



US 20060156620A1

(19) **United States**(12) **Patent Application Publication** (10) **Pub. No.: US 2006/0156620 A1****Clayton et al.**(43) **Pub. Date: Jul. 20, 2006**(54) **FUELS FOR COMPRESSION-IGNITION
ENGINES**(52) **U.S. Cl. 44/457; 123/294**(76) Inventors: **Christopher William Clayton**, Chester
(GB); **Mary Ann Dahlstrom**, Katy, TX
(US); **George Robert Lee**, Chester
(GB); **Richard John Price**, Chester
(GB); **Susan Jane Smith**, Chester
(GB); **Nigel Peter Tait**, Chester (GB);
Jessica F. Wallington, Chester (GB)(57) **ABSTRACT**Correspondence Address:
SHELL OIL COMPANY
P O BOX 2463
HOUSTON, TX 772522463

A fuel composition containing a major amount of a fuel suitable for use in a compression-ignition engine, which fuel contains 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 zinc, in said at least one hydrocarbon component, said treatment including physical separation of the hydrocarbon component from the metal adsorbing or absorbing phase, is used to operate a compression-ignition engine, and/or a vehicle which is driven by a compression-ignition engine, for the purpose of reducing subsequent formation of deposits, preferably combustion related deposits, during engine operation in the compression-ignition engine into which the fuel composition is introduced and/or of removing from the engine previously incurred deposits.

(21) Appl. No.: **11/314,590**(22) Filed: **Dec. 21, 2005**(30) **Foreign Application Priority Data**Dec. 23, 2004 (EP) 04258093.6
Apr. 12, 2005 (EP) 05252268.7**Publication Classification**(51) **Int. Cl.**
C10L 1/12 (2006.01)

FUELS FOR COMPRESSION-IGNITION ENGINES**FIELD OF THE INVENTION**

[0001] The present invention relates to the use of certain fuels in the operation of compression-ignition engines.

BACKGROUND OF THE INVENTION

[0002] 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 processes employed, and the handling, storage and distribution history of the fuel.

[0003] U.S. Pat. No. 2,090,007, U.S. Pat. No. 2,338,142 or GB-A-614636 describe treatment of hydrocarbons by passing them through filtering or adsorbing material such as Fuller's Earth or charcoal.

DETAILED DESCRIPTION OF THE INVENTION

[0004] GB-A-437023 describes 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 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 stabilising fractionation and thereupon subjecting the stabilised hydrocarbons, whilst still hot, to said refining treatment.

[0005] U.S. Pat. No. 3,529,944 describes 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 acetoxyl ethyl 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.

[0006] In U.S. Pat. No. 4,225,319, 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.

[0007] U.S. Pat. No. 5,951,851 relates to a process for removing elemental sulfur from fluids, particularly fuels

such as gasoline, jet fuel, diesel, kerosene and fuel additives such as ethers. The process involves contacting the sulfur contaminated fluid with layered double hydroxide (or hydrotalcite) $Mg_2Al(NO_3)_3 \cdot mH_2O$ or $Mg_3Al(NO_3)_3 \cdot mH_2O$, where m is the number of waters of hydration. In Example 1, it can be seen that Attapulgus clay, molecular sieve 5 Å, silica gel, alumina, bayerite, tetraphenylphosphonium-montmorillonite, Kao-EG.9.4 Å, Kao-tetraethylene glycol, Al_{13} pillared montmorillonite, tetramethylammonium-montmorillonite, palygorskite-PF1-s, Kaolinite KGa-1, Kao-cellosolve and Iron (III) montmorillonite are ineffective in removing elemental sulfur, whilst the hydrotalcites Al_2LiCl , $Mg_2Al(NO_3)_3$, $Mg_2Fe(NO_3)_3$, $Mg_3Fe(NO_3)_3$ and $Mg_3Al(NO_3)_3$ are particularly effective in removing elemental sulfur.

[0008] 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, (8) sepiolite, attapulgite and palygorskite and (9) mixed layer clay minerals.

[0009] Group (8), sepiolite, attapulgite and palygorskite, are described as fibrous clay minerals, and these have, as an important structural element, the amphibole double silica chain which is orientated parallel to the c axis.

[0010] 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 impair engine performance. To reduce fouling, a detergent-containing additive may be included in the fuel.

[0011] However, when at least one hydrocarbon component of 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 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.

[0012] For the purpose of this disclosure, "heavier metals" are defined as metals with atomic numbers of 20 or greater.

[0013] In accordance with one embodiment of the present invention there is 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 hydrocarbon component 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.

[0014] In accordance with one embodiment of 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 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.

[0015] In accordance with another embodiment of 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, said compression-ignition engine having a combustion chamber, which method comprising 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 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.

[0016] In accordance with another embodiment of 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, said compression-ignition engine having a combustion chamber, which method comprising introducing into the combustion chamber a fuel composition comprising a major amount of a fuel suitable for use in a compression-ignition engine, said fuel comprising 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 effective to reduce the level of at least one metal in said at least one hydrocarbon component, said metal adsorbing or absorbing material being in a different physical phase from the hydrocarbon component(s), said treatment including physical separation of the hydrocarbon component from the metal adsorbing or absorbing material, thereby reducing subsequent formation

of deposits during engine operation in the compression-ignition engine and/or of removing from the engine previously incurred deposits.

[0017] In accordance with another embodiment of 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 zinc, in said at least one hydrocarbon component, said treatment including physical separation of the hydrocarbon component from the metal adsorbing or absorbing phase.

[0018] In accordance with another embodiment of 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 comprises replacing a fuel composition by 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 zinc, in said at least one hydrocarbon component, said treatment including physical separation of the hydrocarbon component from the metal adsorbing or absorbing phase.

[0019] Most preferably, 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.

[0020] 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.

[0021] 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.

[0022] Preferably the fibrous clay mineral is sepiolite, attapulgite, or Fuller's Earth.

[0023] Preferably, the 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.

[0024] Preferably, examples of said diatomaceous earths are DAMOLIN MOLER (available ex. Damolin) and HYFLO SUPER CEL (available ex. Aldrich).

[0025] Preferably, the 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, sulfur materials such as sulphides, sulphones, sulphoxides, sulphonates, thiols, anionic materials such as carboxylates, oxygen species such as 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 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.

[0026] Preferably, the ion-exchange resins are selected from mineral species, such as silica gels, and polymers 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.

[0027] Preferably, a blend of at least two of said hydrocarbon components has been treated with the metal adsorbing or absorbing material.

[0028] In this specification, the terms "reduce", "reducing" and "reduction" mean as compared to prior to the treatment with the metal adsorbing or absorbing 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 partial removal.

[0029] 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.

[0030] The fuel compositions to which the present invention relates include diesel fuel compositions for use in 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 (non-distilled) components.

[0031] The base fuel may itself contain a mixture of two or more different diesel fuel components, and/or be additivated as described below.

[0032] Such diesel fuel compositions will contain one or 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 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 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.

[0033] Such industrial gas oils will contain a base fuel which may comprise fuel fractions such as the kerosene or 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 5-40, more preferably 5-31, yet more preferably 6-25, most preferably 9-25, and such fractions have a density at 15° C. of 650-1000 kg/m³, a kinematic viscosity at 20° C. of 1-80 mm²/s, and a boiling range of 150-400° C.

[0034] 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 be derived from natural gas, natural gas liquids, petroleum or shale oil, petroleum or shale oil processing residues, coal or biomass.

[0035] The amount of Fischer-Tropsch derived fuel used in a diesel fuel composition may be from 0.5 to 100% v of the 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 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.

[0036] An industrial gas oil composition will preferably comprise more than 50 wt %, more preferably more than 70 wt %, of a Fischer-Tropsch derived fuel component.

[0037] 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 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, 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, U.S. Pat. No. 5,766,274, U.S. Pat. No. 5,378,348, U.S. Pat. No. 5,888,376 and U.S. Pat. No. 6,204,426.

[0038] 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 sulfur and nitrogen will be very low and normally below the detection limits for such compounds. For this reason the sulfur content of a fuel composition containing a Fischer-Tropsch product may be very low.

[0039] The fuel composition preferably contains no more than 5000 ppmw sulfur, more preferably no more than 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 sulfur.

[0040] The base fuel may itself be additivated (additive-containing) or unadditivated (additive-free). If 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 additives, antioxidants and wax anti-settling agents.

[0041] 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.

[0042] 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 polyisobutylene amine succinamides, aliphatic amines, Mannich bases or amines and polyolefin (e.g. polyisobutylene) maleic anhydrides. Succinimide dispersant additives are described for example in GB-A-960493, EP-A-0147240, EP-A-0482253, EP-A-0613938, EP-A-0557516 and WO-A-98/42808. Particularly preferred are polyolefin substituted succinimides such as polyisobutylene succinimides.

[0043] The additive may contain other components in addition to the detergent. Examples are lubricity 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 those disclosed in U.S. Pat. No. 4,208,190 at column 2, line 27 to column 3, line 21); anti-rust agents (e.g. a propane-1,2-diol semi-ester of tetrapropenyl succinic acid, or polyhydric alcohol esters of a succinic acid derivative, the succinic acid derivative having on at least one of its alpha-carbon atoms an unsubstituted or substituted aliphatic hydrocarbon group containing from 20 to 500 carbon atoms, e.g. the pentaerythritol diester of polyisobutylene-substituted succinic acid); corrosion inhibitors; reodorants; anti-wear additives; anti-oxidants (e.g. phenolics such as 2,6-di-tert-butylphenol, or phenylenediamines

such as N,N'-di-sec-butyl-p-phenylenediamine); metal deactivators; and combustion improvers.

[0044] 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) sulfur content. In the additivated fuel composition, the 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 literature, in particular in connection with their use in low sulfur content diesel fuels, for example in:

[0045] the paper by Danping Wei and H. A. Spikes, "The Lubricity of Diesel Fuels", Wear, III (1986) 217-235;

[0046] WO-A-95/33805—cold flow improvers to enhance lubricity of low sulfur fuels;

[0047] WO-A-94/17160—certain esters of a carboxylic acid and an alcohol wherein the acid has from 2 to 50 carbon atoms and the alcohol has 1 or more carbon atoms, particularly glycerol monooleate and di-isodecyl adipate, as fuel additives for wear reduction in a diesel engine injection system;

[0048] U.S. Pat. No. 5,490,864—certain dithiophosphoric diester-dialcohols as anti-wear lubricity additives for low sulfur diesel fuels; and

[0049] 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 sulfur diesel fuels.

[0050] It is also preferred that the additive contain an anti-foaming agent, more preferably in combination with an anti-rust agent and/or a corrosion inhibitor and/or a lubricity additive.

[0051] 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.

[0052] 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.

[0053] 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 member companies of the Royal Dutch/Shell Group under the trade mark "SHELLSOL".

[0054] The total content of the additives may be suitably between 0 and 10000 ppmw and preferably below 5000 ppmw.

[0055] In this specification, amounts (concentrations, % v, ppmw, wt %) of components are of active matter, i.e. exclusive of volatile solvents/diluent materials.

[0056] The treatment according to the present invention may be applied before or after any additives are blended into the fuel composition, as appropriate.

[0057] 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.

[0058] 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.

[0059] 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.

[0060] 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.

[0061] In the diesel fuel composition, hydrocarbons can be supplemented by oxygenates such as esters known for use in diesel fuel.

[0062] 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 temperature, the treatment may very conveniently be effected at atmospheric pressure.

[0063] Whilst when it is known that a particular hydrocarbon refinery component or combination/components of a fuel composition is at least predominantly 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 fully pre-blended fuel composition may also be treated.

[0064] 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.

[0065] 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 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, 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.

[0066] 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.

[0067] 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.

[0068] The present invention will now be further described by reference to the following illustrative embodiments that are provided for illustrative purposes and are not meant as limiting the invention. Unless otherwise indicated, parts and percentages are by weight, and temperatures are in degrees Celsius.

EXAMPLES

Example 1

[0069] The fuels referred to in Example 1 were as set out in

TABLE 1

Property	Fuel A	Fuel B
Density @ 15° C. (kg/m ³)	835.7	835.5
Cetane	52.7	53.3
Sulfur 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

TABLE 1-continued

Property	Fuel A	Fuel B
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

[0070] 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.

[0071] 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 sulfur content were also essentially unchanged by said treatment, as were the distillation characteristics.

Metals Content and Clay Filtration

[0072] 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 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. 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 quadrupole mass spectrometer. The results (in ppbw) are set out in Table 2 below.

[0073] 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 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.

[0074] Fuel A at ambient temperature (20° C.) was then poured into the column, to a depth of 25 to 30 cm above the 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

[0075] 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.

[0076] 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.

[0077] The clay which was employed was Attapulgit, mesh size 30-60, 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

[0078] 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. (g/cm ³)	0.8394	0.8391	0.8391	0.8394	0.8395

[0079] Fuel C was a 275 ppmw sulfur 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.

[0080] It can be seen that the density of Fuels C to G was essentially unchanged.

Metals Content and Filtration

[0081] 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.

[0082] 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.

[0083] Fuel D was obtained when Fuel C was treated in a column approximately 1 m high with a diameter of about 7.5 cm and a tap at the bottom. Approximately 250 g of dry solid was loaded into the column, on top of a layer of glass wool. The solid filled the column to approximately 20 cm above the tap. The fuel was passed once through the column with the first ~100 ml being discarded.

[0084] Fuels E, F, and G were obtained when Fuel C was treated in columns about 50 cm high with a diameter of 2 cm and a tap at the bottom. In each case, approximately 40 g of solid was loaded into the column, on top of a layer of glass wool. The solid filled the column to approximately 30 cm above the tap. The fuels were passed once through the columns, with the first ~100 ml being discarded.

[0085] 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

[0086] 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.

[0087] 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.

[0088] 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, in turn, can reduce any power loss in the engine or improve the power generated by the engine.

[0089] The reduction in the level of zinc was particularly marked.

[0090] 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.

[0091] 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

[0092] 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
Sulfur 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

[0093] Fuel H was a zero sulfur 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 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).

[0094] The density, sulfur level and distillation 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.

[0095] Similarly, the density, sulfur level and 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

[0096] 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

TABLE 6-continued

Metal	Fuel H	Fuel I	Fuel J
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

[0097] 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

[0098] 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

[0099] The engine was fitted on a test bed and the exhaust gas recirculation (EGR) was blanked off to disable it.

[0100] The engine was run using the test fuels for 3 hours at 90 Nm torque and 2000 rpm.

[0101] 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.

[0102] 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

[0103] 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 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).

[0104] Also, it can be seen from Table 6 that the level of the metals copper, iron and zinc had been greatly reduced 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.

[0105] 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, sulfur content and distillation characteristics of Fuels H and K were essentially the same.

[0106] 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 expected that Fuel J would have generated the same Fouling Index as Fuel K.

[0107] Thus, the clay treatment resulted in a fuel having essentially the same density, sulfur 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.

[0108] The reduced fouling, in turn, can reduce any power loss in the engine or improve the power generated by the engine.

We claim:

1. 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 hydrocarbon component 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.

2. The method of claim 1 wherein the metal adsorbing or absorbing material is selected from the group consisting of fibrous clay minerals, diatomaceous earths, graphite, charcoal, polymeric adsorbents or absorbents, ion-exchange resins, and complexing or chelating agents.

3. A method of operating a compression-ignition engine, and/or a vehicle which is driven by a compression-ignition engine, said compression-ignition engine having a combustion chamber, which method comprising introducing into the

combustion chamber a fuel composition comprising a major amount of a fuel suitable for use in a compression-ignition engine, said fuel comprising 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 effective to reduce the level of at least one metal in said at least one hydrocarbon component, said metal adsorbing or absorbing material being in a different physical phase from the hydrocarbon component(s), said treatment including physical separation of the hydrocarbon component from the metal adsorbing or absorbing material, thereby reducing subsequent formation of deposits during engine operation in the compression-ignition engine and/or of removing from the engine previously incurred deposits.

4. A method of reducing subsequent formation of deposits during engine operation 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 comprising: providing 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, said fuel comprising one or more hydrocarbon components boiling within the diesel boiling range, at least one of which hydrocarbon compo-

nents has been treated with a metal adsorbing or absorbing material effective to reduce the level of at least one metal in said at least one hydrocarbon component, said metal adsorbing or absorbing material being in a different physical phase from the hydrocarbon component(s), said treatment including physical separation of the hydrocarbon component from the metal adsorbing or absorbing material.

5. The method of claim 4 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.

6. The method of claim 4 wherein the metal adsorbing or absorbing material is selected from the group consisting of fibrous clay minerals, diatomaceous earths, graphite and charcoal.

7. The method of claim 4 wherein the metal adsorbing or absorbing material is selected from polymeric adsorbents or absorbents and ion-exchange resins.

8. The method of claim 4 wherein the metal adsorbing or absorbing material is selected from complexing or chelating agents.

* * * * *