but not exclusively, to one or more of metals content, density, sulphur content and distillation characteristics of the fuel compositions.

In accordance with the present invention there is yet further provided a method of preparing a fuel composition comprising (a) providing a major amount of a fuel suitable for use in a compression-ignition engine, which fuel comprises one or more hydrocarbon components boiling within the diesel boiling range; (b) treating at least one of said hydrocarbon components with a metal adsorbing or absorbing material which is in a different physical phase from the hydrocarbon component, thereby reducing the level of at least one metal in said at least one hydrocarbon component; and (c) physically separating the thus-treated hydrocarbon component from the metal adsorbing or absorbing material.

In accordance with the present invention there is yet further provided a method of treating a fuel composition comprising a major amount of a fuel suitable for use in a compression-ignition engine, which fuel comprises one or more hydrocarbon components boiling within the diesel boiling range, which method comprises (a) adding one or more metals, preferably selected from copper, iron and zinc, to said fuel composition; (b) treating at least one of said hydrocarbon components with a metal adsorbing or absorbing material which is in a different physical phase from the hydrocarbon component, thereby reducing the level of at least one of said metals in said at least one hydrocarbon component; and (c) physically separating the thus-treated hydrocarbon component from the metal adsorbing or absorbing material.

Preferably, the metal adsorbing or absorbing material is selected from fibrous clay minerals, diatomaceous earths, graphite, charcoal, polymeric adsorbents or absorbents, ion-exchange resins, and complexing or chelating agents, which materials may be in liquid form which is immiscible (including having minimal

or low solubility) with the hydrocarbon component, or solids, more preferably solids. Said complexing or chelating agents preferably comprise molecules having one or more functional groups acting as a ligand or forming a complex or being otherwise metal-attracting.

The fibrous clay mineral of the sepiolite, attapulgite and palygorskite group must at least contain at least one mineral of the sepiolite, attapulgite and palygorskite groups. The term "Fuller's Earth" is used in published literature on clays in a number of different ways, but in the context of the present invention "Fuller's Earth" comprises at least one fibrous clay mineral of the sepiolite, attapulgite and palygorskite groups. One type of Fuller's Earth may comprise a mixture of montmorillonite and palygorskite.

Preferably the fibrous clay mineral is sepiolite, attapulgite, or Fuller's Earth.

Preferably, said polymeric material is selected from polyolefins such as polyacrylate or polystyrene, polyester, polyether, polyamide, polyamine and polysulphone materials, for example AMBERLITE XAD-4, AMBERLITE XAD-7 and AMBERLITE XAD-16 non-ionic polymeric adsorbents and polyethylene imine on silica gel (available ex. Aldrich), said polymeric materials being in solid form, or bound to a solid, or in liquid or suspension or dissolved form which is immiscible (including having minimal or low miscibility) with the hydrocarbon component.

Preferably, examples of said diatomaceous earths are DAMOLIN MOLER (available ex. Damolin) and HYFLO SUPER CEL (available ex. Aldrich).

Preferably, said complexing or chelating agents are selected from nitrogen materials such as amines, amides, polyamines, cyclic polyamines including but not limited

to porphyrins, derivatives of N,N'-disalicylidene-propanediamine, sulphur materials such as sulphides, sulphones, sulphoxides, sulphonates, thiols, anionic materials such as carboxylates, oxygen species such as
5 alcohols, ketones, phenols and ethers, including polyethers and cyclic polyethers (crown ethers), and species containing both nitrogen and oxygen such as cryptands and oxazoles and derivatives thereof, said complexing or chelating agents being in solid form, or
10 bound to a solid, or in liquid or suspension or dissolved form which is immiscible (including having minimal or low miscibility) with the hydrocarbon component.

Preferably, said ion-exchange resins are selected from mineral species, such as silica gels, and polymers
15 with functional groups such as sulphonate and carboxylate, such as some of the products available from Aldrich under the trade names AMBERLITE, AMBERLYST, DOWEX and SEPHADEX.

Preferably, a blend of at least two of said
20 hydrocarbon components has been treated with the metal adsorbing or absorbing material.

In this specification, the terms "reduce", "reducing" and "reduction" mean as compared to prior to the treatment with the metal adsorbing or absorbing
25 material or as compared to when using a diesel fuel composition components of which have not been subjected to said treatment, as appropriate. In the context of the present invention, "reducing" includes complete prevention and "removing" embraces both complete and
30 partial removal.

The processes of adsorption or absorption of trace elements on to clay are not completely understood. One possibility is that the metals bond to the surface in the same way that they bond to ligands. Ligands are

molecules or ions that function as electron donors and attract metal atoms or ions.

The fuel compositions to which the present invention relates include diesel fuel compositions for use in
5 automotive compression ignition engines, as well as in other types of engine such as for example marine, railroad and stationary engines, and industrial gas oils for use in heating applications (e.g. boilers), provided that these non-automotive fuels do not contain residual
10 (non-distilled) components.

The base fuel may itself comprise a mixture of two or more different diesel fuel components, and/or be additivated as described below.

Such diesel fuel compositions will contain one or
15 more base fuels which may typically comprise liquid hydrocarbon middle distillate gas oil(s), for instance petroleum derived gas oils. Such fuel compositions will typically have boiling points within the usual diesel range of 150 to 400°C, depending on grade and use. They
20 will typically have a density from 750 to 1000 kg/m³, preferably for automotive uses from 780 to 860 kg/m³, at 15°C (e.g. ASTM D4502 or IP 365) and a cetane number (ASTM D613) of from 35 to 120, more preferably from 40 to 85. They will typically have an initial boiling point in
25 the range 150 to 230°C and a final boiling point in the range 290 to 400°C. Their kinematic viscosity at 40°C (ASTM D445) might suitably be from 1.5 to 6 mm²/s.

Such industrial gas oils will contain a base fuel which may comprise fuel fractions such as the kerosene or
30 gas oil fractions obtained in traditional refinery processes, which upgrade crude petroleum feedstock to useful products. Preferably such fractions contain components having carbon numbers in the range 5 to 40, more preferably 5 to 31, yet more preferably 6 to 25,

most preferably 9 to 25, and such fractions have a density at 15°C of 650 to 1000 kg/m³, a kinematic viscosity at 20°C of 1 to 80 mm²/s, and a boiling range of 150 to 400°C.

5 Optionally, non-mineral oil based fuels, such as Fischer-Tropsch derived fuels, biomass-derived materials, biofuel components such as fatty acid methyl esters, or shale oils, may also form or be present in the fuel composition. Such Fischer-Tropsch fuels may for example
10 be derived from natural gas, natural gas liquids, petroleum or shale oil, petroleum or shale oil processing residues, coal or biomass.

The amount of Fischer-Tropsch derived fuel used in a diesel fuel composition may be from 0.5 to 100%v of the
15 overall diesel fuel composition, preferably from 5 to 75%v. It may be desirable for the composition to contain 10%v or greater, more preferably 20%v or greater, still more preferably 30%v or greater, of the Fischer-Tropsch derived fuel. It is particularly preferred for the
20 composition to contain 30 to 75%v, and particularly 30 or 70%v, of the Fischer-Tropsch derived fuel. The balance of the fuel composition is made up of one or more other fuels.

An industrial gas oil composition will preferably
25 comprise more than 50 wt%, more preferably more than 70 wt%, of a Fischer-Tropsch derived fuel component.

Such a Fischer-Tropsch derived fuel component is any fraction of the middle distillate fuel range, which can be isolated from the (hydrocracked) Fischer-Tropsch
30 synthesis product. Typical fractions will boil in the naphtha, kerosene or gas oil range. Preferably, a Fischer-Tropsch product boiling in the kerosene or gas oil range is used because these products are easier to handle in for example domestic environments. Such

products will suitably comprise a fraction larger than 90 wt% which boils between 160 and 400°C, preferably to about 370°C. Examples of Fischer-Tropsch derived kerosene and gas oils are described in EP-A-0583836, 5 WO-A-97/14768, WO-A-97/14769, WO-A-00/11116, WO-A-00/11117, WO-A-01/83406, WO-A-01/83648, WO-A-01/83647, WO-A-01/83641, WO-A-00/20535, WO-A-00/20534, EP-A-1101813, US-A-5766274, US-A-5378348, US-A-5888376 and US-A-6204426.

10 The Fischer-Tropsch product will suitably contain more than 80 wt% and more suitably more than 95 wt% iso and normal paraffins and less than 1 wt% aromatics, the balance being naphthenics compounds. The content of sulphur and nitrogen will be very low and normally below 15 the detection limits for such compounds. For this reason the sulphur content of a fuel composition containing a Fischer-Tropsch product may be very low.

The fuel composition preferably contains no more than 5000 ppmw sulphur, more preferably no more than 20 500 ppmw, or no more than 350 ppmw, or no more than 150 ppmw, or no more than 100 ppmw, or no more than 50 ppmw, or most preferably no more than 10 ppmw sulphur.

The base fuel may itself be additivated (additive-containing) or unadditivated (additive-free). If 25 additivated, e.g. at the refinery, it will contain minor amounts of one or more additives selected for example from anti-static agents, pipeline drag reducers, flow improvers (e.g. ethylene/vinyl acetate copolymers or acrylate/maleic anhydride copolymers), lubricity 30 additives, antioxidants and wax anti-settling agents.

Detergent-containing diesel fuel additives are known and commercially available. Such additives may be added to diesel fuels at levels intended to reduce, remove, or slow the build up of engine deposits.

Examples of detergents suitable for use in fuel additives for the present purpose include polyolefin substituted succinimides or succinamides of polyamines, for instance polyisobutylene succinimides or
5 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,
10 EP-A-0557516 and WO-A-98/42808. Particularly preferred are polyolefin substituted succinimides such as polyisobutylene succinimides.

The additive may contain other components in addition to the detergent. Examples are lubricity
15 enhancers; dehazer compositions, e.g. those containing alkoxyated phenol formaldehyde polymers; anti-foaming agents (e.g. polyether-modified polysiloxanes); ignition improvers (cetane improvers) (e.g. 2-ethylhexyl nitrate (EHN), cyclohexyl nitrate, di-tert-butyl peroxide and
20 those disclosed in US-A-4208190 at column 2, line 27 to column 3, line 21); anti-rust agents (e.g. a propane-1,2-diol semi-ester of tetrapropenyl succinic acid, or polyhydric alcohol esters of a succinic acid derivative, the succinic acid derivative having on at
25 least one of its alpha-carbon atoms an unsubstituted or substituted aliphatic hydrocarbon group containing from 20 to 500 carbon atoms, e.g. the pentaerythritol diester of polyisobutylene-substituted succinic acid); corrosion inhibitors; reodorants; anti-wear additives;
30 anti-oxidants (e.g. phenolics such as 2,6-di-tert-butylphenol, or phenylenediamines such as N,N'-di-sec-butyl-p-phenylenediamine); metal deactivators; and combustion improvers.

It is particularly preferred that the additive include a lubricity enhancer, especially when the fuel composition has a low (e.g. 500 ppmw or less) sulphur content. In the additivated fuel composition, the
5 lubricity enhancer is conveniently present at a concentration less than 1000 ppmw, preferably between 5 and 1000 ppmw. Suitable commercially available lubricity enhancers include ester- and acid-based additives. Other lubricity enhancers are described in the patent
10 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
15 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,
20 as fuel additives for wear reduction in a diesel engine injection system;
- US-A-5490864 - certain dithiophosphoric diester-dialcohols as anti-wear lubricity additives for low sulphur diesel fuels; and
- 25 - 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.

It is also preferred that the additive contain an
30 anti-foaming agent, more preferably in combination with an anti-rust agent and/or a corrosion inhibitor and/or a lubricity additive.

Unless otherwise stated, the (active matter) concentration of each such additional component in the

additivated 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. The (active matter) concentration of any dehazer in the fuel composition will preferably be in the range from 0.1 to 20 ppmw, more preferably from 1 to 15 ppmw, still more preferably from 1 to 10 ppmw, advantageously from 1 to 5 ppmw. The (active matter) concentration of any ignition improver present will preferably be 2600 ppmw or less, more preferably 2000 ppmw or less, conveniently from 300 to 1500 ppmw.

If desired, the additive components, as listed above, may be co-mixed, preferably together with suitable diluent(s), in an additive concentrate, and the additive concentrate may be dispersed into the fuel, in suitable quantity to result in a composition of the present invention.

In the case of a diesel fuel composition, for example, the additive will typically contain a detergent, optionally together with other components as described above, and a diesel fuel-compatible diluent, which may be a carrier oil (e.g. a mineral oil), a polyether, which may be capped or uncapped, a non-polar solvent such as toluene, xylene, white spirits and those sold by Shell companies under the trade mark "SHELLSOL".

The total content of the additives may be suitably between 0 and 10000 ppmw and preferably below 5000 ppmw.

In this specification, amounts (concentrations, %v, ppmw, wt%) of components are of active matter, i.e. exclusive of volatile solvents/diluent materials.

The treatment according to the present invention may be applied before or after any additives are blended into the fuel composition, as appropriate.

The level of formation of deposits during engine operation in a diesel engine may be measured in its fuel injection system, with reference to the degree of fouling of the injector nozzles. Degree of nozzle fouling may be assessed in a number of ways, for instance visually, by measuring the mass of deposits in a fouled nozzle or by measuring the fluid flow (for instance, fuel flow or more preferably air flow) properties of the fouled nozzle relative to those of the clean nozzle.

An appropriate test might for example determine the degree of nozzle fouling (conveniently in the form of a percentage injector fouling index) in a suitable diesel engine, for instance based on the change in air flow rate through one or more of the nozzles as a result of using the fuel composition. Conveniently the results are averaged over all of the injector nozzles of the engine.

The present invention is particularly applicable where the fuel composition is used or intended to be used in a direct injection diesel engine, for example of the rotary pump, in-line pump, unit pump, electronic unit injector or common rail type, in an indirect injection diesel engine or in a homogeneous charge compression ignition engine. The fuel composition may be suitable for use in heavy and/or light duty diesel engines.

As mentioned above, it is also applicable where the fuel composition is used in heating applications, for example boilers. Such boilers include standard boilers, low temperature boilers and condensing boilers, and are typically used for heating water for commercial or domestic applications such as space heating and water heating.

In the diesel fuel composition, hydrocarbons can be supplemented by oxygenates such as esters known for use in diesel fuel.

In the process of the present invention the treatment with metal adsorbing or absorbing material is effected with the hydrocarbons in the liquid phase, very conveniently at ambient temperature. At ambient
5 temperature, the treatment may very conveniently be effected at atmospheric pressure.

Whilst when it is known that a particular hydrocarbon refinery component or combination/components of a fuel composition is at least predominantly
10 responsible for the presence of metals to be removed, that component or combination of components may be treated with the metal adsorbing or absorbing material before blending with at least the other hydrocarbon refinery component to form the fuel composition, the
15 fully pre-blended fuel composition may also be treated.

The level of formation of deposits during engine operation may for example be measured by assessing the degree of fouling of the injector nozzles in the fuel injection system of the engine, as described above.

20 If formation of deposits in the fuel injectors during vehicle operation are to be measured, the test cycles involve running the engine on the relevant fuel composition for a given period of time and/or for a given number of miles. The tests may be conducted on the
25 engine alone or driving a vehicle - in the latter case they may be conducted under simulated driving conditions (such as using a chassis dynamometer) or involve regular road driving. The tests may be conducted in "Keep-Clean" mode (i.e. by running the engine on treated fuel,
30 followed by examination of the engine) or in "Clean-Up" mode (i.e. by running one test cycle on untreated fuel to generate deposits, followed by running a second test cycle on treated fuel). In the latter case, the engine running and/or driving conditions should be the same or

comparable for both the first test cycle and the second test cycle.

By way of example, in "Clean-Up" tests the duration of the "first test cycle" should be sufficient to cause a significant, and at least detectable, build up of combustion related deposits. An appropriate duration for the "second test cycle" is typically from 10 to 100%, preferably from 50 to 100%, most suitably 100%, of that of the first test cycle. It may in cases be 80% or 75% or even 50% or less of the duration of the "first test cycle". For assessing reductions in (as opposed to removal of) combustion related deposits, it may be up to 120% or 150% or even 200% of the duration of the "first test cycle", although it could be even greater.

In any type of testing, the test may be conducted on only a part of the engine (for example, the fuel injection system) or on a simulated engine or engine part.

The present invention will now be further described by reference to the following Examples, in which, unless otherwise indicated, parts and percentages are by weight, and temperatures are in degrees Celsius:

EXAMPLES

Example 1

The fuels referred to in Example 1 were as set out in Table 1:

Table 1

| Property | Fuel A | Fuel B |
|--|--------|--------|
| Density @ 15°C (kg/m ³) | 835.7 | 835.5 |
| Cetane | 52.7 | 53.3 |
| Sulphur mg/kg | 212 | 210 |
| Distillation (°C) | | |
| IBP | 183.0 | 185.3 |
| 10% rec | 208.5 | 210.5 |
| 20% rec | 221.5 | 222.8 |
| 30% rec | 235.0 | 235.5 |
| 40% rec | 248.5 | 249.1 |
| 50% rec | 263.0 | 263.6 |
| 60% rec | 277.5 | 278.2 |
| 70% rec | 293.5 | 293.9 |
| 80% rec | 311.5 | 310.6 |
| 90% rec | 333.0 | 331.9 |
| 95% rec | 350.0 | 348.3 |
| FBP | 361.0 | 361.1 |
| HPLC aromatics (%m/m) | | |
| Mono | 26.8 | 26.7 |
| Di | 4.5 | 4.2 |
| Tri | 0.7 | 0.5 |
| Total | 32 | 31.4 |

5 Fuel A was a market fuel from Hungary that is compliant with EN590 and which was used without any further treatment. Fuel B was Fuel A which had been treated by being passed through a clay column as described below.

10 By comparing the characteristics of Fuels A and B set out in Table 1 it can be seen that the physical properties (density and cetane number) were essentially unchanged by the clay treatment. It can also be seen

that the aromatic (mono-, di- and tri-) content and sulphur content were also essentially unchanged by said treatment, as were the distillation characteristics.

Metals content and clay filtration

5 The metal content of Fuel A was determined using the following technique, ICP-MS (Inductively Coupled Plasma-Mass Spectrometry). Said technique involves spraying the fuel containing the metals into a spray chamber to form a fine spray. Here the larger droplets
10 are removed and 1 to 2% of the sample solution enters into the inductively coupled plasma. The plasma is produced in a quartz torch, via the interaction of an intense magnetic field and flowing argon. The plasma discharge has a high temperature, approximately 10000°C.
15 In ICP-MS the plasma is used to generate positively charged ions. Once the ions are produced in the plasma, they are directed into the mass spectrometer via the interface region from where the positive ions are focused down a quadruple mass spectrometer. The results (in
20 ppbw) are set out in Table 2 below.

 A glass column of about 1 metre in height and diameter of 7.5 cm, having a tap at the bottom and a loose glass cap on top, was fitted with a glass wool layer immediately above the tap and was then loaded with
25 0.5 kg of dry clay, in powder form. The clay filled the column to about 40 cm above the tap, and the glass wool layer prevented clay from falling into the tap.

 Fuel A at ambient temperature (20°C) was then poured into the column, to a depth of 25 to 30 cm above the
30 clay. Flow rate was adjusted to 1 litre/hour, and the column was regularly topped up with fuel. A total volume of 50 litres was passed through the column. The first litre of permeate was discarded, and subsequently 5 litre samples (Fuel B) were collected. The 2nd, 4th, 6th, 8th

and final samples (Fuel B) were tested for metal content. The average values (in ppbw) were as set out in Table 2 below:

Table 2

| Metal | Fuel A | Fuel B |
|-------|--------|--------|
| Ag | <50 | <50 |
| B | <50 | <50 |
| Cr | 14 | <5 |
| Cu | <50 | <50 |
| Fe | 84 | <5 |
| Mg | 76 | <5 |
| Mn | 8 | <5 |
| Mo | <50 | <50 |
| Ni | <50 | <50 |
| Pb | 50 | <40 |
| Sn | <50 | <50 |
| Ti | <50 | <50 |
| Zn | 1500 | 26 |
| V | <50 | <50 |

5

It is to be noted that the levels of chromium (Cr), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn) and zinc (Zn) were all reduced after the clay treatment. The reduction in the level of zinc was particularly marked.

10

The levels of metals could be further reduced by optimisation of the operating conditions of the process, or by passing the fuel through a second bed of solid, or by other means.

15

The clay which was employed was Attapulgite, mesh size 30-60 (0.500 to 0.250 mm), ex. Wilfrid Smith Limited (manufactured by Millwhite). Other suitable clays include Fuller's Earth, e.g. mesh size 30-60, ex. Aldrich, and Sepiolite, e.g. grade 30-60, ex. Steetly Bentonite & Absorbents Ltd.

Example 2

The fuels referred to in Example 2 were as set out in Table 3:

Table 3

| Property | Fuel C | Fuel D | Fuel E | Fuel F | Fuel G |
|--|--------|--------|--------|--------|--------|
| Density @ 15°C (kg/m ³) | 839.4 | 839.1 | 839.1 | 839.4 | 839.5 |

5

Fuel C was a 275ppmw sulphur diesel fuel. Fuels D, E, F, and G were Fuel C which had been treated by being passed through DAMOLIN MOLER (diatomaceous earth ex. Damolin), AMBERLITE XAD-7 (polymeric adsorbent ex. Aldrich), polyethylene imine on silica gel (ex. Aldrich), and AMBERLYST 15 (ion-exchange resin, ex. Aldrich), respectively, as described below.

10

It can be seen that the density of Fuels C to G was essentially unchanged.

15 Metals content and filtration

The metals content of Fuel C was determined using the technique described in Example 1 with respect to Fuel A. The results (in ppbw) are set out in Table 4 below.

20

Fuel C was then treated at ambient temperature (20°C) with the metal adsorbing or absorbing materials DAMOLIN MOLER, AMBERLITE XAD-7, polyethylene imine on silica gel, and AMBERLYST 15, to produce Fuels D to G respectively, as described below.

25

Fuel D was obtained when Fuel C was treated in a column approximately 1m high with a diameter of about 7.5cm and a tap at the bottom. Approximately 250g of dry solid was loaded into the column, on top of a layer of glass wool. The solid filled the column to approximately 20cm above the tap. The fuel was passed once through the column with the first ~100ml being discarded.

30

Fuels E, F, and G were obtained when Fuel C was treated in columns about 50cm high with a diameter of 2cm and a tap at the bottom. In each case, approximately 40g of solid was loaded into the column, on top of a layer of glass wool. The solid filled the column to approximately 30cm above the tap. The fuels were passed once through the columns, with the first ~100ml being discarded.

Fuels D to G were then tested for metals content. The average values (in ppbw) were as set out in Table 4 below:

Table 4

| Metal | Fuel C | Fuel D | Fuel E | Fuel F | Fuel G |
|-------|--------|--------|--------|--------|--------|
| Ag | <20 | <20 | <20 | <20 | <20 |
| Al | <100 | <100 | <100 | <100 | nd |
| B | <500 | <500 | <500 | <500 | nd |
| Cr | <20 | <20 | <20 | <20 | <5 |
| Cu | 275 | <10 | 30 | 145 | 130 |
| Fe | 10 | <5 | <5 | <5 | <5 |
| Mg | <100 | <100 | <100 | <100 | <5 |
| Mn | <5 | <5 | <5 | <5 | <5 |
| Mo | <20 | <20 | <20 | <20 | <20 |
| Ni | <20 | <20 | <20 | <20 | nd |
| Pb | <100 | <100 | <100 | <100 | <50 |
| Sn | <50 | <50 | <50 | <50 | <50 |
| Ti | <20 | <20 | <20 | <20 | <20 |
| V | <50 | <50 | <50 | <50 | nd |
| Zn | 1740 | <5 | 5 | 160 | 590 |

nd = not determined

It is to be noted that the levels of copper (Cu), iron (Fe) and zinc (Zn) were reduced after the treatment with each of the metal adsorbing or absorbing materials. The reduction in the level of zinc was particularly marked.

The levels of metals in the fuel may be reduced further by optimisation of the conditions of the process,

or by passing the fuel through a second process of contact with metal adsorbing or absorbing material, or by alternative means. Further reductions in metal level may be desirable to achieve the optimum reduction in the formation of deposits during engine operation, preferably combustion related deposits.

The degree of fouling of the injector nozzles in the fuel injection system of an engine, caused by such deposits, can be reduced by the treatment according to the present invention. This has been demonstrated by the tests described in Example 3.

Example 3

The fuels used in the tests described below included those set out in Table 5:

Table 5

| Property | Fuel H | Fuel K |
|--|--------|--------|
| Density @ 15°C (kg/m ³) | 841.8 | 841.8 |
| Sulphur mg/kg | 7.1 | 7.2 |
| Distillation (°C) | | |
| IBP | 167.5 | 169.2 |
| 10% rec | 202.8 | 203.2 |
| 20% rec | 221.5 | 221.8 |
| 30% rec | 237.2 | 238.1 |
| 40% rec | 250.9 | 251.8 |
| 50% rec | 263.3 | 265.3 |
| 60% rec | 276.6 | 276.9 |
| 70% rec | 290.1 | 290.2 |
| 80% rec | 305.7 | 305.7 |
| 90% rec | 326.3 | 327.1 |
| 95% rec | 342.8 | 344.6 |
| FBP | 352.6 | 352.5 |

Fuel H was a zero sulphur diesel fuel, which was doped with copper, iron and zinc, using metallo-organic solutions of said metals, to form a Fuel I. Fuel K was produced by passing Fuel I through a clay column, using
5 the technique as described above in Example 1, to form a Fuel J, to which then were added 1 ppmw of an anti-static additive ("STADIS 450", ex. Du Pont) and 400 ppmw of a lubricity additive ("R655", ex. Infineum).

The density, sulphur level and distillation
10 characteristics of Fuel I were not measured as they would have been the same as those of Fuel H, i.e. as they would have been essentially unchanged by the above-mentioned doping with metals.

Similarly, the density, sulphur level and
15 distillation characteristics of Fuel J were not measured as they would have been the same as those of Fuel K, i.e. they would have been essentially unchanged by the above-mentioned addition of additives.

Metals content and filtration

20 The metals content of Fuels H, I and J was determined using the technique described in Example 1 with respect to Fuel A. The average values (in ppbw) were as set out in Table 6 below:

Table 6

| Metal | Fuel H | Fuel I | Fuel J |
|-------|--------|--------|--------|
| Ag | <20 | <20 | <20 |
| Al | <100 | <100 | <100 |
| B | <20 | <50 | nd |
| Ba | <5 | <5 | <5 |
| Ca | <5 | 10 | <5 |
| Cd | <5 | <5 | <5 |
| Cr | <5 | <5 | <5 |
| Cu | <5 | 1300 | <5 |
| Fe | 5 | 1600 | 8 |
| Mg | <5 | <5 | <5 |
| Mn | <5 | <5 | <5 |
| Mo | <20 | <20 | <20 |
| Na | nd | <200 | nd |
| Ni | <20 | <20 | <20 |
| P | <50 | 270 | nd |
| Pb | <50 | <50 | <50 |
| Si | <50 | <50 | <50 |
| Sn | <50 | <50 | <50 |
| Ti | <20 | <20 | <20 |
| V | <20 | <20 | <20 |
| Zn | 5 | 1400 | <5 |

nd = not determined

5 The metals content of Fuel K was not measured as it would have been the same as that of Fuel J, i.e. unchanged by the above-mentioned addition of additives, both of which are non-metallic materials.

Injector fouling

The engine used in tests to determine injector fouling was as shown in Table 7:

Table 7

| | |
|---------------------|--|
| Type | Turbocharged indirect injection (IDI) diesel engine, type AAZ (from a Volkswagen Passat passenger car) |
| Number of cylinders | 4 |
| Displaced volume | 1.896 L |
| Bore | 79.5 mm |
| Stroke | 95.5 mm |
| Rated power | 75 kW @ 4200 rpm |
| Nozzles | Bosch DNOSD308 type |

5

The engine was fitted on a test bed and the exhaust gas recirculation (EGR) was blanked off to disable it.

The engine was run using the test fuels for 3 hours at 90 Nm torque and 2000 rpm.

10

Percentage fouling is a measure of the blocking of the injectors by deposits. This is measured by comparing the flow rate of air sucked through at X mm injector needle lift before the fouling test with the flow rate after the fouling test. The air flow is measured by rotameters. For each of the four injectors on the engine, for each of three values of X (0.1, 0.2 and 0.3), this produces a ratio (e.g. 20 units of air flow through the new injector, 13 units of flow after the injector was dirtied by the test, therefore 7 units of flow lost and the fouling index of that injector at that needle lift was $7/20 = 35\%$). The $3 \times 4 = 12$ values are then averaged to produce one Fouling Index for that run.

15

20

The above procedure was carried out using each of Fuels H, I and K in said engine. The measured Fouling

Index in respect of each of said fuels was as set out in Table 8:

Table 8

| | Fuel H | Fuel I | Fuel K |
|-----------------|--------|--------|--------|
| Fouling Index % | 33.56 | 33.73 | 23.74 |

5 It can be seen from the results in Table 8 that when using Fuel I in the engine, the Fouling Index was 33.73%. However, when using Fuel K in the engine, the Fouling Index was substantially lower, at 23.74%. As described above, Fuel K was Fuel I which had been passed through a
10 clay column to form Fuel J, to which then were added an anti-static additive ("STADIS 450", ex. Du Pont) and lubricity additive ("R655", ex. Infineum).

 Also, it can be seen from Table 6 that the level of the metals copper, iron and zinc had been greatly reduced
15 by said clay treatment, i.e. as between Fuel I and Fuel J and therefore as between Fuel I and Fuel K. This shows quite clearly that the reduction of the level of metals in the fuel had resulted in a greatly reduced Fouling Index.

20 Moreover, the results in Tables 5, 6 and 8 also show that the Fouling Index when using Fuel K was substantially lower than that when using Fuel H, despite the fact that the levels of metals in Fuels H and K were essentially the same and the fact that the density,
25 sulphur content and distillation characteristics of Fuels H and K were essentially the same.

 The presence of said anti-static additive and lubricity additive would have had no effect on the fouling of the injectors and therefore it would have been
30 expected that Fuel J would have generated the same Fouling Index as Fuel K.

Thus, the clay treatment resulted in a fuel having essentially the same density, sulphur content and distillation characteristics, but exhibiting a much lower Fouling Index, than that of each of the zero diesel fuel and that fuel when doped with copper, iron and zinc.

5

The reduced fouling, in turn, can reduce any power loss in the engine or improve the power generated by the engine.

C L A I M S

1. Use of a fuel composition comprising a major amount of a fuel suitable for use in a compression-ignition engine, which fuel comprises one or more hydrocarbon components boiling within the diesel boiling range, at least one of which hydrocarbon components has been
5 treated with a metal adsorbing or absorbing material in a different physical phase from the hydrocarbon component(s), preferably to reduce the level of at least one metal, more preferably the level of at least one heavier metal, most preferably the level of copper and/or
10 iron and/or zinc, in said at least one hydrocarbon component, said treatment including physical separation of the hydrocarbon component from the metal adsorbing or absorbing phase, for the purpose of reducing subsequent formation of deposits, preferably combustion related
15 deposits, during engine operation in a compression-ignition engine into which the fuel composition is introduced and/or of removing from the engine previously incurred deposits, preferably wherein the level of
20 deposits in the engine after engine operation with said fuel composition in the engine is lower than the level of deposits in the engine after engine operation with an alternative fuel composition in the engine, said alternative fuel composition having essentially the same
25 characteristics as said fuel composition but the hydrocarbon components of which have not been treated with said metal adsorbing or absorbing material.
2. A use according to claim 1 wherein reducing subsequent formation of deposits in the compression-
30 ignition engine and/or removing from the engine previously incurred deposits has the effect of reducing

any power loss in the engine or improving the power generated by the engine, preferably wherein the power loss in the engine is lower or the power generated in the engine is greater during engine operation with said fuel composition in said engine, as compared to the power loss or power generated respectively during engine operation with said alternative fuel composition in the engine.

5
10
3. A use according to claim 1 or 2 wherein the metal adsorbing or absorbing material is selected from fibrous clay minerals, diatomaceous earths, graphite, charcoal, polymeric adsorbents or absorbents, ion-exchange resins, and complexing or chelating agents.

15
20
25
30
4. A method of operating a compression-ignition engine, and/or a vehicle which is driven by a compression-ignition engine, which method involves introducing into a combustion chamber of the engine a fuel composition comprising a major amount of a fuel suitable for use in a compression-ignition engine, which fuel comprises one or more hydrocarbon components boiling within the diesel boiling range, at least one of which hydrocarbon components has been treated with a metal adsorbing or absorbing material in a different physical phase from the hydrocarbon component(s), preferably to reduce the level of at least one metal, more preferably the level of at least one heavier metal, most preferably the level of copper and/or iron and/or zinc, in said at least one hydrocarbon component, said treatment including physical separation of the hydrocarbon component from the metal adsorbing or absorbing phase, for the purpose of reducing subsequent formation of deposits, preferably combustion related deposits, during engine operation in the compression-ignition engine and/or of removing from the engine previously incurred deposits, preferably wherein the level of deposits in the engine after engine

operation with said fuel composition in the engine is lower than the level of deposits in the engine after engine operation with an alternative fuel composition in the engine, said alternative fuel composition having
5 essentially the same characteristics as said fuel composition but the hydrocarbon components of which have not been treated with said metal adsorbing or absorbing material.

5. A method of reducing subsequent formation of
10 deposits during engine operation, preferably combustion related deposits, during engine operation in a compression-ignition engine into which a fuel composition is introduced and/or of removing from the engine
previously incurred deposits, which method comprises
15 bringing into the combustion chambers of such engine a fuel composition comprising a major amount of a fuel suitable for use in a compression-ignition engine, which fuel comprises one or more hydrocarbon components boiling within the diesel boiling range, at least one of which
20 hydrocarbon components has been treated with a metal adsorbing or absorbing material in a different physical phase from the hydrocarbon component(s), preferably to reduce the level of at least one metal, more preferably the level of at least one heavier metal, most preferably
25 the level of copper and/or iron and/or zinc, in said at least one hydrocarbon component, said treatment including physical separation of the hydrocarbon component from the metal adsorbing or absorbing phase, preferably wherein
the level of deposits in the engine after engine
30 operation with said fuel composition in the engine is lower than the level of deposits in the engine after engine operation with an alternative fuel composition in the engine, said alternative fuel composition having essentially the same characteristics as said fuel

composition but the hydrocarbon components of which have not been treated with said metal adsorbing or absorbing material.

5 6. A method of reducing subsequent formation of deposits, preferably combustion related deposits, during engine operation in a compression-ignition engine into which a fuel composition is introduced and/or of removing from the engine previously incurred deposits, which comprises replacing a fuel composition in said engine by
10 another fuel composition comprising a major amount of a fuel suitable for use in a compression-ignition engine, which fuel comprises one or more hydrocarbon components boiling within the diesel boiling range, at least one of which hydrocarbon components has been treated with a
15 metal adsorbing or absorbing material in a different physical phase from the hydrocarbon component(s), preferably to reduce the level of at least one metal, more preferably the level of at least one heavier metal, most preferably the level of copper and/or iron and/or
20 zinc, in said at least one hydrocarbon component, said treatment including physical separation of the hydrocarbon component from the metal adsorbing or absorbing phase, preferably wherein the level of deposits in the engine after engine operation with said fuel
25 composition in the engine is lower than the level of deposits in the engine after engine operation with said replaced fuel composition in the engine, said replaced fuel composition having essentially the same characteristics as said fuel composition but the
30 hydrocarbon components of which have not been treated with said metal adsorbing or absorbing material.

7. A method according to claim 4, 5 or 6 wherein reducing subsequent formation of deposits in the compression-ignition engine and/or removing from the

engine previously incurred deposits has the effect of reducing any power loss in the engine or improving the power generated by the engine, preferably wherein the power loss in the engine is lower or the power generated
5 in the engine is greater during engine operation with said fuel composition in said engine, as compared to the power loss or power generated respectively during engine operation with said replaced fuel composition in the engine.

10 8. A method according to any one of claims 4 to 7 wherein the metal adsorbing or absorbing material is selected from fibrous clay minerals, diatomaceous earths, graphite, charcoal, polymeric adsorbents or absorbents, ion-exchange resins, and complexing or chelating agents.

15 9. A method of preparing a fuel composition comprising (a) providing a major amount of a fuel suitable for use in a compression-ignition engine, which fuel comprises one or more hydrocarbon components boiling within the diesel boiling range; (b) treating at least one of said
20 hydrocarbon components with a metal adsorbing or absorbing material which is in a different physical phase from the hydrocarbon component, thereby reducing the level of at least one metal in said at least one hydrocarbon component; and (c) physically separating the
25 thus-treated hydrocarbon component from the metal adsorbing or absorbing material.

10. A method of treating a fuel composition comprising a major amount of a fuel suitable for use in a compression-ignition engine, which fuel comprises one or
30 more hydrocarbon components boiling within the diesel boiling range, which method comprises (a) adding one or more metals, preferably selected from copper, iron and zinc, to said fuel composition; (b) treating at least one of said hydrocarbon components with a metal adsorbing or

- 37 -

absorbing material which is in a different physical phase from the hydrocarbon component, thereby reducing the level of at least one of said metals in said at least one hydrocarbon component; and (c) physically separating the
5 thus-treated hydrocarbon component from the metal adsorbing or absorbing material.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2006/061549

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10L1/08 C10G25/00 C10G25/02 C10L10/04

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 C10G

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 practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX, API Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|-----------------------|
| X | US 5 300 218 A (GRAIFF ET AL) 5 April 1994 (1994-04-05) column 1, line 8 - column 2, line 60 column 3, line 41 - line 55 column 4, line 1 - line 40 | 1-10 |
| Y | US 5 133 851 A (BITTER ET AL) 28 July 1992 (1992-07-28) column 1, line 14 - line 26; example | 1-9 |
| Y | US 6 077 421 A (PURANIK ET AL) 20 June 2000 (2000-06-20) column 1, line 36 - line 48; claims | 1-9 |
| | ----- -/-- | |

Further documents are listed in the continuation of Box C.

See patent family annex.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2006/061549

| C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|--|---|-----------------------|
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| A | US 4 383 915 A (JOHNSON ET AL) 17 May 1983 (1983-05-17) column 1, line 23 - line 32 column 2, line 5 - line 12 column 3, line 21 - line 32 example I table i claims 1-3 ----- | 1-10 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2006/061549

| Patent document cited in search report | | Publication date | Patent family member(s) | Publication date |
|--|---|------------------|-------------------------|------------------|
| US 5300218 | A | 05-04-1994 | NONE | |
| US 5133851 | A | 28-07-1992 | GB 2246308 A | 29-01-1992 |
| US 6077421 | A | 20-06-2000 | US 6297191 B1 | 02-10-2001 |
| US 4383915 | A | 17-05-1983 | NONE | |