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(54) Title: COMPOSITION

(57) Abstract: The present invention provides a fuel additive composition comprising (i) at least one primary antiknock component selected from (a) iron or an iron compound; (b) lead or a lead compound; (c) manganese or manganese compound; and (d) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium; (ii) at least one secondary antiknock component selected from (a) oxyhydrocarbyl compounds; and (b) nitrohydrocarbyl compounds; (iii) at least one of (a) a sulphur passivating agent, (b) a material capable of preventing and/or inhibiting valve seat recession of an internal combustion engine.



WO 2005/087901 A2

COMPOSITION

The present invention relates to a fuel additive composition. In particular the present invention relates to a fuel additive composition for increasing the octane number of a fuel. The present invention further relates to a fuel containing such a fuel additive composition and the use of the fuel additive composition.

Combustion knock, commonly known as "pinking", is a fault which occurs when a gasoline charge in a part of a combustion chamber of an internal combustion engine ignites spontaneously instead of burning gradually. The driver usually becomes aware of pinking as a light rattle under acceleration. If it disappears after a few seconds it is relatively harmless, but a severe knock subjects the engine to high pressure. It may raise the temperature of the metal in the endgas region sufficiently to melt the piston crown.

Combustion knock often occurs when the ignition timing of a given engine does not match the properties of the combusted fuel. In particular, fuel must meet certain specification with regard to octane number for combustion knock to be avoided/minimised and to allow engine designers to increase engine compression ratio to maximise engine performance and efficiency.

The octane number of fuel may be enhanced by a number of means. The principal ones are addition of octane enhancing additives and treatment by further refining or catalysis. It is for this reason that octane numbers, such as the Research Octane Number (RON) and Motor Octane Number (MON), feature in gasoline or petrol specifications throughout the world.

For many years lead alkyl antiknock compounds have provided refiners with a cost effective means of meeting octane specifications. The need to produce gasoline with no, or very low contents of elemental lead, in order to meet the requirements of catalytic converters, incorporating noble metal catalysts, to reduce emissions from spark ignition engines has focussed attention on other antiknock compounds.

Typically these antiknock compounds have had a restricted range of application, have been affected by fuel quality, in particular the sulphur content of the fuel, and have not been able to deliver the full octane boost required by refineries, in an effective manner,

with a single additive. In addition they have not been able to fully provide the vital additional performance benefit of exhaust valve seat recession protection that lead alkyl antiknocks offer.

- 5 A wide range of organo-metallic antiknocks exist and the use of mixtures of antiknocks containing different metals has been previously considered.

WO 98/36039 for instance considers lead and iron to achieve a nominal octane gain of 2RON. Earlier examples of lead and iron being considered are FR-A-1078519 and US
10 3341311.

Iron and manganese are considered in US 4139349.

- A major deficiency of organo-metallic antiknocks, other than lead, is their inability to
15 provide adequate exhaust valve seat protection in vehicles designed for leaded gasoline. GB 865343 considers this for manganese. WO 01/16257 considers this for both iron and manganese.

- Another deficiency for organo-metallic antiknocks is that their responses are not additive
20 and mixtures follow the typical logarithmic response curve of a single antiknock. Hence, the octane improvement from addition of the second organo-metallic antiknock can be expected to be significantly smaller than if the antiknock were simply used alone.

- A wide range of organic antiknocks have also been considered. Mackinven , 'A search
25 for an ashless replacement for lead in gasoline' presented at DGMK in October 1974 gives an overview. US 2758916, US2881061, US 3009793, US 3706541, and US 4294587 provide specific examples. Whilst, Burns 'Organic Antiknocks, ChemTech December 1984 and Stournas 'Influence of structure and other characteristics of substitute fuel components in petrol on engine efficiency and pollution' EC Contractors
30 Meeting on Combustion Research, April 1988 in Brussels provide further review.

Organic antiknocks can potentially be used alone, as single compounds, as mixtures, or in combinations with organo-metallic antiknocks. However, they have the disadvantage of typically needing to be used at high additive levels (500-5000ppm) and this makes

selection of components vitally important if other fuel properties are to be unaffected. They also have the disadvantage of not typically providing exhaust valve seat protection.

Co-additives to stabilise fuels, stabilise additives or eliminate harmful effects of additive use in engines have been extensively proposed. Phenol antioxidants and halogen scavengers with tetraethyl lead antiknock Compound is an obvious practical example. Other less obvious and significant examples are GB1003303 which considers modifying lead alkyl response at high concentrations and providing enhanced engine performance, US 4005992 and US 4005993 which considers control of fouling of catalytic converters by methyl cyclopentadienyl manganese tricarbonyl, US 4141693 which considers reducing misfire in gasolines containing methyl cyclopentadienyl manganese tricarbonyl and US 3615293 and US 3755195 which consider the use of another organometallic compound to provide this protection against misfire.

The present invention alleviates the problems of the prior art.

In one aspect the present invention provides a fuel additive composition comprising (i) at least one primary antiknock component selected from (a) iron or an iron compound; (b) lead or a lead compound; (c) manganese or manganese compound; and (d) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium; (ii) at least one secondary antiknock component selected from (a) oxyhydrocarbyl compounds; and (b) nitrohydrocarbyl compounds; (iii) at least one of (a) a sulphur passivating agent, (b) a material capable of preventing and/or inhibiting valve seat recession of an internal combustion engine.

In one aspect the present invention provides a fuel composition comprising (A) fuel additive composition comprising (i) at least one primary antiknock component selected from (a) iron or an iron compound; (b) lead or a lead compound; (c) manganese or manganese compound; and (d) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium; (ii) at least one secondary antiknock component selected from (a) oxyhydrocarbyl compounds; and (b) nitrohydrocarbyl compounds; (iii) at least one of (a) a sulphur passivating agent, (b) a material capable of preventing and/or inhibiting valve seat recession of an internal combustion engine.; and (B) a fuel.

In one aspect the present invention provides use of a composition for the prevention and/or inhibition of combustion knock in an internal combustion engine, wherein the composition is a fuel additive composition comprising (i) at least one primary antiknock component selected from (a) iron or an iron compound; (b) lead or a lead compound; (c) manganese or manganese compound; and (d) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium; (ii) at least one secondary antiknock component selected from (a) oxyhydrocarbyl compounds; and (b) nitrohydrocarbyl compounds; (iii) at least one of (a) a sulphur passivating agent, (b) a material capable of preventing and/or inhibiting valve seat recession of an internal combustion engine.

In one aspect the present invention provides use of a composition for the prevention and/or inhibition of spark plug fouling in an internal combustion engine, wherein the composition is a fuel additive composition comprising (i) at least one primary antiknock component selected from (a) iron or an iron compound; (b) lead or a lead compound; (c) manganese or manganese compound; and (d) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium; (ii) at least one secondary antiknock component selected from (a) oxyhydrocarbyl compounds; and (b) nitrohydrocarbyl compounds; (iii) at least one of (a) a sulphur passivating agent, (b) a material capable of preventing and/or inhibiting valve seat recession of an internal combustion engine.

In one aspect the present invention provides use of a composition for the prevention and/or inhibition of catalyst poisoning in an internal combustion engine, wherein the composition is a fuel additive composition comprising (i) at least one primary antiknock component selected from (a) iron or an iron compound; (b) lead or a lead compound; (c) manganese or manganese compound; and (d) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium; (ii) at least one secondary antiknock component selected from (a) oxyhydrocarbyl compounds; and (b) nitrohydrocarbyl compounds; (iii) at least one of (a) a sulphur passivating agent, (b) a material capable of preventing and/or inhibiting valve seat recession of an internal combustion engine.

In one aspect the present invention provides use of a composition for increasing the

octane number of a fuel, wherein the composition is a fuel additive composition comprising (i) at least one primary antiknock component selected from (a) iron or an iron compound; (b) lead or a lead compound; (c) manganese or manganese compound; and (d) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium; (ii) at least one secondary antiknock component selected from (a) oxyhydrocarbyl compounds; and (b) nitrohydrocarbyl compounds; (iii) at least one of (a) a sulphur passivating agent, (b) a material capable of preventing and/or inhibiting valve seat recession of an internal combustion engine.

10

In one aspect the present invention provides a process for the prevention and/or inhibition of combustion knock in an internal combustion engine, wherein the process comprises contacting a fuel with a fuel additive composition comprising (i) at least one primary antiknock component selected from (a) iron or an iron compound; (b) lead or a lead compound; (c) manganese or manganese compound; and (d) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium; (ii) at least one secondary antiknock component selected from (a) oxyhydrocarbyl compounds; and (b) nitrohydrocarbyl compounds; (iii) at least one of (a) a sulphur passivating agent, (b) a material capable of preventing and/or inhibiting valve seat recession of an internal combustion engine, prior to combustion of the fuel.

20

In one aspect the present invention provides a process for the prevention and/or inhibition of spark plug fouling in an internal combustion engine, wherein the process comprises contacting a fuel with a fuel additive composition comprising (i) at least one primary antiknock component selected from (a) iron or an iron compound; (b) lead or a lead compound; (c) manganese or manganese compound; and (d) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium; (ii) at least one secondary antiknock component selected from (a) oxyhydrocarbyl compounds; and (b) nitrohydrocarbyl compounds; (iii) at least one of (a) a sulphur passivating agent, (b) a material capable of preventing and/or inhibiting valve seat recession of an internal combustion engine, prior to combustion of the fuel.

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In one aspect the present invention provides a process for the prevention and/or inhibition of catalyst poisoning in an internal combustion engine, wherein the process comprises contacting a fuel with a fuel additive composition comprising (i) at least one primary antiknock component selected from (a) iron or an iron compound; (b) lead or a lead compound; (c) manganese or manganese compound; and (d) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium; (ii) at least one secondary antiknock component selected from (a) oxyhydrocarbyl compounds; and (b) nitrohydrocarbyl compounds; (iii) at least one of (a) a sulphur passivating agent, (b) a material capable of preventing and/or inhibiting valve seat recession of an internal combustion engine, prior to combustion of the fuel.

In one aspect the present invention provides a process for increasing the octane number of a fuel, wherein the process comprises contacting a fuel with a fuel additive composition comprising (i) at least one primary antiknock component selected from (a) iron or an iron compound; (b) lead or a lead compound; (c) manganese or manganese compound; and (d) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium; (ii) at least one secondary antiknock component selected from (a) oxyhydrocarbyl compounds; and (b) nitrohydrocarbyl compounds; (iii) at least one of (a) a sulphur passivating agent, (b) a material capable of preventing and/or inhibiting valve seat recession of an internal combustion engine.

We have found that by providing at least one primary antiknock component and at least one secondary antiknock component, in combination with a sulphur passivating agent, and/or a material capable of preventing and/or inhibiting valve seat recession of an internal combustion engine, an enhanced increase in octane number can be achieved for a given fuel.

Furthermore we have found that by "balancing" the amounts of primary antiknock component, secondary antiknock component, and one of a sulphur passivating agent, and/or a material capable of preventing and/or inhibiting valve seat recession of an internal combustion engine, one may provide an increase in octane number for a given fuel. Thus it is possible by use of this particular combination of components to tailor a fuel additive package to provide a require octane increase for a fuel. In a typically aspect

the constituents of the composition and their relative and absolute amounts will be tailored to provide an RON increase of at least 2 or approximately 2.

Yet further, we have found that the "balancing" of the amounts of components allows for
5 reduction in the overall amount of (metallic) primary antiknock compound or metal. The presence of metals in fuel combustion is considered in some applications to be advantageous.

Furthermore we have found that the particular components of the composition of the or
10 used in the present invention, allow one to address problems of particular fuels in particular the components allow one to counter the negative effects of undesirable sulphur content and/or undesirable olefin content in a fuel.

For ease of reference, these and further aspects of the present invention are now
15 discussed under appropriate section headings. However, the teachings under each section are not necessarily limited to each particular section

PREFERRED ASPECTS

20 PRIMARY ANTIKNOCK COMPONENT

The primary antiknock component may be selected from (a) iron or an iron compound;
(b) lead or a lead compound; (c) manganese or manganese compound; and (d) a metal
selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a
25 metal selected from rare earth metals, lithium, nickel, and thallium.

IRON OR AN IRON COMPOUND

Preferably the primary antiknock component is selected from iron or an iron compound.
30

Preferably the iron and/or iron compound is an iron compound.

Preferably the iron compound is a ferrocene and/or a substituted ferrocene.

35 Preferably the iron and/or iron compound is a ferrocene and/or a substituted ferrocene.

Preferably the iron compound is a ferrocene.

Preferably the iron and/or iron compound is a ferrocene.

5

Preferably the iron compound is an iron complex selected from bis-cyclopentadienyl iron and substituted bis-cyclopentadienyl iron.

Preferably the iron and/or iron compound is an iron complex selected from bis-cyclopentadienyl iron and substituted bis-cyclopentadienyl iron.

10

Preferably the iron compound is bis-cyclopentadienyl iron.

Preferably the iron and/or iron compound is bis-cyclopentadienyl iron.

15

The iron compound may be an iron complex of bis-cyclopentadienyl or substituted bis-cyclopentadienyl complex of iron, wherein the substituents can be, for example, one or more C₁₋₃₀ alkyl groups, preferably C₁₋₂₀ alkyl groups, preferably C₁₋₁₀ alkyl groups, preferably C₁₋₅ alkyl groups, preferably C₁₋₂ alkyl groups. A combination of such iron complexes may also be used.

20

Suitable alkyl-substituted-dicyclopentadienyl iron complexes are cyclopentadienyl-(methylcyclopentadienyl) iron, cyclopentadienyl(ethyl-cyclopentadienyl) iron, bis-(methylcyclopentadienyl) iron, bis-(ethylcyclopentadienyl) iron, bis-(1,2-dimethyl-cyclopentadienyl) iron, and bis-(1-methyl-3-ethylcyclopentadienyl) iron. These iron complexes can be prepared by the processes taught in US-A-2680756, US-A-2804468, GB-A-0733129 and GB-A-0763550. Another volatile iron complex is iron pentacarbonyl.

25

Suitable iron complexes are bis-cyclopentadienyl iron and/or bis-(methylcyclopentadienyl) iron.

30

A highly preferred iron complex is ferrocene (i.e. bis-cyclopentadienyl iron).

The co-ordination chemistry relevant to the solubilisation of transition metals, including iron, in hydrocarbon solvents, e.g. diesel fuel, is well known to those skilled in the art

35

(see e.g. WO-A-87/01720 and WO-A-92/20762).

A wide range of so-called "substituted ferrocenes" are known and may be used in the present invention (see e.g. Comprehensive Organic Chemistry, Eds. Wilkinson et al., Pergamon 1982, Vol. 4:475-494 and Vol. 8:1014-1043). Substituted ferrocenes for use in the invention include those in which substitution may be on either or both of the cyclopentadienyl groups. Suitable substituents include, for example, one or more C₁₋₃₀ alkyl groups, preferably C₁₋₂₀ alkyl groups, preferably C₁₋₁₀ alkyl groups, preferably C₁₋₅ alkyl groups, preferably C₁₋₂ alkyl groups.

10

Particularly suitable alkyl-substituted-dicyclopentadienyl iron complexes (substituted ferrocenes) include cyclopentadienyl(methylcyclopentadienyl) iron, bis-(methylcyclopentadienyl) iron, bis-(ethylcyclopentadienyl) iron, bis-(1,2-dimethylcyclopentadienyl) iron and 2,2-diethylferrocenyl-propane.

15

Other suitable substituents that may be present on the cyclopentadienyl rings include cycloalkyl groups such as cyclopentyl, aryl groups such as tolylphenyl, and acetyl groups, such as present in diacetyl ferrocene. A particularly useful substituent is the hydroxyisopropyl group, resulting in (α -hydroxyisopropyl) ferrocene. As disclosed in WO-A-94/09091, (α -hydroxyisopropyl)ferrocene is a room temperature liquid.

20

Ferrocenes linked by a "bridge" may used in the present invention. Suitable compounds are taught in WO 02/18398 and WO 03/020733.

Other organometallic complexes of iron may also be used in the invention, to the extent that these are fuel compatible and stable. Such complexes include, for example, iron pentacarbonyl, di-iron nonacarbonyl, (1,3-butadiene)-iron tricarbonyl, and (cyclopentadienyl)-iron dicarbonyl dimer. Salts such as di-tetralin iron tetraphenylborate ($\text{Fe}(\text{C}_{10}\text{H}_{12})_2(\text{B}(\text{C}_6\text{H}_5)_4)_2$) may also be employed.

30

As a result of a combination of their solubility, stability, high iron content and, above all, volatility, the substituted ferrocenes are particularly preferred iron compounds for use in the invention. Ferrocene itself is an especially preferred iron compound on this basis. Ferrocene of suitable purity is sold in a range of useful forms as PLUTOcen^{RTM} and as solutions, Satacen^{RTM} both by Octel Deutschland GmbH.

35

The iron compounds for use in the invention need not feature iron-carbon bonds in order to be fuel compatible and stable. Salts may be used; these may be neutral or overbased. Thus, for example, overbased soaps including iron stearate, iron oleate and iron naphthenate may be used. Methods for the preparation of metal soaps are described in The Kirk-Othmer Encyclopaedia of Chemical Technology, 4th Ed, Vol. 8:432-445, John Wiley & Sons, 1993. Suitable stoichiometric, or neutral, iron carboxylates for use in the invention include the so-called 'drier-iron' species, such as iron tris(2-ethylhexanoate) [19583-54-1].

10

Iron complexes not featuring metal-carbon bonds and not prepared using carbonation may also be used in the invention provided these are adequately fuel compatible and stable. Examples include complexes with β -diketonates, such as tetramethylheptanedionate.

15

Iron complexes of the following chelating ligands are also suitable for use in the invention:

- aromatic Mannich bases such as those prepared by reaction of an amine with an aldehyde or ketone followed by nucleophilic attack on an active hydrogen containing compound, e.g. the product of the reaction of two equivalents of (tetrapropenyl)phenol, two of formaldehyde and one of ethylenediamine,
- hydroxyaromatic oximes, such as (polyisobutenyl)-salicylaldoxime. These may be prepared by reaction of (polyisobutenyl)phenol, formaldehyde and hydroxylamine;
- Schiff bases such as those prepared by condensation reactions between aldehydes or ketones (e.g. (tert-butyl)-salicylaldehyde) and amines (e.g. dodecylamine). A tetradentate ligand may be prepared using ethylenediamine (half equivalent) in place of dodecylamine;
- substituted phenols, such as 2-substituted-8-quinolinols, for example 2-dodecenyl-8-quinolinol or 2-N-dodecenylamino-methylphenol;
- substituted phenols, such as those wherein the substituent is NR_2 or SR in which R is a long chain (e.g. 20-30 C atoms) hydrocarbyl group. In the case of both α - and β -substituted phenols, the aromatic rings may beneficially be further substituted with hydrocarbyl groups, e.g. lower alkyl groups;
- carboxylic acid esters, in particular succinic acid esters such as those prepared by reaction of an anhydride (e.g. dodecenyl succinic anhydride) with a single equivalent

of an alcohol (e.g. triethylene glycol);

- acylated amines. These may be prepared by a variety of methods well known to those skilled in the art. However, particularly useful chelates are those prepared by reaction of alkenyl substituted succinates, such as dodecenyl succinic anhydride, with an amine, such as N,N'-dimethyl ethylene diamine or methyl-2-methylamino-benzoate;
- amino-acids, for example those prepared by reaction of an amine, such as dodecylamine, with an α,β -unsaturated ester, such as methylmethacrylate. In cases where a primary amine is used, this may be subsequently acylated, such as with oleic acid or oleyl chloride;
- hydroxamic acids, such as that prepared from the reaction of hydroxylamine with oleic acid,
- linked phenols, such as those prepared from condensation of alkylated phenols with formaldehyde. Where a 2:1 phenol:formaldehyde ratio is used the linking group is CH_2 . Where a 1:1 ratio is employed, the linking group is CH_2OCH_2 ;
- alkylated, substituted pyridines, such as 2-carboxy-4-dodecylpyridine;
- borated acylated amines. These may be prepared by reaction of a succinic acylating agent, such as poly(isobutylene)succinic acid, with an amine, such as tetraethylenepentamine. This procedure is then followed by boronation with a boron oxide, boron halide or boronic acid, amide or ester. Similar reactions with phosphorus acids result in the formation of phosphorus-containing acylated amines, also suitable for providing an oil-soluble iron chelate for use in the invention;
- pyrrole derivatives in which an alkylated pyrrole is substituted at the 2-position by OH, NH_2 , NHR, CO_2H , SH or C(O)H . Particularly suitable pyrrole derivatives include 2-carboxy-t-butylpyrroles;
- sulphonic acids, such as those of the formula $\text{R}^1\text{SO}_3\text{H}$, where R^1 is a C_{10} to about C_{60} hydrocarbyl group, e.g. dodecylbenzene sulphonic acid;
- organometallic complexes of iron, such as ferrocene, substituted ferrocenes, iron naphthenate, iron succinates, stoichiometric or over-based iron soaps (carboxylate or sulphonate), iron picrate, iron carboxylate and iron -diketonate complexes.

Suitable iron picrates for use in the invention include those described in US-A-4,370,147 and US-A-4,265,639.

Other iron-containing compounds for use in the invention include those of the formula

M(R)_x.nL wherein: M is an iron cation; R is the residue of an organic compound RH in which R is an organic group containing an active hydrogen atom H replaceable by the metal M and attached to an O, S, P, N or C atom in the group R; x is 2 or 3; n is 0 or a positive integer indicating the number of donor ligand molecules forming a dative bond
5 with the metal cation; and L is a species capable of acting as a Lewis base.

In one aspect the iron and/or an iron compound provides iron in an amount of at least 8 mg per kg of fuel.

10 In one aspect the iron and/or an iron compound provides iron in an amount of at least 9 mg per kg of fuel.

In one aspect the iron and/or an iron compound provides iron in an amount of at least 15 mg per kg of fuel.

15

In one aspect the iron and/or an iron compound provides iron in an amount of at least 18 mg per kg of fuel.

In one aspect the iron and/or an iron compound provides iron in an amount of at least
20 22.5 mg per kg of fuel.

In one aspect the iron and/or an iron compound provides iron in an amount of at least 30 mg per kg of fuel.

25 In one aspect the iron and/or an iron compound provides iron in an amount of from 15 to 30 mg per kg of fuel.

In one aspect the iron and/or an iron compound provides iron in an amount of from 9 to 18 mg per kg of fuel.

30

In one aspect the iron and/or an iron compound provides iron in an amount of from 8 to 18 mg per kg of fuel.

LEAD OR A LEAD COMPOUND

Preferably the primary antiknock component is selected from lead or a lead compound.

- 5 Preferably the lead and/or lead compound is a lead compound.

A broad range of lead compounds have been claimed to be suitable as a means to deliver lead, in fuel-soluble forms, for various purposes including gasoline soluble forms for use as anti-knock additives.

10

In a preferred aspect the lead compound is a tetraalkyl lead compound.

In a preferred aspect the lead and/or lead compound is a tetraalkyl lead compound.

- 15 Usually the tetraalkyl lead compound will be a tetra-lower alkyl lead, such as tetramethyl lead, tetraethyl lead (otherwise, commonly known as "TEL"), trimethyl ethyl lead, dimethyl diethyl lead, tri-ethyl methyl lead, tetraisopropyl lead, and the like, including mixtures thereof.

- 20 There are numerous references to tetraalkyl lead compounds - such as TEL - in the art. For example, reference may be made to any one of the following US patents: 1705723, 1798593, 2004160, 2029301, 2000069, 241453, 2400383, 2043224, 3151142, 2515821, 2477465, 2464398, 1645375, 1652812, 1661809, 1661810, 1717961, 1907701, 1962173 and 2686799 (the contents of which are incorporated herein by reference).

25

The tetraalkyl lead compound is typically prepared by known processes wherein lead/sodium alloy (PbNa) is reacted with an alkyl halide.

- 30 There are numerous references to the preparation of tetraalkyl lead compounds - such as TEL - in the art. For example, reference may be made to any one of the following US patents: 2411453, 1661809 and 1661810 (the contents of which are incorporated herein by reference).

Preferably, the tetraalkyl lead compound is TEL.

35

Typically, the TEL is prepared by the reaction of lead/sodium alloy (PbNa) with ethyl chloride.

The tetraalkyl lead compound and the iron complex can be used in conjunction with at least one lead scavenger - such as a poly-halo-hydrocarbon lead scavenger. A typical lead scavenger comprises from 2 to 8 carbon atoms and from 2 to 3 halogen atoms and has a boiling point less than 300°C, preferably less than 210°C. Suitable scavengers are ethylene dibromide and ethylene dichloride. A preferred scavenger is dichloroethane or dibromoethane.

10

In one preferred aspect the lead and/or lead compound provides lead in an amount of at least 3 mg per kg of fuel.

In one preferred aspect the lead and/or lead compound provides lead in an amount of at least 5 mg per kg of fuel.

In one preferred aspect the lead and/or lead compound provides lead in an amount of at least 10 mg per kg of fuel.

In one preferred aspect the lead and/or lead compound provides lead in an amount of at least 13 mg per kg of fuel.

In one preferred aspect the lead and/or lead compound provides lead in an amount of at least 20 mg per kg of fuel.

25

In one preferred aspect the lead and/or lead compound provides lead in an amount of at least 40 mg per kg of fuel.

In one preferred aspect the lead and/or lead compound provides lead in an amount of at least 67 mg per kg of fuel.

In one preferred aspect the lead and/or lead compound provides lead in an amount of from 13 to 67 mg per kg of fuel. In one preferred aspect the lead and/or lead compound provides lead in an amount of from 13 to 40 mg per kg of fuel. In one preferred aspect the lead and/or lead compound provides lead in an amount of from 13 to 20 mg per kg of

35

fuel.

In one preferred aspect the lead and/or lead compound provides lead in an amount of from 20 to 67 mg per kg of fuel. In one preferred aspect the lead and/or lead compound provides lead in an amount of from 20 to 40 mg per kg of fuel.

In one preferred aspect the lead and/or lead compound provides lead in an amount of from 40 to 67 mg per kg of fuel.

In one preferred aspect the lead and/or lead compound provides lead in an amount of at least 0.0023g per litre of fuel. In one preferred aspect the lead and/or lead compound provides lead in an amount of at least 0.0038g per litre of fuel. In one preferred aspect the lead and/or lead compound provides lead in an amount of at least 0.0077g per litre of fuel. In one preferred aspect the lead and/or lead compound provides lead in an amount of at least 0.01g per litre of fuel. In one preferred aspect the lead and/or lead compound provides lead in an amount of at least 0.015g per litre of fuel. In one preferred aspect the lead and/or lead compound provides lead in an amount of at least 0.03g per litre of fuel. In one preferred aspect the lead and/or lead compound provides lead in an amount of at least 0.05g per litre of fuel. In one preferred aspect the lead and/or lead compound provides lead in an amount of at least 0.1g per litre of fuel.

MANGANESE OR MANGANESE COMPOUND

Preferably the primary antiknock component is selected from manganese or a manganese compound.

Preferably the manganese and/or manganese compound is a manganese compound.

The most desirable general type of manganese carbonyl compounds utilised in accordance with this invention comprise organomanganese polycarbonyl compounds. For best results, use should be made of a cyclopentadienyl manganese tricarbonyl compound of the type described in U.S. Pat. Nos. 2,828,417 and 3,127,351. Thus use can be made of such compounds as cyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, dimethylcyclopentadienyl manganese tricarbonyl, trimethylcyclopentadienyl

manganese tricarbonyl, propylcyclopentadienyl manganese tricarbonyl, isopropylcyclopentadienyl manganese tricarbonyl, butylcyclopentadienyl manganese tricarbonyl, pentylcyclopentadienyl manganese tricarbonyl, hexylcyclopentadienyl manganese tricarbonyl, ethylmethylcyclopentadienyl manganese tricarbonyl, 5 dimethyloctylcyclopentadienyl manganese tricarbonyl, dodecylcyclopentadienyl manganese tricarbonyl, indenyl manganese tricarbonyl, and like compounds in which the cyclopentadienyl moiety contains up to about 18 carbon atoms.

A preferred organomanganese compound is cyclopentadienyl manganese tricarbonyl. 10 Particularly preferred for use in the practice of this invention is methylcyclopentadienyl manganese tricarbonyl.

Methods for the synthesis of cyclopentadienyl manganese tricarbonyls are well documented in the literature. See for example, in addition to U.S. Pat. Nos. 2,818,417 15 and 3,127,351 noted above, U.S. Pat. Nos. 2,868,816; 2,898,354; 2,960,514; and 2,987,529, among others.

Other organomanganese compounds which may be employed include the non-ionic diamine manganese tricarbonyl halide compounds and bromo manganese tricarbonyl 20 halide compounds such as bromo manganese dianiline tricarbonyl and bromo manganese dipyridine tricarbonyl, described in U.S. Pat. No. 2,902,489; the acyl manganese tricarbonyls such as methylacetyl cyclopentadienyl manganese tricarbonyl and benzoyl methyl cyclopentadienyl manganese tricarbonyl, described in U.S. Pat. No. 2,959,604; the aryl manganese pentacarbonyls such as phenyl manganese 25 pentacarbonyl, described in U.S. Pat. 3,007,953; and the aromatic cyanomanganese dicarbonyls such as mesitylene cyanomanganese dicarbonyl, described in U.S. Pat. No. 3,042,693. Likewise, use can be made of cyclopentadienyl manganese dicarbonyl compounds of the formula $\text{RMn}(\text{CO})_2\text{L}$, where R is a substituted or unsubstituted cyclopentadienyl group having 5 to 18 carbon atoms, and L is a ligand, such as an olefin, 30 an amine, a phosphine, SO_2 , tetrahydrofuran, or the like. Such compounds are referred to, for example in, Herberhold, M., *Metal π -Complexes*, Vol. II, Amsterdam, Elsevier, 1967 or Giordano, P.J. and Weighton, M. S., *Inorg. Chem.*, 1977, 16, 160. Manganese pentacarbonyl dimer (dimanganese decacarbonyl) can also be employed if desired.

35 Preferably the manganese compound is a manganese complex.

Preferably the manganese compound is selected from cyclopentadienyl manganese tricarbonyl and substituted cyclopentadienyl manganese tricarbonyl.

- 5 The manganese compound may be cyclopentadienyl manganese tricarbonyl and substituted cyclopentadienyl manganese tricarbonyl, wherein the substituents can be, for example, one or more C₁₋₅ alkyl groups, preferably C₁₋₂ alkyl groups. A combination of such manganese complexes may also be used.

- 10 Preferably the manganese compound is methylcyclopentadienyl manganese tricarbonyl.

Preferably the manganese and/or the manganese compound is selected from cyclopentadienyl manganese tricarbonyl and substituted cyclopentadienyl manganese tricarbonyl.

15

Preferably the manganese and/or the manganese compound is methylcyclopentadienyl manganese tricarbonyl.

- In one preferred aspect the manganese and/or manganese compound provides
20 manganese in an amount of at least 3 mg per kg of fuel. In one preferred aspect the manganese and/or manganese compound provides manganese in an amount of at least 5 mg per kg of fuel. In one preferred aspect the manganese and/or manganese compound provides manganese in an amount of at least 15 mg per kg of fuel. In one preferred aspect the manganese and/or manganese compound provides manganese in
25 an amount of at least 25 mg per kg of fuel. In one preferred aspect the manganese and/or manganese compound provides manganese in an amount of at least 30 mg per kg of fuel. In one preferred aspect the manganese and/or manganese compound provides manganese in an amount of at least 36 mg per kg of fuel.

- 30 In one preferred aspect the manganese and/or manganese compound provides manganese in an amount of from 3 to 25 mg per kg of fuel.

In one preferred aspect the manganese and/or manganese compound provides manganese in an amount of from 3 to 20 mg per kg of fuel.

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In one preferred aspect the manganese and/or manganese compound provides manganese in an amount of from 5 to 15 mg per kg of fuel.

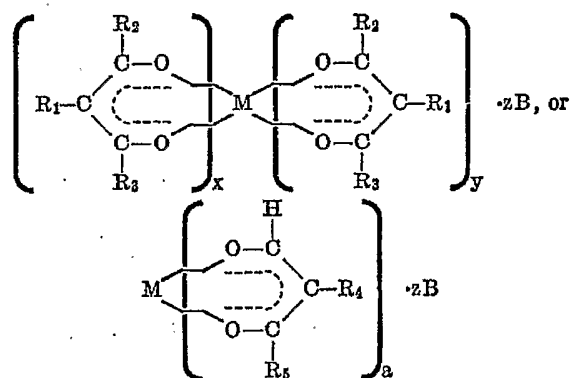
In one preferred aspect the manganese and/or manganese compound provides
5 manganese in an amount of from 6 to 12 mg per kg of fuel.

RARE EARTH METAL

Preferably the primary antiknock component is selected from rare earth metals or a rare
10 earth metal compounds.

The rare earth metal may be selected from the group consisting of lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium
15 (Tm), ytterbium (Yb), lutetium (Lu), scandium (SC), yttrium (Y) and mixtures thereof.

As discussed in US 3794473 suitable rare earth metals antiknock compounds may be rare earth beta-ketoenolates having the following general formulae:



20

wherein M is a rare earth element selected from the group consisting of lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu), scandium (SC), yttrium (Y) and mixtures thereof R1 is
25 selected from the group consisting of hydrogen, alkyl, phenyl, fluorine, chlorine, bromine and iodine, the alkyl radical preferably containing from 1 to 16 carbon atoms; R2 and R3 are individually selected from the group consisting of alkyl, halogen-substituted alkyl, aryl, halogen-substituted aryl, cycloalkyl, hetero atom-substituted alkyl, and hetero atom-

substituted aryl; R1 and R2 together are d-camphor and R3 is as indicated; where the total number of carbon atoms in the R1, R2 and R3 groups is greater than 3 and the maximum number of carbon atoms in any one of the R2 and R3 groups is preferably 35 or less; R4 is hydrogen or methyl; R5 is ethyl; B is an adducting agent such as water or a
5 compound containing a donor group; (x+y) equals the valence of the element M or n equals zero and y equals the valence of the element M; a equals the valence of the element M; and z is zero to 5, inclusive.

Specific examples of groups that can be substituted for R2 and R3 in Formula 1 include
10 methyl, trifluoromethyl, ethyl, propyl, isopropyl, heptafluoropropyl, butyl, tertiary butyl, pentyl, heptyl, octyl, dodecyl, hexadecyl, eicosyl, hexacosyl, triacontyl, tritriacontyl, phenyl, biphenyl, phenoyl, naphthyl, naphthoyl, toluyl, beta-fluorobenzoyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, triethylamino, tetramethylamino, pyridyl, pyrimidyl, pyrolyl, pyrrolidyl, thienyl, thenoyl, furoyl, p-methoxyphenyl, and the like.

15 As indicated above, B in the formulae is water or a compound containing a donor group. The adducting agent can also be defined as a compound having a moiety containing an electron pair capable of bonding to the rare earth element ion. Examples of compounds containing donor groups include ammonia; alcohols, such as methanol, ethanol,
20 isopropanol, and butanol; esters, such as ethyl acetate, n-butyl acetate, ethyl propionate, methyl n-butyrate, ethyl isovalerate, and dimethyl succinate; amines (primary, secondary and tertiary), such as ethylamine, aniline, diethylamine, ethylphenylamine, triethylamine, methyldiethylamine, tripropylamine, triethanolamine, diphenylbenzylamine, pyridine and piperidine; phosphates, such as tricresylphosphate and tributylphosphate; amides, such
25 as formamide, dimethylformamide, acetamide, ethylacetamide and dibenzamide; ethers, such as ethyl ether, dimethyl ether, methylethyl ether, dimethoxymethane, and dimethoxypropane; sulfoxides, such as dimethylsulfoxide, diethylsulfoxide, dipropylsulfoxide; sulfides, such as dimethylsulfide, diethylsulfide, dibenzylsulfide and diphenylsulfide; ketones, such as acetone, pinacolone, acetylacetone, methyl-4,6-
30 heptanedione, 2-methyl-3,5-octanedione, 2,4-decanedione, and 6,8-tridecanedione; and the like.

The following are examples of rare earth β -ketoenolates that can be used in the practice of the present invention:

- tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato) cerium(IV),
 tris(2,2,6,6-tetramethyl-3,5-heptanedionato)ytterbium(III),
 tris(2,2,6,6-tetramethyl-3,5-heptanedionato) praseodymium(III),
 tris(2,2,6,6-tetramethyl-3,5-heptanedionato) neodymium(III),
 5 tris(2,2,6,6-tetramethyl-3,5-heptanedionato) lanthanum(III), - -
 tetrakis(2,2-dimethyl-3,5-hexanedionato)cerium(IV),
 tris(2,2-dimethyl-3,5-hexanedionato)praseodymium(III),
 tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato) neodymium(III)hydrate,
 tris(1,1,1-trifluoro-3-methyl-2;4-hexanedionato) samarium(III),
 10 tris (1, 1, 1-trifluoro-3-isopropyl-6-methyl-2,4-heptanedionato) europium(III),
 tetrakis(1,3-diphenyl-1,3-propanedionato)cerium(IV),
 tris(1,3-diphenyl-2,4-octanedionato)gadolinium(III),
 tris(1,1,1-trifluoro-4-phenyl-2,4-butanedionato) terbium(III),
 tris(1-beta-fluorobenzoyl-2,4-butanedionato) dysprosium(III),
 15 tris [1, 1, 1-trifluoro-4 (beta-biphenyl) -2;4-butanedionato] holmium(III),
 tris(2-naphthoyltrifluoroacetylacetonato)erbium(III),
 tetrakis(1,3-dicyclopropyl-1,3-propanedionato) cerium (IV),
 tris (1,3-dicyclohexyl) -2,4-butanedionato) cerium(III),
 tris(2-furoyltrifluoroacetylacetonato)thulium(III),
 20 tris(1-cyclopentyl-1,3-butanedionato)ytterbium(III),
 tris(tropolonato)scandium(III),
 tetrakis (2-pyroyltrifluoroacetylacetonato) cerium (IV),
 tris(thenoyltrifluoroacetylacetonato) lanthanum (III),
 tris[1,1,1,2,2,3,3-heptafluoro-6(2-thienyl)-4,6-hexanedionato] praseodymium(III),
 25 tris (2-pyroyltrifluoroacetylacetonato) europium(III),
 bis (2-methyl-4,6-nonanedionato) europium (II),
 bis(2,6-dimethyl-3,5-heptanedionato)samarium(II),
 tris(trifluoroacetyl-d-camphorato)europium(III),
 tris(1,1,1,5,5,5-hexafluoro-4,6-pentanedionato) dysprosium(III)hydrate,
 30 tetrakis(3,5-pentanedionato)cerium(IV),
 tris(2-methyl-1,3-pentanedionato)lanthanum(III),
 dimethylformamide adduct of tris(2,2-dimethyl-3,5- hexanedionato)(lanthanum(III),
 triethylamine adduct of tris (1, 1, 1-trifluoro-3-isopropyl-6- methyl-2,4-heptanedionato)
 europium (III),
 35 butanol adduct of tris(3-methyl-2,4-pentanedionato) praseodymium (III),

trimesylphosphate adduct of tris(2-methyl-4,6-heptanedionato) neodymium(III),
ethylacetate adduct of tris(2,2,6,6-tetramethyl-3,5-heptanedionato) ytterbium(III),
ethyl ether adduct of tris(3-ethyl-2,4-heptanedionato) gadolinium(III),
dimethoxy propane adduct of tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)erbium(III);

5

The β -ketoenolates represented by the above formulae (except for those in which R1 and R2 together are d-camphor) and methods for their synthesis are described in the literature. In this regard attention is directed to Inorganic Chemistry, 6, 110.5 (1967), Inorganic Chemistry, 10, 498 (1971), Inorganic Synthesis, 11, 94-98 (1968), and Journal
10 of the American Chemical Society. 87. 5254 (1965), which are incorporated herein by reference. The β -ketoenolates in which R1 and R2 are d-camphor and R3 is, for example, a fluoroalkyl, can be synthesized by preparing an alcohol solution of tritluoroacetyl-d-camphor- [H(facam)] and adding this solution to an aqueous solution of a chloride of one of the aforementioned rare earth elements. For example, in the synthesis
15 of tris(trifluoroacetyl - d - camphorato)praseodymium(III) [Pr(facam)3], a first solution is prepared by stirring 15 millimoles (3.70 grams) of H(facam) in 100 milliliters of a 50 percent alcohol solution. A 10 percent ammonium hydroxide solution is slowly added until all of the H(facam) is dissolved. A second solution is prepared by adding 5 milliliters of a 1 molar aqueous solution of praseodymium chloride (5 millimols) to 30 milliliters of
20 alcohol. The first solution is then added dropwise to the second solution while stirring vigorously. The precipitate that forms is stirred in the mother liquor for an additional time, e.g., for about one hour, after all of the first solution has been added. The mixture is then filtered and the precipitate is washed with 100 milliliters of a 50 percent alcohol solution. After the precipitate is air dried overnight, it is recovered and the product obtained is
25 determined by analysis to be Pr(facam)3.

In one preferred aspect the rare earth metal and/or rare earth metal compound provides rare earth metal in an amount of at least 3 mg per kg of fuel. In one preferred aspect the rare earth metal and/or rare earth metal compound provides rare earth metal in an
30 amount of at least 20 mg per kg of fuel. In one preferred aspect the rare earth metal and/or rare earth metal compound provides rare earth metal in an amount of at least 50 mg per kg of fuel. In one preferred aspect the rare earth metal and/or rare earth metal compound provides rare earth metal in an amount of at least 100 mg per kg of fuel.

35 In one preferred aspect the rare earth metal and/or rare earth metal compound provides

rare earth metal in an amount of from 20 to 500 mg per kg of fuel. In one preferred aspect the rare earth metal and/or rare earth metal compound provides rare earth metal in an amount of from 50 to 500 mg per kg of fuel. In one preferred aspect the rare earth metal and/or rare earth metal compound provides rare earth metal in an amount of from
5 100 to 500 mg per kg of fuel.

CERIUM

Preferably the rare earth metal is cerium (Ce).

10

Preferably the cerium and/or cerium compound is a cerium compound.

The cerium metal or the cerium compound may be delivered in a manner analogous to that given herein in respect of potassium. Each of the forms of potassium disclosed
15 herein may be used to provide the analogous cerium compound.

Preferred sources of cerium include overbased cerium salts, particularly cerium oxide, otherwise known as ceria. Such overbased cerium salts are often referred to as sols, that is, suspensions of finely divided cerium salt crystals comprising surface-bound
20 sulphonc or especially carboxylic acids. An example of a suitable sulphonc acid would be dodecylbenzene sulphonc acid. Examples of suitable carboxylic acids would include long-chain fatty acids, such as C₈ to C₃₀ fatty acids and C₁₂ to C₂₄ fatty acids, especially the naturally occurring mixtures of acids known as tall-oil fatty acids.

25 Other preferred cerium compounds would include neutral carboxylate salts of the acids described above. Further preferred compounds would include β -diketonate salts, especially salts of 2,2,6,6-tetramethylheptane-3,5-dione (TMHD).

Suitable cerium compounds are disclosed in US 3794473 and are discussed herein.
30 Particularly preferred are the cerium compounds discussed above in respect of rare earth metals.

Of the rare earth metals β -ketoenolate derivatives discussed herein it is preferred to use those in which the rare earth element is cerium. For example, tetrakis(2,2,6,6-
35 tetramethyl-3,5-heptanedionato) cerium(IV) has been found to be a particularly effective

antiknock agent. However, from an economic standpoint, it is often desirable to employ those which are derived from naturally occurring ores so that M in the foregoing formula is a mixture of rare earth elements. Also, it is often preferred to utilize an ore which is rich in cerium.

5

In one preferred aspect the cerium and/or cerium compound provides cerium in an amount of at least 3 mg per kg of fuel. In one preferred aspect the cerium and/or cerium compound provides cerium in an amount of at least 20 mg per kg of fuel. In one preferred aspect the cerium and/or cerium compound provides cerium in an amount of at least 50 mg per kg of fuel. In one preferred aspect the cerium and/or cerium compound provides cerium in an amount of at least 100 mg per kg of fuel.

In one preferred aspect the cerium and/or cerium compound provides cerium in an amount of from 20 to 500 mg per kg of fuel. In one preferred aspect the cerium and/or cerium compound provides cerium in an amount of from 50 to 500 mg per kg of fuel. In one preferred aspect the cerium and/or cerium compound provides cerium in an amount of from 100 to 500 mg per kg of fuel.

LITHIUM

20

Preferably the primary antiknock component is selected from lithium or lithium compounds.

Preferably the lithium and/or lithium compound is a lithium compound.

25

Suitable lithium compounds are disclosed in GB1387767.

Preferred lithium compounds are

- lithium salts of alkyl and dialkyl amino-alkyl phenols
- 30 • lithium salt of 2-(di-iso-butylaminomethyl)-4-cresol
- lithium salts of 2-dimethylaminomethyl-4-cresol
- lithium salt of 2-(dimethylamino-methyl)-5-cresol
- lithium salt of 2-(diethylaminomethyl)-4-cresol

Suitable lithium compounds are disclosed in WO 98/26028 and include: lithium bis(dimethylsilyl)amide, lithium bis(trimethylsilyl)amide, oxamic acid, P-aminosalicylic acid lithium salt, lithium salt 5-nitroorotic acid, lithium D-gluconate, lithium hexacyanoferrate(III) ($\text{Li}_3\text{Fe}(\text{CN})_6$), lithium diphenylphosphide, lithium acetate, lithium acetate acid, lithium salt acetic acid, lithium acetamide, lithium anilide, lithium azide, lithium benzamide, lithium antimonide, lithium orthoarsenate, lithium orthoarsenite, lithium meta-arsenite, lithium diborane, lithium pentaborate, lithium dihydroxy diborane, lithium borohydride, lithium cadmium iodide, lithium chloride, lithium calcium chloride, lithium carbide, lithium carbonate, lithium hydrogen carbonate, lithium carbonate, lithium carbonyl, lithium cobalt (II) cyanide, lithium cobalt (III) cyanide, lithium cobaltinitrite, lithium cynomanganate (II), lithium cynomanganate (III), lithium citrate, lithium ferricyanide, lithium ferrocyanide, lithium hydride, lithium hydroxide, lithium manganate, lithium permanganate, lithium methionate, lithium naphthenate, lithium nitride, lithium nitrate, lithium nitrite, lithium nitrobenzene (e.g. lithium p-nitrobenzene), lithium nitrophenoxide, lithium etherate, lithium chromate, lithium oleate, lithium oxalate, lithium oxalatoferrate (II), lithium oxalatoferrate (III), lithium monoxide, lithium oxide, lithium peroxide, lithium , lithium mono- orthophosphate, lithium hypophosphite, lithium orthophosphite, lithium hydroxoplumbate, lithium rhodium cyanide, lithium selenide, lithium selenite, lithium selenocynate, lithium selenocyanoplatinate, lithium disilicate, lithium metasilicate, lithium sodium carbonate, lithium sodium ferricyanide, lithium hydroxostannate, lithium disulfide, lithium hydrosulfide, lithium pentasulfide, lithium tetrasulfide, lithium trisulfide, lithium telluride, lithium thioarsenate, lithium thioarsenite, lithium trithiocarbonate, lithium thiocyanate, lithium amide, lithium salt (E,E)-2,4-hexadienoic acid, dilithium fluorophosphate, dilithium fluorophosphite, trilithium phosphate, trilithium phosphite, lithium perchlorate, propanoic acid lithium salt, lithium formate, lithium cyanate, lithium hexacyanocobaltate (III), lithium hypophosphite, lithium hexafluorsilicate, lithium nitroprusside, lithium phenoxide, lithium phosphate (dibasic, monobasic, tribasic), lithium salicylate, lithium selenide, lithium tetracyanonickelate (II), lithium tetrafluoroborate, lithium xanthogenate, lithium -p-aminobenzoate, lithium copper ferrocyanide, lithium cupric ferrocyanide, lithium hexafluorophosphate, lithium hexanitricobaltate III, lithium naphthenate, lithium -Bnaphthoxide, lithium polysulfide, lithium - sodium phosphate, lithium stearate, lithium sulfide, lithium sulfite, lithium sulfate, lithium thiocyanate, lithium xanthate, lithium fluorosilicate, Nlithiummethylenediamine, oxalic acid dilithium salt, lithium betahydropyruvic acid, lithium 1 ,l- dimethylurea, lithium 1 ,l-diethylurea, lithium 1 ,l-diepropylurea, lithium xanthate, lithium ethylxanthate, lithium

methylxanthate, lithium salt thiophenol, lithium triphenylmethyllithium, methyl- lithium, ethyllithium, lithiumethynyl(acetylide), propyllithium, isopropyllithium, butyllithium, isobutyllithium, secbutyllithium, tertbutyllithium, pentalithium, hexyllithium, heptalithium, amyllithium, isoamyllithium, benzyllithium, dimethylbenzyllithium, toyllithium, 5 dodecylithium, cyclopentadienyllithium, methyl- cyclopentadienyllithium, cyclohexyllithium, lithiumheptyl, lithiumdodecyl, lithium tetradecyl, lithium hexadecyl, lithium octadecyl, phenyllithium, lithium o-tolyl, lithium m-tolyl, lithium p-tolyl, lithium-p-chlorophenyl, lithium pbromophenyl, lithium lithium o- anisyl, lithium m-anisyl, lithium p-anisyl, lithium diethoxyphenyl, lithium dimethoxyphenol, lithium m-cumyl, lithium p-ethoxyphenyl, lithium m-dimethylaminophenyl, lithium 9- flourene, lithium a-napthyl, 10 lithium b-napthyl, lithium p-phenylphenyl, lithium 9-phenylanthryl, lithium 9-anthryl, lithium g-methyl- phenanthryl, lithium pyridyl, lithium 2-pyridyl, lithium 3-pyridyl, lithium 6-bromo-2- pyridyl, lithium 5bromo-2-pyridyl, lithium dibenzofuryl, lithium 3- quinoyl, lithium 2-lepidyl, lithium triphenylmethyl, lithium 2,4,6- trimethylphenyl, lithium 2,4,6- 15 triisopropylphenyl, lithium 2,3,5,6- tetraisopropylphenyl, lithium tetrabutylphenyl, thiophenedilithium, toluenedilithium, dipheny- lethylenedilithium, lithiumamylethynyl, lithiumphenylethynyl, lithiummethoxybromophenyl, lithium phenylisopropyl, lithium tetraphenylboron, lithium tetramethylboron, lithium a-thienyl, lithium m-trifluoromethylphenyl, phenylethynyllithium, 3-furyl- lithium, phenylisopropyllithium, 20 dibenzofuranyllithium, lithium dimethylbenzyl, lithium selenocyanate, lithium trimethylsilanolate, diphenylphosphide, lithium benzoate, lithium tert-butyl carbonate, lithium azide, di-lithiumcyanamide, lithium cyanide, lithium dicyanamide, cyclohexanebutyric acid lithium salt, cyclohexane acid lithium salt, cyclopentadientyllithium, lithium tri-tert-butoxy- aluminum hydride, lithium 25 triethylborohydride, lithium trimethyl- borohydride, lithium tripropylborohydride, lithium triisopropyl- borohydride, lithium tributylborohydride, lithium triisobutyl- borohydride, lithium tri-secbutylborohydride, lithium tri-tert- butylborohydride, lithium trisiamylborohydride, lithium chlorate, lithium tert-butoxide, lithium secbutoxide, iso-butoxide, lithium antimonate, lithium diphenylphosphide, lithium bis(trismethylsilyl) amide, 30 trilithium phosphite, lithium selenocyanate, lithium tri- set-butylborohydride, lithium triethylsilanolate, lithiumthiocyan- ate, lithium acetylide, lithium chlorate, lithium salicylate, lithium di-lithium tetracarbonylferrate, lithium tetraphenylborate, lithium triethylborohydride, lithium triacetoxyborohydride, lithium triphenylborane, lithium hydroxide, lithium diphenylphosphide, lithium methoxide, lithium ethoxide, lithium tri-sec- 35 butyl- borohydride, tri-tert-butylborohydride, lithium triethylborohydride, lithium

triphenylborohydride, lithium trisiamylboro- hydride, lithium metavanadate, lithium cyclohexanebutyrate, lithium hexachloroplatinate, lithium thiocyanate, lithium selenocyanate, lithium cyanate, lithium floride, lithium hexafluoroantimonate, lithium hexafluoroaluminate, lithiumaluminate, lithiumaluminum-tri- tertbutoxide, lithium

5 hexafluoroarsenate, lithium hexafluorosili- cate, lithium hexacyanocobalt(II)ferrate(II), lithium ferrosilicon, dilithiumhexacyanocobalt(II)ferrate(II), lithium hexafluorotitan- ate, lithium hexafluorozirconate, lithium hexahydroxyantimonate, lithium hexachlororuthenate, lithium hexachloropalladate, lithium formate, lithium tetracyanonickelate, lithium tetrafluoroaluminate, lithium tetrafluoroborate, lithium thioacetate, L-glutamic acid

10 monolithium salt, fumaric acid lithium salt, oxamic acid lithium salt, lithium salt diphenylphospene, P-aminobenzoic lithium salt, aminobenzole acid lithium salt, alpha-naphthaleneacetic acid lithium salt, dilithium salt 2,6- naphthalenedicarboxylic acid, lithium cyclohexanetherate, lithium phthalimide, P-aminosalicylic acid lithium salt, lithium salt 3,5- dimethylcyclohexyl sulfate, indolebutyric acid lithium salt, indole-3- butyric acid

15 lithium salt, diphenylphosphide, lithium dimethylsilanolate, lithium triethyl- borohydride, lithium propoxide, lithium isopropoxide, lithium butoxide, lithium set-butoxide, lithium pentoxide, lithium tertpentoxide, lithium hydrogenphthalate, lithium oxalate, lithium hydrogensulfate, monolithium acetylenedicarboxylic acid, lithium pyrophosphate, lithium dihydrogenphosphate, lithium hexoate (lithium salt hexoic acid), lithium

20 diphenylphosphide, lithium trimethylsilanolate, lithium phthalic acid, P-aminobenzoic acid lithium salt, monolithium Laspartic acid, tetraphenyldilithium (C₆H₅)₂CLi₂C(C₆H₅)₂, lithiummethylphenyl (LiCH₂C₆H₅), lithium bromate, lithium hydrogenphosphate, monolithium salt D-shaccharic acid, DI-aspartic lithium salt, (R)-alpha-hydroxymethylaspartic acid lithium salt, lithium fluoride, lithium iodate, lithium salt ethyl malonate, lithium thioacetate,

25 lithium phenol, lithium salt aminobenzoic acid, lithium aminophenol salt, lithium cyclohexenol, lithium methylcyclohexenol, lithium cyclopropanol, lithium methylcyclopropanol, lithium cyclobutanol, lithium methylcyclobutanol, lithium methylcyclopentanol, lithium cyclopentanol, lithium cyclohexenol, lithium methylcyclohexenol, lithium dimethylcyclohexenols (e.g. lithium 3,5-

30 dimethylcyclohexanol, lithium 2,3- dimethylcyclohexanol, lithium 2,6- dimethylcyclohexanol, lithium 2,5- dimethylcyclohexanol, 3,5-dimethylcyclohexanol), lithium oethylxanthic acid, monolithium salt 2-ketoglutaric acid, dilithium salt, ketomalonic acid, lithium salt lactic acid, dilithium thiosulfate, lithium antimony tartrate, lithium dichloroacetate, lithium dimethylacetate, lithium diethylacetate, lithium dipropyl- acetate,

35 lithium metaborate, lithium tetraborate, lithium tetra- chlorocuprate, lithium acetoacetate,

lithium diisopropylamide, lithium diethylamide, lithium dimethylamide, lithium bis(dimethyl- silyl)amide, dilithium phthalocyanine, dilithiumtetrabromocuprate, dilithium tetrabromonickelate, dilithiumtetrachloromanganate, dilithiumbutadiyne, lithium cyclopentadienide, lithium dicyclo- hexylamide, lithium diethylamide, lithium dimethylamide, lithium dipropylamide, lithium diisopropylamide, lithium thexylborohydride, lithium tri-tert-butoxyaluminumhydride, lithium trimethyl- silyl)acetylide, lithium triethylsilyl)acetylide, lithium tris[(3- ethyl-3-pentyl)oxy]aluminumhydride, (phenylethynyl)lithium, 2- thienyllithium, lithium diethyldihydroaluminate, lithium dimethyldihydroaluminate, lithium aluminum hydride, lithium bifluoride, lithium biphenyl, lithium biselenite, lithium bis(2-methoxyethoxy)-aluminum hydride, lithium bismuthate, lithium borate, lithium chlorite, lithium cobaltnitrite, lithium cyanoborohydride, lithium cyclopentadienide, lithium dicyanamide, lithium hexametaphosphate, lithium hexanitrocolbaltate, lithium hydrogenphosphite, lithium hydrogenselenite, lithium hydrogensulfite, lithium hydrosulfite, lithium hypochloride, lithium metaarsenite, lithium metabisulfide, lithium metaperiodate, lithium methacrylate, lithium nitrofer- ricyanide, oxybate, lithium pentamethylcyclopentadienide, lithium phenolate, polyphosphate, lithium polyphosphite, lithium propion- ate, lithium pyrophosphate, lithium selenate, lithium selenite, lithium tetrachloroaluminate, lithium thiomethoxide, lithium thiosulfate, lithium thiosulfide, lithium thiosulfite, lithium tri- actoxyborohydride, lithium lithium trimethylsilonate, lithium triethylsilonate, lithium tris(lpyrazoly) borohydride, including analogues, homologue, isomers and derivatives thereof. See Lithium Chemistry: A Theoretical and Experimental Overview, Sapse, Schleyer, John Wiley & Sons, N.Y. (1995), incorporated herein by reference

25 NICKEL

Preferably the primary antiknock component is selected from nickel or nickel compounds.

Suitable nickel compounds are disclosed in WO 98/26028, GB 972630, GB 737092, GB950147, GB966860, and GB 803140, and are discussed herein.

Suitable nickel compounds include: alkyl, aryl, alkyloxy, alkylanol, aryloxy, di/trialkyl, diltriaryl, di/trialkyloxy, di/trialkyanol, di/triaryloxy, and/or cyclomatic complexes, including, biscyclopentadienyl nickel, cyclopentadienyl methylcyclopentadienyl nickel, bis(methylcyclopentadienyl) nickel, bis(triphenylphosphine)dicarbonyl nickel,

bis(isopropylcyclopentadienyl) nickel, bisindenyl nickel, cyclopentadienyl nickel nitrosyl, methylcyclopentadienyl nickel nitrosyl, including analogue, homologue, isomer, and derivatives thereof.

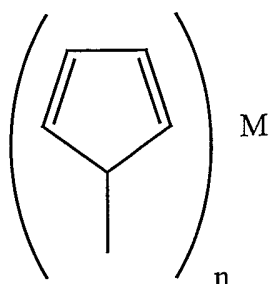
- 5 In one preferred aspect the nickel and/or nickel compound provides nickel in an amount of at least 3 mg per kg of fuel. In one preferred aspect the nickel and/or nickel compound provides nickel in an amount of at least 5 mg per kg of fuel. In one preferred aspect the nickel and/or nickel compound provides nickel in an amount of at least 10 mg per kg of fuel. In one preferred aspect the nickel and/or nickel compound provides nickel in an amount of at least 50 mg per kg of fuel. In one preferred aspect the nickel and/or nickel compound provides nickel in an amount of at least 100 mg per kg of fuel. In one preferred aspect the nickel and/or nickel compound provides nickel in an amount of at least 200 mg per kg of fuel.
- 10
- 15 In one preferred aspect the nickel and/or nickel compound provides nickel in an amount of from 3 to 500 mg per kg of fuel. In one preferred aspect the nickel and/or nickel compound provides nickel in an amount of from 5 to 500 mg per kg of fuel. In one preferred aspect the nickel and/or nickel compound provides nickel in an amount of from 10 to 500 mg per kg of fuel. In one preferred aspect the nickel and/or nickel compound provides nickel in an amount of from 50 to 500 mg per kg of fuel. In one preferred aspect the nickel and/or nickel compound provides nickel in an amount of from 100 to 500 mg per kg of fuel. In one preferred aspect the nickel and/or nickel compound provides nickel in an amount of from 200 to 500 mg per kg of fuel.
- 20

25 THALLIUM

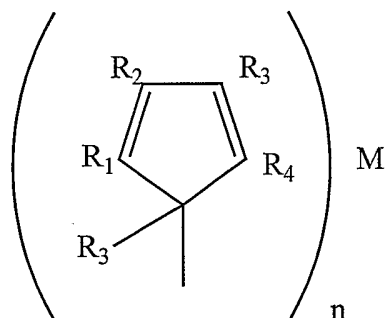
Preferably the primary antiknock component is selected from thallium or thallium compounds.

- 30 Preferably the thallium and/or thallium compound is a thallium compound.

Suitable thallium compounds are disclosed in US3328440, and are discussed herein. Suitable thallium compounds include compounds represented by the general formula



wherein n is a integer from one to four, and wherein M is thallium. In preferred compounds, the cyclopentadienyl moiety can be mono-, di-, tri-, tetra-, or pentasubstituted with monovalent radicals, and in addition said moiety can be directly
 5 bonded with at least one fused ring structure. For example, the cyclopentadienyl moiety can be substituted with monovalent radicals providing antiknock agents of the instant invention which can be represented by the general formula



wherein each of R_1 , R_2 , R_3 , R_4 , and R_5 can be the same or different and are selected
 10 from the class consisting of hydrogen and organic radicals; and wherein n is a integer from one to four and M is thallium.

Thus, the R_1 , R_2 , R_3 , R_4 , and R_5 groups of the antiknock agents of our invention can be alkyl radicals such as, for example, methyl ethyl, n -propyl, isopropyl, n -butyl, isobutyl,
 15 sec-butyl 't'-butyl, n -amyl, and the various positional isomers thereof as, for example, 1-methylbutyl, 2-methyl-butyl, 3-methyl-butyl, 1,1-dimethyl-propyl, 1,2- dimethyl-propyl, 2,2-dimethyl-propyl, and 1-ethyl-propyl, and likewise the corresponding straight and branched chain isomers, of hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nondecyl, eicosyl and the like.
 20 In addition, these monovalent hydrocarbon radicals may be alkenyl radicals such as ethenyl, Δ^1 -propenyl, Δ^2 -propenyl, isopropenyl, Δ -butenyl, Δ^2 - butenyl, Δ^3 -butenyl, and the corresponding branched chain isomers thereof as, for example, Δ^1 -isobutenyl, Δ^2 -isobutenyl, Δ -sec-butenyl, Δ^2 -see- butenyl, including 1-methylene- Δ^2 propenyl, Δ^1 -pentenyl, Δ^Z -pentenyl, Δ^3 -- pentenyl, Δ^4 -pentenyl, and the corresponding branched

chain isomers thereof; Δ^1 -hexenyl, Δ^2 -hexenyl, Δ^3 -hexenyl, Δ^4 -hexenyl, Δ^5 -hexenyl, and the corresponding branched chain isomers thereof, including 3,3-dimethyl- Δ^1 -butenyl; 2,3-dimethyl Δ^1 -butenyl; 2,3-dimethyl- Δ^2 -butenyl; 2,3-dimethyl- Δ^3 -butenyl; and 1-methyl- Δ^1 -ethyl- Δ^2 -propenyl; and similarly, the various isomers of heptenyl, octenyl, nonyl, 5 decenyl, undecenyl, dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, eicosenyl, and the like.

Particularly preferred is cyclopentadienyl thallium.

10 SECONDARY ANTIKNOCK COMPONENT

The present invention comprises or utilises at least one secondary antiknock component selected from (a) oxyhydrocarbyl compounds and (b) nitrohydrocarbyl compounds.

15 In one aspect the at least one secondary antiknock component is an oxyhydrocarbyl compound.

In one aspect the at least one secondary antiknock component is a nitrohydrocarbyl compound.

20

OXYHYDROCARBYL COMPOUNDS

OXYHYDROCARBYL

25 The term "oxyhydrocarbyl" compound as used herein means a compound comprising at least C, H and O and may optionally comprise one or more other suitable elements or substituents. Examples of such elements will be apparent to those skilled in the art and include, for instance, sulphur and nitrogen.. Examples of such substituents may include halo-, alkoxy-, nitro-, an alkyl group, a cyclic group etc. If the oxyhydrocarbyl group 30 comprises more than one C then those carbons need not necessarily be linked to each other. For example, at least two of the carbons may be linked *via* a suitable element or group. Thus, the oxyhydrocarbyl group may contain hetero atoms. Suitable hetero atoms will be apparent to those skilled in the art and include, for instance, sulphur and nitrogen.

35

In one embodiment of the present invention, the oxyhydrocarbyl compound is a oxyhydrocarbon compound.

Here the term "oxyhydrocarbon" compound means a compound comprising only (i.e. consisting of) C, H and O and may not optionally comprise one or more other suitable elements

In one embodiment of the present invention, the oxyhydrocarbyl compound comprises a group selected from alcohols, phenols, carboxylic acids, esters, and ethers.

10

NITROHYDROCARBYL COMPOUNDS

The term "nitrohydrocarbyl" group as used herein means a compound comprising at least C, H and N and may optionally comprise one or more other suitable elements or substituents. Examples of such elements will be apparent to those skilled in the art and include, for instance, sulphur and oxygen.. Examples of such substituents may include halo-, alkoxy-, an alkyl group, a cyclic group etc. If the nitrohydrocarbyl group comprises more than one C then those carbons need not necessarily be linked to each other. For example, at least two of the carbons may be linked *via* a suitable element or group. Thus, the oxyhydrocarbyl group may contain hetero atoms. Suitable hetero atoms will be apparent to those skilled in the art and include, for instance, sulphur and oxygen.

20

In one embodiment of the present invention, the nitrohydrocarbyl group is a nitrohydrocarbon group.

25

Here the term "nitrohydrocarbon" means a compound comprising only (i.e. consisting of) C, H and N and may not optionally comprise one or more other suitable elements.

Preferably the at least one secondary antiknock component is selected from an antiknock component selected from

30

I. Cyclic amines

A. Monoaromatics 1. Monoamines

a. Unsubstituted (aniline)

35

b. Ring-substituted

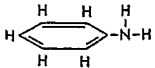
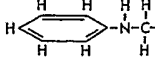
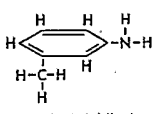
- (1) Monoalkyl
- (a) Methyl
 - (b) Ethyl
 - (c) Propyl
 - 5 (d) Butyl
 - (e) Amyl
 - (f) Vinyl
- (2) Polyalkyl
- (a) Dimethyl
 - 10 (b) Trimethyl
 - (c) Diethyl
 - (d) Isopropyl I-methyl
- (3) Functional
- (a) O-containing
- 15 1. Acids and esters
 - 2. Hydroxy
 - 3. Alkoxy
 - 4. Miscellaneous
- (b) Halogen-containing
- (c) N-containing
- 20 (d) S-containing
- (e) Multiple groups
- (4) Alkyl and functional
- c. N-substituted
- 25 (I) Alkyl
- (a) Methyl (mono- and di-)
 - (b) Ethyl (mono- and di-)
 - (c) Methyl-ethyl
 - (d) Propyl (mono- and di-)
 - 30 (e) Butyl (mono- and di-)
 - (f) Amyl
 - (g) Allyl
- (2) Functional
- (3) Alkyl and functional
- 35 d. Ring and N-substituted

- (1) Alkyl (ring)-Alkyl (N)
- (a) Methyl-methyl (mono- and di-)
 - (b) Methyl-ethyl (mono- and di-)
 - (c) Methyl-isopropyl
 - 5 (d) Methyl-alkyl
 - (e) Dimethyl-methyl (mono- and di-)
 - (f) Trimethyl-methyl (mono- and di-)
 - (g) Ethyl-methyl
 - (h) Isopropyl-alkyl
 - 10 (i) Butyl-alkyl
 - (j) Amyl-alkyl
 - (k) Alkyl-alkyl
- (2) Alkyl (ring)-functional (N)
- (3) Functional (ring)-alkyl (N)
- 15 (4) Functional (ring) - functional (N)
2. Polyamines
- a. Unsubstituted
 - b. Ring-substituted
 - c. N-substituted
- 20 3. Organic metallic derivatives
- a. Chelates
 - b. Organo-metallic
 - c. Miscellaneous
- 25 B. Polyaromatics (uncondensed)
1. Monoamines
- a. Unsubstituted b. N-substituted
 - (1) Secondary amines
 - (a) Diphenylamine
 - 30 (b) Benzyaniline
 - (c) Miscellaneous
 - (2) Tertiary amines
 - (a) Triphenylamines
 - (b) Miscellaneous
 - 35 c. Ring and N-substituted

- 2. Polyamines
 - a. Unsubstituted
 - b. Ring-substituted
 - c. N-substituted
 - 5 d. Ring and N-substituted
- 3. Organic metallic derivatives
- C. Condensed ring compounds
 - I. Unsubstituted
 - 10 2. Ring-substituted
 - 3. N-substituted
 - a. Alkyl
 - b. Aryl
 - c. Miscellaneous
 - 15 4. Organic metallic derivatives
- D. Heterocyclics
 - 1. Heteronitrogen
 - E. Hydroaromatics
- 20 II. Aromatic amides
 - A. C-substituted
 - B. N-substituted
 - 1. Monoamides
 - 2. Diamides
 - 25 C. C- and N-substituted
 - 1. Aryl and/or alkyl
 - 2. Aryl and/or functional
 - D. Organic metallic derivatives
- 30 III. Aliphatic amines
 - A. Monamines
 - 1. Unsubstituted
 - 2. C-substituted (functional)
 - 3. N-substituted
 - 35 a. Alkyl

- b. Functional
 - c. Alkyl and functional
 - 4. C- and N-substituted
 - B. Diamines
 - 5 C. Polyamines
 - D. Imines
 - E. Organic metallic derivatives
 - 1. Chelates
 - 2. Miscellaneous
- 10
- IV. Aliphatic amides
- A. Unsubstituted
 - B. C-substituted
 - C. N-substituted
 - 15 D. C- and N-substituted
 - E. Organic metallic derivatives
 - 1. Silver acetamide derivatives
 - 2. Copper urea derivatives
 - 3. Miscellaneous
- 20
- V. Aralkylamines
- VI. Heterocyclics (Heteronitrogens)
- A. Mono-N
 - 25 1. Pyridine and derivatives
 - 2. Piperidine and derivatives
 - 3. Quinoline and derivatives
 - 4. Miscellaneous
 - B. Poly-N
 - 30 C. N and other hetero atoms
 - D. Organic metallic derivatives
- VII. Functional N groups
- A. Nitrates
 - 35 B. Nitrites

- C. Nitro
 - 1. Aliphatic
 - 2. Cyclic
 - a. Mono-N
 - b. Poly-N
 - D. Nitroso
 - E. Cyanogen derivatives
 - 1. Aliphatic nitriles
 - 2. Aromatic nitriles
 - 3. Organic metallic derivatives
 - F. Oximes
 - 1. Organic metallic derivatives
 - G. Hydrazines
 - 1. Substituted
 - a. Phenyl
 - H. Cyanic acid and derivatives
 - 1. Organic metallic derivatives
 - I. Carbamic acid derivatives
 - 1. Organic metallic derivatives
 - J Azo compounds
 - K. Azoxy and hydrazo compounds
 - L. Azide compounds
- VIII. Poly-N functions
- A. Guanidine derivatives
 - B. Amidine derivatives
 - C. Nitrosoamines
 - D. Azoamines
 - E. Thiourea derivatives
 - F. Carbazides
 - G. Acetanilide derivatives
 - H. Cyanogen derivatives

FUNCTIONAL GROUP	CLASS	COMPOUND
NH ₂	AROMATIC AMINE	 (Aniline)
	AROMATIC AMINE With amine hydrogen replaced by methyl or ethyl group *	 (N-methylaniline)
NH ₂ CH ₂	AROMATIC AMINE With separate methyl or ethyl attachment *	 (m-toluidine)

*Alkyls larger than ethyl decrease antiknock effectiveness

Preferably the at least one secondary antiknock component is selected from an antiknock component selected from (a), (b) and (c) below:

5

(a) Compounds containing only carbon, hydrogen and oxygen

Oxygenated compounds considered in five groups;

- (a) alcohols and phenols,
 - 10 b) carboxylic acids,
 - (c) esters
 - (d) ethers and
 - (e) miscellaneous oxygen compounds.
- 15 Preferred carboxylic acids include aliphatic and aromatic, monobasic, dibasic and polybasic acids, aliphatic esters, aromatic esters, formates, acetates, propionates (including cyclopropionates and acrylates), benzoates, oxalates, malonates, succinates and carbonates.
- 20 Preferred ethers and cyclic ethers include methyl t-butyl ether and di-isopropyl ether.

Preferred miscellaneous oxygenated compounds include aldehydes and ketones, 4-acetylbiphenyl, compounds containing a biphenyl moiety and quinones.

(b) Compounds containing nitrogen

Compounds containing the elements carbon, hydrogen, nitrogen and, optionally, oxygen and halogen may be used. Optionally compounds containing nitrogen with phosphorus
5 and/or sulphur may be used

Preferred compounds include amines, hydrazines, N-nitrosamines, nitrogen heterocycles, nitro compounds, C-nitroso compounds, nitriles, nitrogen derivatives of acids and aldehydes, ureas and urethanes

10

Preferred compounds include toluidine, N-methylaniline, 3-aminomethylpyridine N - methyldiphenylamine, N-phenyl-N-benzyl-naphthylamine, primary and secondary aromatic amines (i.e. containing at least one benzene ring), aminopyridines, anilines, 4-methoxyaniline, 5-amino-2-methoxypyridine, naphthalene, fluorene, chrysene, pyrrole,
15 pyrazole, triazole, tetrazole, pyrimidine, triazine, indazole, benzimidazole, benzotriazole, purine, quinoline, quinoxaline and anthraquinone, aromatic diamines and polyamines, diamines based on the benzene ring (i. e. the phenylene diamines), diamines based on other aromatic ring structures (e.g. pyridine and triazine), hydrazines, N,N'-diphenyl-N'-di-p-tolylhydrazine, N-nitrosamines, N-nitroso-4-methyldiphenyl-amine

20

Particularly preferred compounds are toluidine and N-methylaniline.

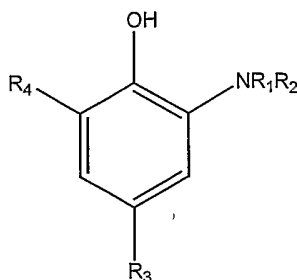
(c) Nitrogen compounds, heterocyclics, nitro, C-nitroso, nitriles, acid and aldehyde derivatives etc

25

Preferred compounds are carbazole and phenoxazine.

Also preferred are amino cresols and in particular amino cresols of general formula methyl phenol-NR₁R₂ and methyl phenol-CH₂-NR₁R₂. where R₁ and R₂ are
30 independently hydrogen or alkyl wherein the 3,4, and 6 positions of the phenyl group are unsubstituted.

Dimethylaminomethyl phenols of the formula



wherein each of R₁, R₂, R₃ and R₄ are independently selected from independently hydrogen or alkyl such as H, CH₃, C₂H₅, (CH₃)₂CH, C₃H₇, and (CH₃)₃C

5

Preferred compounds include those disclosed in Lyle D Burns, Organic Antiknock Chemicals, Chemtech, December 1984.

Preferably the at least one secondary antiknock component is selected from an antiknock component selected from (A) and (B) below:

10

(A) Compounds containing oxygen, carbon and hydrogen

Aliphatic alcohols; typically small benefits, decreasing with increased molecular weight.

15

Phenols; medium benefits, particularly for substituted molecules. Exceptions were 2,4,6-tri-t-butyl phenol and 4-hydroxytetraphenylmethane which were pro-knock.

Dihydroxy benzenes, catechol and hydroquinone; typically weak activity and poor solubility.

20

Carboxylic acids; low activity for aliphatic, aromatic, monobasic and dibasic compounds.

Esters; compounds considered included formates, acetates, propionates, benzoates, oxalates, malonates, succinates and carbonates. Aromatic formates are consistently the more effective group. In general aromatic compounds showed highest activity. Aliphatic oxalates were predominately pro-knock.

25

Ethers and cyclic ethers; aliphatic ethers typically have small antiknock effectiveness.

30

Aldehydes and ketones; typically show negligible effect.

(B) Compounds containing nitrogen, carbon and hydrogen

- 5 Aliphatic amines and polyamines; typically no or low activity.

Tertiary amines; typically no or low activity.

- 10 Primary and secondary aromatic amines; generally effective antiknocks, although dependant on other ring substituents and their placement. 4-methoxy aniline is highly effective.

- Amines of other aromatic ring structures; typically less effective than phenyl derivative. Alternatives considered include pyridine, naphthalene, fluorene, chrysene, pyrrole, pyrazole, triazole, tetrazole, pyrimide, triazine, indazole, benzimidazole, benzotriazole, purine, quinoline, quinoxaline and anthraquinone.
- 15

Diphenyl amines; can be highly effective such as 4, 4' -dimethyldiphenylamine.

- 20 Aromatic diamines and polyamines; typically have high antiknock activity. Again the phenyl derivative is more effective than other aromatic structures.

Hydrazines; variable, although N,N'- diphenyl-N'- di-p-tolylhydrazine is highly effective.

- 25 N-nitrosamines; variable, although N-nitroso-4-methyldiphenylamine is highly effective. Diaromatic N-nitrosoamines are generally antiknock depending on type and positioning of substituent on phenyl group.

- 30 Carbazole and phenoxazine, bridged diphenylamine molecules; are antiknocks, along with benzohydroxamic acid, maleimide, phthalimide and 1,2,3,4-tetrahydroquinoline.

Compounds without amino groups are in general poor antiknocks i.e. amides, ureas, nitro compounds and heterocycles with more than 2 nitrogens are hard to dissolve in gasoline.

SULPHUR PASSIVATING AGENT

As discussed herein the present invention provides and utilises a sulphur passivating agent. By the term "sulphur passivating agent" it is meant a material which reduces and/or inhibits one or more undesired activities of sulphur. In particular it is meant a material which reduces and/or inhibits one or more undesired activities of sulphur in respect of the primary or secondary antiknock component (preferably the primary antiknock component) wherein the sulphur is present in a fuel. Preferably the undesired activities of sulphur which is reduced and/or inhibited is the reduction of the octane enhancement and/or antiknock effect of the primary or secondary antiknock component (preferably the primary antiknock component) by sulphur.

In one aspect the composition comprises the sulphur passivating agent. In this aspect the composition comprised (i) at least one primary antiknock component selected from (a) iron or an iron compound; (b) lead or a lead compound; (c) manganese or manganese compound; and (d) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium; (ii) at least one secondary antiknock component selected from (a) oxyhydrocarbyl compounds; and (b) nitrohydrocarbyl compounds; (iii) a sulphur passivating agent.

In one aspect the sulphur passivating compound is selected from a manganese and/or manganese compound, a fuel compatible s block metal and an acetate compound.

In one aspect the sulphur passivating compound is a free radical generating oxygenate, such as an acetate compound.

MANGANESE OR MANGANESE COMPOUND

Preferably the manganese and/or manganese compound is a manganese compound.

The most desirable general type of manganese carbonyl compounds utilised in accordance with this invention comprise organomanganese polycarbonyl compounds. For best results, use should be made of a cyclopentadienyl manganese tricarbonyl compound of the type described in U.S. Pat. Nos. 2,828,417 and 3,127,351. Thus use

can be made of such compounds as cyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, dimethylcyclopentadienyl manganese tricarbonyl, trimethylcyclopentadienyl manganese tricarbonyl, propylcyclopentadienyl manganese tricarbonyl, isopropylcyclopentadienyl manganese tricarbonyl, butylcyclopentadienyl manganese tricarbonyl, pentylcyclopentadienyl manganese tricarbonyl, hexylcyclopentadienyl manganese tricarbonyl, ethylmethylcyclopentadienyl manganese tricarbonyl, dimethyloctylcyclopentadienyl manganese tricarbonyl, dodecylcyclopentadienyl manganese tricarbonyl, indenyl manganese tricarbonyl, and like compounds in which the cyclopentadienyl moiety contains up to about 18 carbon atoms.

A preferred organomanganese compound is cyclopentadienyl manganese tricarbonyl. Particularly preferred for use in the practice of this invention is methylcyclopentadienyl manganese tricarbonyl.

15

Methods for the synthesis of cyclopentadienyl manganese tricarbonyls are well documented in the literature. See for example, in addition to US 2,818,417 and US 3,127,351 noted above, US 2,868,816; US 2,898,354; US 2,960,514; and US 2,987,529, among others.

20

Other organomanganese compounds which may be employed include the non-ionic diamine manganese tricarbonyl halide compounds such as bromo manganese tricarbonyl halide compounds such as bromo manganese dianiline tricarbonyl and bromo manganese dipyridine tricarbonyl, described in US 2,902,489; the acyl manganese tricarbonyls such as methylacetyl cyclopentadienyl manganese tricarbonyl and benzoyl methyl cyclopentadienyl manganese tricarbonyl, described in US 2,959,604; the aryl manganese pentacarbonyls such as phenyl manganese pentacarbonyl, described in U.S. Pat. 3,007,953; and the aromatic cyanomanganese dicarbonyls such as mesitylene cyanomanganese dicarbonyl, described in U.S. Pat. No. 3,042,693. Likewise, use can be made of cyclopentadienyl manganese dicarbonyl compounds of the formula $\text{RMn}(\text{CO})_2\text{L}$, where R is a substituted or unsubstituted cyclopentadienyl group having 5 to 18 carbon atoms, and L is a ligand, such as an olefin, an amine, a phosphine, SO_2 , tetrahydrofuran, or the like. Such compounds are referred to, for example in, Herberhold, M., *Metal π -Complexes*, Vol. II, Amsterdam, Elsevier, 1967 or Giordano, P.J. and Weighton, M. S., *Inorg. Chem.*, 1977, 16, 160. Manganese pentacarbonyl dimer

35

(dimanganese decarbonyl) can also be employed if desired.

Preferably the manganese compound is a manganese complex.

- 5 Preferably the manganese compound is selected from cyclopentadienyl manganese tricarbonyl and substituted cyclopentadienyl manganese tricarbonyl.

The manganese compound may cyclopentadienyl manganese tricarbonyl and substituted cyclopentadienyl manganese tricarbonyl, wherein the substituents can be, for example,
10 one or more C₁₋₅ alkyl groups, preferably C₁₋₂ alkyl groups. A combination of such manganese complexes may also be used.

Preferably the manganese compound is methylcyclopentadienyl manganese tricarbonyl.

- 15 Preferably the manganese and/or the manganese compound is selected from cyclopentadienyl manganese tricarbonyl and substituted cyclopentadienyl manganese tricarbonyl.

Preferably the manganese and/or the manganese compound is methylcyclopentadienyl
20 manganese tricarbonyl.

In one preferred aspect the manganese and/or manganese compound provides manganese in an amount of at least 3 mg per kg of fuel. In one preferred aspect the manganese and/or manganese compound provides manganese in an amount of at least
25 18 mg per kg of fuel. In one preferred aspect the manganese and/or manganese compound provides manganese in an amount of at least 36 mg per kg of fuel.

S BLOCK

30 In one aspect the sulphur passivating compound is a fuel compatible metal selected from the s block of the periodic table ("an s block metal") or a fuel compatible compound comprising a metal selected from the s block of the periodic table ("an s block compound").

35 Preferably the s block metal or the s block metal of the s block compound is selected

from magnesium and calcium.

The s block metal may be magnesium.

- 5 The s block metal may be calcium.

Preferably the s block metal and/or s block metal compound is an s block metal compound.

- 10 A very extensive range of compounds have been claimed to be suitable as a means to provide s block metals, in particular magnesium and/or calcium, in fuel-soluble forms for various purposes.

- 15 The s block metal or the s block compound may be delivered in a manner analogous to that given herein in respect of potassium. Each of the forms of potassium disclosed herein may be used to provide the analogous s block compound, such as the analogous calcium or magnesium compound.

- 20 Particularly preferred s block compounds are overbased carboxylic acid salts of the respective s block metal, such as overbased carboxylic acid salts of magnesium and/or calcium.

- 25 In one preferred aspect the s block metal and/or s block compound provides the s block metal in an amount of at least 10 mg per kg of fuel. In one preferred aspect the s block metal and/or s block compound provides the s block metal in an amount of at least 20 mg per kg of fuel. In one preferred aspect the s block metal and/or s block compound provides the s block metal in an amount of at least 30 mg per kg of fuel. In one preferred aspect the s block metal and/or s block compound provides the s block metal in an amount of from 30 to 50 mg per kg of fuel.

30

FUEL COMPATIBLE MG COMPOUND

Suitable magnesium compounds are disclosed in GB2248068, GB2254610, and WO 98/26028 and are discussed herein.

35

GB2248068 teaches compounds in the form of salts of organic acids. As examples of organic acids, there may be mentioned carboxylic acids and their anhydrides, phenols, sulphurized phenols, and sulphonic acids.

5 The carboxylic acid may be, for example:

i) An acid of the formula:

R-COOH where R is hydrogen, or a substituted or unsubstituted alkyl, cycloalkyl, alkenyl,
10 cycloalkenyl, or aryl group. Examples of such acids include formic acid, acetic acid, propionic acid, butyric acid, valeric acid, palmitic acid, stearic acid, cyclohexanecarboxylic acid, 2-methylcyclohexane carboxylic acid, 4-methylcyclohexane carboxylic acid, oleic acid, linoleic acid, linolenic acid, cyclohex-2-eneoic acid, benzoic acid, 2-methylbenzoic acid, 3-methylbenzoic acid, 4-methyl benzoic acid, salicylic acid,
15 2-hydroxy-4-methylbenzoic acid, 2-hydroxy-4-ethylbenzoic acid, p-hydroxybenzoic acid, 3,5-di-tert-butyl-4-hydroxybenzoic acid, o-aminobenzoic acid, p-aminobenzoic acid, o-methoxybenzoic acid and p-methoxybenzoic acid.

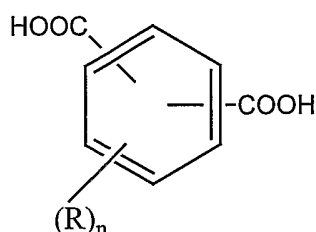
ii) A dicarboxylic acid of the formula $\text{HOOC}-(\text{CH}_2)_n\text{COOH}$ where n is zero or an integer,
20 including e.g. oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid and suberic acid. Also included are acids of the formula $\text{R HOOC}-(\text{CH}_2)_x\text{COOH}$ where x is zero or an integer, y is zero or an integer and x and y may be equal or different and R is defined as in (i). Examples of such acids include the alkyl or alkenyl succinic acids, 2-methylbutanedioic acid, 2-ethylpentanedioic acid, 2-n-
25 dodecylbutanedioic acid, 2-n-dodecenylbutanedioic acid, 2-phenylbutanedioic acid, and 2-(p-methylphenyl)butanedioic acid. Also included are polysubstituted alkyl dicarboxylic acids wherein other R groups as described above may be substituted on the alkyl chain. These other groups may be substituted on the same carbon atom or different atoms. Such examples include 2,2-dimethylbutanedioic acid; 2,3-dimethylbutanedioic acid;
30 2,3,4-trimethylpentanedioic acid; 2,2,3-trimethylpentanedioic acid; and 2-ethyl-3-methylbutanedioic acid.

The dicarboxylic acids also include acids of the formula:

$\text{HOOC}-(\text{CrH}_2\text{r}-2)\text{COOH}$ where r is an integer of 2 or more. Examples include maleic acid, fumaric acid, pent-2-enedioic acid, hex-2-enedioic acid; hex-3-enedioic acid, 5-methylhex-2-enedioic acid; 2,3-di-methylpent-2-enedioic acid; 2-methylbut-2-enedioic acid; 2-dodecylbut-2-enedioic acid; and 2-polyisobutylbut-2-enedioic acid.

5

The dicarboxylic acids also include aromatic dicarboxylic acids e.g. phthalic acid, isophthalic acid, terephthalic acid and substituted phthalic acids of the formula:

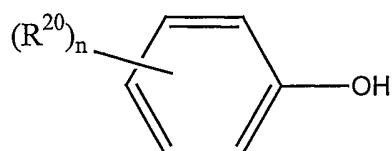


where R is defined as in (i) and $n = 1, 2, 3$ or 4 and when $n > 1$ then the R groups may be the same or different. Examples of such acids include 3-methylbenzene-1,2-dicarboxylic acid; 4-phenylbenzene-1,3-dicarboxylic acid; 2-(1-propenyl)benzene-1,4-dicarboxylic acid, and 3,4-dimethylbenzene-1,2-dicarboxylic acid.

The carboxylic acid anhydrides include the anhydrides that may be derived from the carboxylic acids described above. Also included are the anhydrides that may be derived from a mixture of any of the carboxylic acids described above. Specific examples include acetic anhydride, propionic anhydride, benzoic anhydride, maleic anhydride, succinic anhydride, dodecylsuccinic anhydride, dodecenylsuccinic anhydride, an optionally substituted polyisobutylenesuccinic anhydride, advantageously one having a molecular weight of between 500 and 2000 daltons, phthalic anhydride and 4-methylphthalic anhydride.

The phenols from which the anion may be derived are of many different types. Examples of suitable phenols include:

Phenols of the formula:

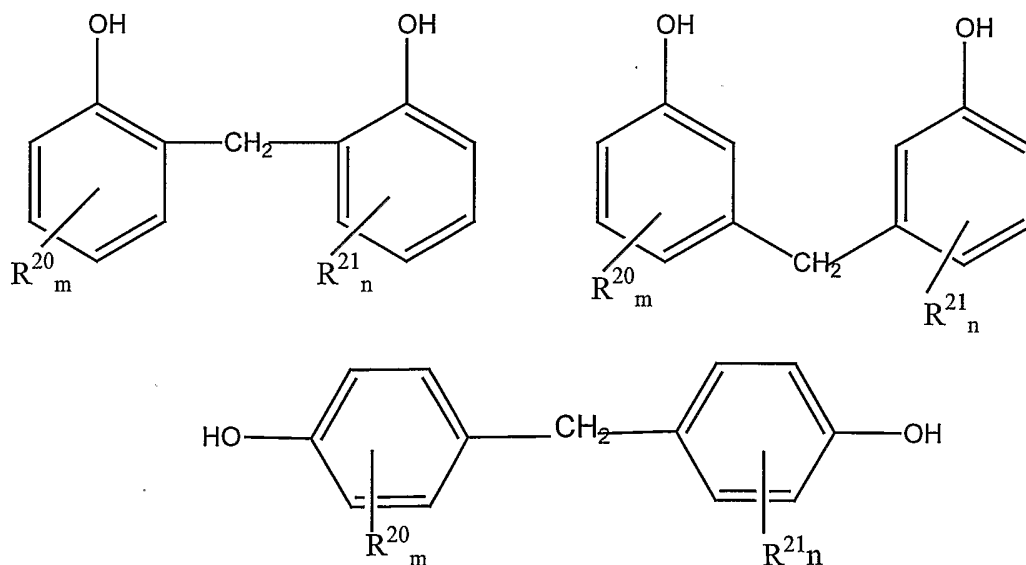


where $n = 1, 2, 3, 4$ or 5 , where R_{20} is defined below and when $n > 1$ then the substituents may be the same or different. R_{20} may be hydrogen, or a substituted or unsubstituted, alkyl, cycloalkyl, alkenyl, cycloalkenyl or aryl group. The hydrocarbon

group(s) may be bonded to the benzene ring by a keto or thio-keto group. Alternatively the hydrocarbon group(s) may be bonded through an oxygen, sulphur or nitrogen atom. Examples of such phenols include o-cresol; m-cresol; p-cresol; 2,3-dimethylphenol; 2, 4-dimethylphenol; 2,3,4-trimethylphenol; 3-ethyl-2,4-dimethylphenol; 2,3, 4,5-tetramethylphenol; 4-ethyl-2,3,5,6-tetramethylphenol; 2-ethylphenol 3- ethylphenol; 4-ethylphenyl; 2-n-propylphenol; 2-isopropylphenol; 4- isopropylphenol; 4-n-butylphenol; 4-isobutylphenol; 4-sec-butylphenol; 4- t-butylphenol; 4-nonylphenol; 2-dodecylphenol; 4-dodecylphenol; 4- octadecylphenol; 2-cyclohexylphenol; 4-cyclohexylphenol; 2-allylphenol; 4-allylphenol; 2-hydroxydiphenyl; 4-hydroxydiphenol; 4-methyl-4'-hydroxydiphenyl; o-methoxyphenol; p-methoxyphenol; p-phenoxyphenol; 2-hydroxydiphenylsulphide; 4-hydroxydiphenylsulphide; 4- hydroxyphenylmethylsulphide; and 4-hydroxyphenyldimethylamine. Also included are alkyl phenols where the alkyl group is obtained by polymerization of a low molecular weight olefin e.g. polypropyl phenol or polyisobutylphenol.

15

Also included are phenols of the formula:

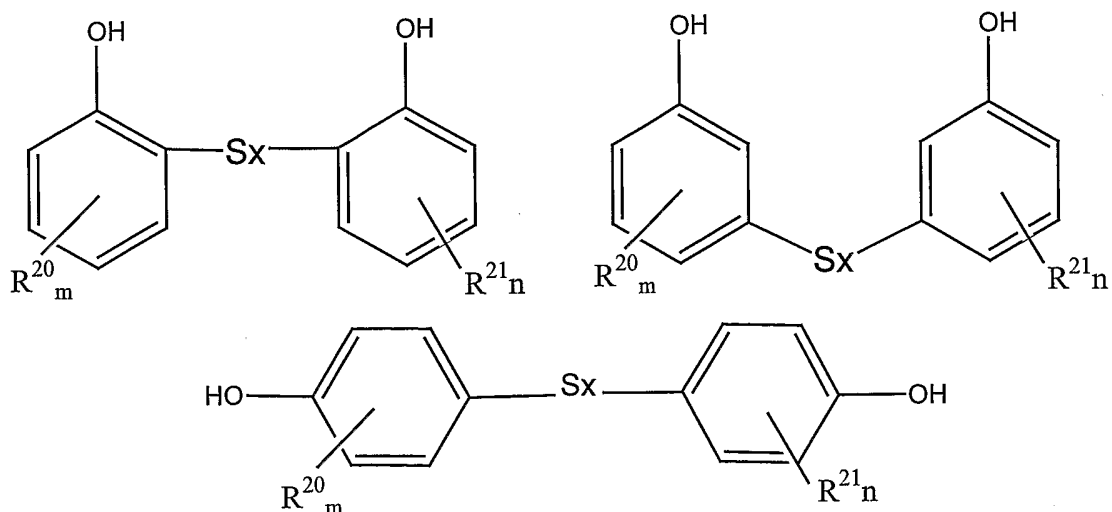


where R20 and R21 which may be the same or different are as defined above for R20 and m and n are integers and for each m or n greater than 1 each R20 and R21 may be the same or different. Examples of such phenols include 2,2'-dihydroxy-5,5'-dimethyldiphenylmethane; 5,5'-dihydroxy-2,2'-dimethyldiphenylmethane; 4,4'-dihydroxy-2,2'-dimethyl-diinethyldiphenylmethane; 2,2'-dihydroxy-5,5'-dinonyldiphenylmethane; 2,2'- dihydroxy-5,5'-didodecyldiphenylmethane; 2,2',4,4'-tetra-t-

20

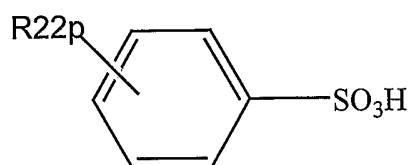
butyl-3,3'-dihydroxy-5,5'-didodecylphenylmethane; and 2,2',4,4'-tetra-*t*-butyl-3,3'-dihydroxydiphenylmethane.

Also included are sulfurized phenols of the formula:



- 5 where R₂₀ and R₂₁ which may be the same or different are as defined above, and m and n are integers, for each m and n greater than 1 each R₂₀ and R₂₁ may be the same or different, and x is 1,2,3 or 4. Examples of such phenols include: 2,2'-dihydroxy-5,5'-dimethyldiphenylsulphide; 5,5'-dihydroxy-2,2'-di-*t*-butyl-4,4'-dihydroxy-3,3'-di-*t*-butyldiphenylsulphide 2,2'-dihydroxy-5,5'-dinonyldiphenyldisulphide; 2,2'-dihydroxy-5,5'-
10 didodecyldiphenyldisulphide; 2,2'-dihydroxy-5,5'- didodecyldiphenyltrisulphide; and 2,2'-dihydroxy-5,5'- didodecyldiphenyltetrasulphide.

- The sulphonic acids from which the anion may be derived include alkyl and aryl sulphonic acids which have a total of 1 to 200 carbon atoms per molecule although the
15 preferred range is 10 to 80 atoms per molecule. Included in this description are aryl sulphonic acids of the formula:



where p = 1, 2, 3, 4, 5 and when p > 1 the substituents may be the same or different, and R₂₂ may represent R₂₀ as defined above.

20

The hydrocarbon group(s) may be bonded to the benzene ring through a carbonyl group or a thio-keto - 11 group. Alternatively the hydrocarbon group(s) may be bonded to the

benzene ring through a sulphur, oxygen or nitrogen atom. Thus examples of sulphonic acids that may be used include: benzene sulphonic acid; o- toluenesulphonic acid, m- toluenesulphonic acid; p-toluene sulphonic acid; 2,3-dimethylbenzenesulphonic acid; 2,4-dinethylbenzenesulphonic acid; 2,3,4-trimethylbenzenesulphonic acid; 4-ethyl-2,3-dinethylbenzenesulphonic acid; 4-ethylbenzenesulphonic acid; 4-n-propylbenzenesulphonic acid; 4-n-butylbenzenesulphonic acid; 4-isobutylbenzenesulphonic acid; 4-sec-butylbenzenesulphonic acid; 4-t-butylbenzenesulphonic acid; 4-nonylbenzenesulphonic acid; 2-dodecylbenzenesulphonic acid; 4-dodecylbenzenesulphonic acid; 4-cyclohexylbenzenesulphonic acid; 2-cyclohexylbenzenesulphonic acid; 2-allylbenzenesulphonic acid; 2-phenylbenzenesulphonic acid; 4(4'-methylphenyl)benzenesulphonic acid; 4-methylmercaptobenzenesulphonic acid; 2-methoxybenzene sulphonic acid; 4-phenoxybenzenesulphonic acid; 4-methylaminobenzenesulphonic acid; 2-dimethylaminobenzenesulphonic acid; and 2-phenylaminobenzenesulphonic acid. Also included are sulphonic acids of the type listed above where R22 is derived from the polymerization of a low molecular weight olefin e.g. polypropylenebenzenesulphonic acid and polyisobutylenebenzenesulphonic acid.

Also included are sulphonic acids of the formula: R23 -SO3H where R23 is substituted or unsubstituted alkyl, cycloalkyl, alkenyl or cycloalkenyl. Examples of such sulphonic acids that may be used include methylsulphonic acid; ethylsulphonic acid; n-propylsulphonic acid; n-butylsulphonic acid; isobutylsulphonic acid; sec-butylsulphonic acid; t-butylsulphonic; nonylsulphonic acid; dodecylsulphonic acid; polypropylsulphonic acid; polyisobutylsulphonic acid; cyclohexylsulphonic acid; and 4methylcyclohexylsulphonic acid.

GB2254610 teaches . metallic salt co-ordination complexes of a metal M and an organic compound RH having an active (acidic) hydrogen atom adjacent an electronegative centre in the organic group R and which is reactive with the metal M to form a salt RM, and which contain a small protic Lewis base ligand L selected from H₂O, NH₃, H₂S, H₂Se and CH₃OH co-ordinating the metal cation M in said salt.

WO 98/26028 teaches magnesium compounds including: alkyl manganese compounds, dialkyl magnesium compounds, magnesium ethylate (ethoxide), magnesium methoxide, dimethylmagnesium, diethylmagnesium, dipropylmagnesium, diisopropylmagnesium,

dibutylmagnesium, di-tert-butylmagnesium, di-iso-butylmagnesium, di-sec-butylmagnesium, diphenylmagnesium, methylmagnesium chloride, methylmagnesium iodide, magnesium methylcarbonate, magnesium hydroxide, magnesium anthracene dianion, bromomagnesium isopropylcyclohexylamide, methylmagnesium bromide,

5 methylmagnesium chloride, ethylmagnesium chloride, magnesium fluoride, magnesium chloride, butylmagnesium chloride, isopropylmagnesium chloride, cyclopentylmagnesium hydride, cyclopentylmagnesium-hydroxide, cyclopentylmagnesiumchloride, cyclopentylmagnesium-methyl, cyclopentylmagnesiummethyl, cyclopentylmagnesiummethylol,

10 cyclopentylmagnesiummethoxy, cyclopentylmagnesiummethoxy, cyclohexylmagnesiumhydride, cyclohexylmagnesiumhydroxide, cyclohexylmagnesiumchloride, cyclohexylmagnesiummethyl, cyclohexylmagnesiummethylol, cyclohexylmagnesiummethylol, cyclohexylmagnesiummethoxy, cyclohexylmagnesiummethoxy, tert-butylmagnesium

15 chloride, isobutylmagnesium chloride, allylmagnesium chloride, benzylmagnesium chloride, benzylmagnesium hydride, benzylmagnesium ethylate, benzylmagnesium methylate, benzylmagnesium ethoxy, benzylmagnesium methoxy, magnesium acetate, magnesium methyl carbonate, trimethylsilylmethyl magnesium chloride, magnesium acetate tetrahydrate, methylmagnesium isopropylcyclohexylamide, magnesium

20 pyrophosphate, phenylethynylmagnesium bromide, methylphenylmagnesiumchloride, methylmagnesium, ethylmagnesium, propylmagnesium, isopropylmagnesium, butylmagnesium, isobutylmagnesium, tert-butylmagnesium, sec-butylmagnesium, phenylmagnesium, magnesium acetate, magnesium hydrogenphosphate, cyclopentylmagnesium, cyclopentylmagnesium-hydroxide, cyclopentylmethylmagnesium,

25 methylcyclopentylmethylmagnesium, allylmagnesium, benzylmagnesium, pentylmagnesium, 1,1-dimethylpropylmagnesiumhydroxide, 1,1-dimethylpropylmethylmagnesium, phenylmagnesium, phenolmagnesium, magnesium hydroxide, magnesiumcarbonate, magnesiumsilicide, magnesium phosphate, magnesium phosphite, magnesium bisulfite, L-aspartic acid magnesium, DL-aspartic

30 acid magnesium, including analogue, homologue, isomer, and derivative thereof. Corresponding beryllium, calcium, strontium, barium, radium and zinc compounds are contemplated in the practice of this invention. See The Organic Compounds of Magnesium, Beryllium, Calcium, Strontium, and Barium, Ioffe, Nesmeyanov, Amsterdam (1967), Organomagnesium Methods in Organic Synthesis, Wakefield, Academic Press,

35 FL (1995), incorporated by reference. The mixture of dialkyl magnesium compounds with

pyrophoric metallics is specifically contemplated

In one preferred aspect the magnesium and/or magnesium compound provides the magnesium in an amount of at least 10 mg per kg of fuel. In one preferred aspect the
5 magnesium and/or magnesium compound provides the magnesium in an amount of at least 20 mg per kg of fuel. In one preferred aspect the magnesium and/or magnesium compound provides the magnesium in an amount of at least 30 mg per kg of fuel. In one preferred aspect the magnesium and/or magnesium compound provides the magnesium in an amount of from 30 to 50 mg per kg of fuel.

10

FUEL COMPATIBLE CA COMPOUND

Suitable calcium compounds are disclosed in GB2248068 and GB2254610 and are discussed herein.

15

Preferred compounds are the calcium analogues of the preferred magnesium compounds discussed herein.

ACETATE COMPOUND

20

In one aspect the sulphur passivating compound is an acetate compound. By acetate compound it is meant a compound comprising an acetate group or which may decompose to form acetic acid or formic acid.

25 Acetate compounds are particularly preferred. The presence of an acetate compound offers multiple advantages. It of course serves to provide a constituent of the present composition - this in itself provides numerous advantages as discussed herein. In addition, it may prevent and/or inhibit of spark plug fouling and/or it may prevent and/or inhibit poisoning of catalysts.

30

In a general sense the acetate compound may be described as a free radical generating oxygenate.

Suitable acetate compounds are disclosed in GB866610 and GB897683 and are
35 discussed herein.

GB866610 teaches compounds defined by the general formulae $R_1(X)_n(R_2)_mCOOR$ or $[R_1(X)_n(R_2)_mCO]_2O$ or R_1CHO where R_1 is hydrogen or a monovalent hydrocarbyl radical with 1-29 carbons and R_2 is a divalent hydrocarbyl radical with 1-18 carbon atoms and R is hydrogen or a tertiary aliphatic hydrocarbyl radical containing 4 to 18 carbon atoms. X is -O- or O=C and n and m are integers having a value of 0 or 1 and the sum of R_1 , R_2 and X is 29.

Preferably the acetate compound is an alkyl acetate

10

In a highly preferred aspect the acetate compound is selected from 2,4-pentane dione and t-butyl acetate.

MATERIAL CAPABLE OF PREVENTING/INHIBITING VSR.

15

VSR is an abbreviation of valve seat recession. In this context it generally means valve seat recession of an internal combustion engine, such as a petrol/gasoline internal combustion engine.

20 The mechanism for VSR protection from a phosphorus additive, for example ValvemasterTM is believed to lie in the formation of P_2O_5 in the engine. Deposits are laid down between the exhaust valve and its seat, preventing metal to metal contact, which leads to valve seat recession.

25 In one aspect the composition comprises the material capable of preventing and/or inhibiting valve seat recession of an internal combustion engine. In this aspect the composition comprised (i) at least one primary antiknock component selected from (a) iron or an iron compound; (b) lead or a lead compound; (c) manganese or manganese compound; and (d) a metal selected from rare earth metals, lithium, nickel, and thallium
30 or a compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium; (ii) at least one secondary antiknock component selected from (a) oxyhydrocarbyl compounds; and (b) nitrohydrocarbyl compounds; (iii) a material capable of preventing and/or inhibiting valve seat recession of an internal combustion engine.

35 In one preferred aspect the material composition material capable of preventing and/or

inhibiting valve seat recession of an internal combustion engine is selected from phosphorus, phosphorus compounds, potassium and potassium compounds.

In one preferred aspect the material composition material capable of preventing and/or
5 inhibiting valve seat recession of an internal combustion engine is selected from phosphorus compounds and potassium compounds.

POTASSIUM

10 The presence of potassium offers multiple advantages. It of course serves to provide a constituent of the present composition - this in itself provides numerous advantages as discussed herein. In addition, it may prevent and/or inhibit of spark plug fouling. This advantage is discussed in further detail in PCT/GB2003/005427.

15 Preferably the potassium and/or potassium compound is a potassium compound.

A very extensive range of compounds have been claimed to be suitable as a means to provide alkali metals, in particular potassium, in fuel-soluble forms for various purposes including gasoline soluble forms for use as VSR additives.

20

Potassium salts used may be acidic, neutral or basic (that is over-based, hyperbased or superbased).

Acidic salts may be prepared with an excess of organic acid over potassium, neutral
25 salts react essentially stoichiometric quantities of acid and base and basic salts contain an excess of cations, and are typically prepared by 'blowing' a suspension of metal base in a solution of organic acid with gaseous CO₂.

In aspects of the present invention colloidal suspensions of inorganic salts of potassium
30 may be used.

Suitable organic acids for use in preparing the potassium compound are extensively reviewed in WO87/01126 to Johnston et al. These include sulphur acids, carboxylic acids and phosphorus acids.

35

Some workers have expressed fears that catalyst poisoning may limit the usefulness of the phosphorus acids.

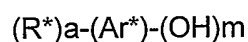
In one aspect the potassium compound is prepared from a sulphur acid.

5

Sulphur acids include sulphonic, sulphamic, thiosulphonic, sulphenic, sulphinic, partial ester sulphuric, sulphurous and thiosulphuric acids. The sulphur acids may be aliphatic or aromatic, including mono- or poly-nuclear aromatic acids or cycloaliphatic compounds. A typical example is alkylbenzene sulphonic acid salt of potassium. Sulphonates from
10 detergent manufacture by-products are frequently encountered.

Carboxylic acids include aliphatic, cycloaliphatic and aromatic mono- and poly-basic carboxylic acids, naphthenic, alkyl or alkenyl cyclopentanoic and hexanoic acids and the corresponding aromatic acids. Branched chain carboxylic acids, including 2-
15 ethylhexanoic acid and propylene tetramer substituted maleic acids may be used. Carboxylic acid fractions featuring various, mixed hydrocarbon chains, such as tall oils which also contain rosins are also encountered. A typical carboxylic acid is the potassium salt of alkyl-arylamide of carboxylic acid (CAS 686603-91-8).

20 Salts of phenols (generally referred to as phenates) may be used. These are of the general formula:



where R^* is an aliphatic group of 4 to 400 C atoms, a is an integer of 1-4, Ar^* is a polyvalent aromatic hydrocarbon nucleus of up to about 14 C atoms and m is an integer
25 from 1-4, provided that there are at least about 8 C atoms per acid equivalent provided by the R^* groups. The R^* groups may be substituted provided that this does not alter the essentially hydrocarbon character of the groups.

Phosphorus acids may also be used, for example the phosphonic and thiophosphonic
30 acids prepared by reaction of P_2S_5 with petroleum fractions such as bright stock or with polymeric materials prepared from C_2 to C_6 mono-olefins, such as poly-(butenes). Appropriate technology for preparation of a range of phosphorus additives is referenced in WO 87/01126.

35 EP 207,560 and EP 555,006 describe ranges of succinic acid derivatives, substituted on

at least one of the alpha carbon atoms with a C₂₀ to C₂₀₀ hydrocarbyl group, optionally connected to the other alpha-carbon atom by a hydrocarbon moiety of from 1 to 6 carbon atoms. Such derivatives may be further derivatised by reaction of one carboxyl group with an alcohol or an amine preparing, respectively, the hemi-ester or the amide. A
5 typical succinic acid derivative is the potassium salt of the hemi-ester of alkenyl PIBSA.

Preferred acid salts are those of potassium with the succinic acid derivatives, as described immediately above, or of alkyl benzene sulphonic acids, especially dodecyl benzene sulphonic acid.

10

Neutral salts are preferred. Salts which are resistant to extraction into aqueous phases are preferred.

The alternative of providing a fuel-stable colloidal suspension of a metal salt having a
15 mean particle size of 1 micron, preferably 0.5 micron or less is illustrated in US-A-5,090,966 to Crawford et al. An emulsion of a solution of a suitable metal salt, whether potassium borate, carbonate, bicarbonate or acetate is prepared, optionally using an emulsifying agent is prepared in some carrier oil. The solvent is then removed, typically by heating whilst subjecting to rapid agitation. Preferred in-situ preparations of metal
20 borate products, preferred carrier oils and preferred emulsifying agents are set out in the Patent. Such colloidal suspensions are also preferred sources of potassium for use according to the invention.

Mixtures of any or all of the above-mentioned acids may be employed in order to provide
25 a fuel-soluble and stable source of potassium ions. Potassium ions may be employed as a mixture of solution and colloidal suspension sources.

In one preferred aspect the potassium compound is a potassium sulphonate.

30 PHOSPHORUS

Preferably the phosphorus and/or phosphorus compound is a phosphorus compound.

Preferably the phosphorus and/or the phosphorus compound is an amine salt of a
35 phosphorus based acid.

All references in the present specification to Valvemaster^{RTM} in the context of phosphorus compounds may be read to mean an amine salt of a phosphorus based acid and/or the reaction product of the following reaction

- 5 C₁₃ alcohol + P₂O₅ → organic acid
organic acid + amine → amine salt of a phosphorus based acid
and/or a product described in US-A-4720288.

- Thus in a preferred aspect the phosphorus based acid is obtainable or obtained from the
10 reaction of (i) the reaction of a C₁₃ alcohol and P₂O₅ to form an organic acid and (ii) the reaction of the organic acid and an amine.

COMPOSITION

- 15 In one preferred aspect the composition comprises each of the components in amount sufficient to provide a RON increase of at least 2.

- In one preferred aspect the composition comprises (i) iron or an iron compound as a primary antiknock component (ii) an oxyhydrocarbyl compound as a secondary antiknock
20 component; and (iii) a sulphur passivating agent.

- In one preferred aspect the composition comprises (i) iron or an iron compound as a primary antiknock component (ii) an oxyhydrocarbyl compound as a secondary antiknock component; and (iii) a material capable of preventing and/or inhibiting valve seat
25 recession of an internal combustion engine.

- In one preferred aspect the composition comprises (i) iron or an iron compound as a primary antiknock component (ii) a nitrohydrocarbyl compound as a secondary antiknock component; and (iii) a sulphur passivating agent.

- 30 In one preferred aspect the composition comprises (i) iron or an iron compound as a primary antiknock component (ii) a nitrohydrocarbyl compound as a secondary antiknock component; and (iii) a material capable of preventing and/or inhibiting valve seat recession of an internal combustion engine.

- 35

In one preferred aspect the composition comprises (i) lead or a lead compound as a primary antiknock component (ii) an oxyhydrocarbyl compound as a secondary antiknock component; and (iii) a sulphur passivating agent.

- 5 In one preferred aspect the composition comprises (i) lead or a lead compound as a primary antiknock component (ii) an oxyhydrocarbyl compound as a secondary antiknock component; and (iii) a material capable of preventing and/or inhibiting valve seat recession of an internal combustion engine.

- 10 In one preferred aspect the composition comprises (i) lead or a lead compound as a primary antiknock component (ii) a nitrohydrocarbyl compound as a secondary antiknock component; and (iii) a sulphur passivating agent.

- 15 In one preferred aspect the composition comprises (i) lead or a lead compound as a primary antiknock component (ii) a nitrohydrocarbyl compound as a secondary antiknock component; and (iii) a material capable of preventing and/or inhibiting valve seat recession of an internal combustion engine.

- 20 In one preferred aspect the composition comprises (i) manganese or a manganese compound as a primary antiknock component (ii) an oxyhydrocarbyl compound as a secondary antiknock component; and (iii) a sulphur passivating agent.

- 25 In one preferred aspect the composition comprises (i) manganese or a manganese compound as a primary antiknock component (ii) an oxyhydrocarbyl compound as a secondary antiknock component; and (iii) a material capable of preventing and/or inhibiting valve seat recession of an internal combustion engine.

- 30 In one preferred aspect the composition comprises (i) manganese or a manganese compound as a primary antiknock component (ii) a nitrohydrocarbyl compound as a secondary antiknock component; and (iii) a sulphur passivating agent.

- 35 In one preferred aspect the composition comprises (i) manganese or a manganese compound as a primary antiknock component (ii) a nitrohydrocarbyl compound as a secondary antiknock component; and (iii) a material capable of preventing and/or inhibiting valve seat recession of an internal combustion engine.

In one preferred aspect the composition comprises (i) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium, as a primary antiknock component (ii) an oxyhydrocarbyl compound as a secondary antiknock component; and (iii) a sulphur passivating agent.

In one preferred aspect the composition comprises (i) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium, as a primary antiknock component (ii) an oxyhydrocarbyl compound as a secondary antiknock component; and (iii) a material capable of preventing and/or inhibiting valve seat recession of an internal combustion engine.

In one preferred aspect the composition comprises (i) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium, as a primary antiknock component (ii) a nitrohydrocarbyl compound as a secondary antiknock component; and (iii) a sulphur passivating agent.

In one preferred aspect the composition comprises (i) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium, as a primary antiknock component (ii) a nitrohydrocarbyl compound as a secondary antiknock component; and (iii) a material capable of preventing and/or inhibiting valve seat recession of an internal combustion engine.

In one preferred aspect the composition comprises at least two primary antiknock components selected from

- (a) iron or an iron compound;
- (b) lead or a lead compound;
- (c) manganese or manganese compound; and
- (d) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium;

In one preferred aspect the composition comprises at least three primary antiknock components selected from

- (a) iron or an iron compound;
- 5 (b) lead or a lead compound;
- (c) manganese or manganese compound; and
- (d) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium;

10

In one preferred aspect the composition comprises

- (a) iron or an iron compound;
- (b) lead or a lead compound;
- (c) manganese or manganese compound; and
- 15 (d) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium;

In one preferred aspect the composition comprises

- 20 (a) iron or an iron compound; and
- (b) lead or a lead compound.

In one preferred aspect the composition comprises

- (a) iron or an iron compound; and
- 25 (c) manganese or manganese compound.

In one preferred aspect the composition comprises

- (a) iron or an iron compound; and
- (d) a metal selected from rare earth metals, lithium, nickel, and thallium or a
- 30 compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium;

In one preferred aspect the composition comprises

- (b) lead or a lead compound; and
- 35 (c) manganese or manganese compound.

In one preferred aspect the composition comprises

(b) lead or a lead compound; and

5 (d) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium;

In one preferred aspect the composition comprises

(c) manganese or manganese compound; and

10 (d) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium;

In one preferred aspect the composition comprises

15 (a) iron or an iron compound;

(b) lead or a lead compound; and

(c) manganese or manganese compound.

In one preferred aspect the composition comprises

20 (a) iron or an iron compound;

(b) lead or a lead compound; and

(d) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium;

25

In one preferred aspect the composition comprises

(a) iron or an iron compound;

(c) manganese or manganese compound; and

30 (d) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium;

In one preferred aspect the composition comprises

(b) lead or a lead compound;

35 (c) manganese or manganese compound; and

(d) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel, and thallium;

5 In one preferred aspect the composition comprises

- (a) oxyhydrocarbyl compounds; and
- (b) nitrohydrocarbyl compounds

In one preferred aspect the composition comprises

- 10 (a) a sulphur passivating agent, and
- (b) a material capable of preventing and/or inhibiting valve seat recession of an internal combustion engine.

AUXILIARY COMPONENTS

15

The additive solution may optionally contain additional components beyond the three essential components. These auxiliary components include corrosion inhibitors, rust inhibitors, gum inhibitors, anti-oxidants, solvent oils, anti-static agents, dyes, anti-icing agents, ashless dispersants and detergents as a non-limiting list. Where any additional

20 component is employed, the use of detergents, especially poly-(butenyl)succinimide based detergents, is preferred.

FUEL

25 In one aspect there is provided a fuel composition comprising (A) a fuel additive composition comprising (i) at least one primary antiknock component selected from (a) iron or an iron compound; (b) lead or a lead compound; (c) manganese or manganese compound; and (d) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel, and

30 thallium; (ii) at least one secondary antiknock component selected from (a) oxyhydrocarbyl compounds; and (b) nitrohydrocarbyl compounds; (iii) a sulphur passivating agent; and (B) a fuel.

The term 'fuel' covers compositions containing a major amount of gasoline base fuel

35 suitable for use in spark-ignition engines. This includes hydrocarbon base fuels boiling in

the so-called gasoline boiling range of 30 to 230°C. These base fuels may comprise mixtures of saturated, olefinic and aromatic hydrocarbons. They can be derived from straight-run gasoline, synthetically produced aromatic hydrocarbon mixtures, thermally or catalytically cracked hydrocarbon feedstocks, hydrocracked petroleum fractions or catalytically reformed hydrocarbons. Motor gasolines are defined by ASTM 4814-03, 5 aviation gasolines typically have a narrower boiling range of 37 to 165°C. The gasoline may also contain various blending components designed to provide octane number, such as MTBE, TAME or ETBE as non-limiting examples. A proportion of the hydrocarbons may also be replaced for example by alcohols, ethers (as above), esters or ketones. 10 Generally the octane number of the gasoline will be greater than 65.

Preferably the fuel is gasoline.

In one aspect the fuel is an aviation gasoline. Aviation gasolines are defined by ASTM 15 910-3 and ASTM 6227-00 for Grade 82 Unleaded Aviation Gasoline. A common aviation gasoline grade is Grade 100LL. This generally contains an aviation alkylate base fuel and lead alkyl based antiknock compound. A conventional aviation gasoline would contain light alkylate, toluene, C4 and C5 paraffinic hydrocarbons and tetraethyl lead aviation Compound. Current formulations would be 75-92% light alkylate, 5-18% toluene, 20 3-20% C4to C5 paraffins and 0.56gPb/l TEL-B Compound. Alternatives to lead alkyls are being sought to enhance the antiknock quality of aviation gasolines

The fuel may further comprise performance-enhancing additives. A non-limiting list would include corrosion inhibitors, rust inhibitors, gum inhibitors, anti-oxidants, solvent 25 oils, anti-static agents, dyes, anti-icing agents, ashless dispersants and detergents.

The fuel additives according to the invention may be added as part of a package to the fuel prior to combustion. This may be done at any stage in the fuel supply chain (for example, at the refinery or distribution terminal) or may be added via a dosing device on- 30 board the vehicle, either to the fuel or even separately direct into the combustion chamber or inlet system. The fuel additives may be added to the fuel in the vehicle fuel tank by the user, a so-called 'aftermarket' treatment.

The invention further comprises an additive solution for addition to a fuel. Such an 35 additive might be dosed at any stage in the fuel supply chain prior to combustion of the

fuel. The fuel additives of the invention may be dosed to the fuel at any stage in the fuel supply chain. Preferably, each additive is added to the fuel close to the engine or combustion systems, within the fuel storage system for the engine at the refinery, distribution terminal or at any other stage in the fuel supply chain, including aftermarket
5 use.

How an additive solution is to be employed significantly influences the optimum formulation. For example, the additive may be added to the fuel at the refinery or at the distribution terminal. Here the components may be added together or separately,
10 providing an additional valuable flexibility in use. If added together, they may be dissolved in the minimum amount of fuel compatible solvent commensurate with the need to provide a pumpable solution and avoid crystallisation/separation of any of the components at low temperatures, e.g. about -30°C.

15 Where the additive combination is intended to be added as an 'aftermarket' treatment, the volume of solvent used will be such as to provide a non-viscous solution, suitable for use in a dispenser bottle or syringe pack. The concentration of components will be such that some convenient and easily recalled treat rate (e.g. about 1 cm³ per litre of fuel) is required. In any case the solvents to be used should be readily fuel soluble and
20 compatible, including with respect to boiling point range. In some aspects solvents to be used will have flash points in excess of 62°C for ease of storage. However solvents having a lower flash point e.g. xylene are envisaged and may be used in the present invention.

25 The invention will now be further described in further detail by way of example only.

EXAMPLES

SULPHUR EFFECT

30

Three fuels were tested with a range of concentrations of two anti-knock components. The relevant properties of the three fuels were as follows.

Property	Basefuel	PU50	PU50/ FCCS Blend
Density	0.73	0.73	0.73
FIA			
Saturates %	59	60	53
Olefins %	12	11	15
Aromatics %	29	29	32
Sulphur ppm	687	46	523
RON	94.5	94.5	94.5

The two anti-knock components tested were Fe (in the form of PLUTOcen, available from Octel Deutschland GmbH) and Mn. The data are shown below.

5

Fuel Sample	RON	Δ RON	MON	Δ MON
Base Fuel containing FCCS	95.3	--	84.7	--
+ 30 mg/kg PLUTOcen G (7 mg Fe/litre)	95.9	0.6	85.0	0.3
+ 45 mg/kg PLUTOcen G (10 mg Fe/litre)	96.1	0.8	85.1	0.4
+ 60 mg/kg PLUTOcen G (14 mg Fe/litre)	96.3	1.0	85.4	0.7
+ 9 mg Mn/litre	96.5	1.2	85.3	0.6
+ 18 mg Mn/litre	97.0	1.7	85.6	0.9

Fuel Sample	RON	Δ RON
PU50	95.3	--
+ 9 mg Fe/litre	96.5	1.2
+ 18 mg Fe/litre	96.8	1.5
+ 9 mg Mn/litre	96.6	1.3
+ 18 mg Mn/litre	97.1	1.8
80% v/v PU50 + 20% v/v FCCS	94.5	--
80% v/v PU50 + 20% v/v FCCS + 9mg Fe/litre	95.3	0.8
80% v/v PU50 + 20% v/v FCCS + 9 mg Mn/litre as MMT	95.8	1.3
80% v/v PU50 + 20% v/v FCCS + 18 mg Fe/litre	95.9	1.4
80% v/v PU50 + 20% v/v FCCS + 18 mg Mn/litre as MMT	96.4	1.9

PRESENT COMPOSITIONS

Fuel Sample	RON	Δ RON
80% v/v PU50 + 20% v/v FCCS	94.5	--
+ 0.1% v/v m-toluidine	94.8	0.3
+ 0.2% v/v m-toluidine	95.0	0.5
+ 0.3% v/v m-toluidine	95.1	0.6
+ 0.4% v/v m-toluidine	95.7	1.2
+ 0.5% v/v m-toluidine	95.5	1.0
+ 0.1% v/v o-toluidine	94.9	0.4
+ 0.2% v/v o-toluidine	95.0	0.5
+ 0.3% v/v o-toluidine	95.2	0.7
+ 0.4% v/v o-toluidine	95.5	1.0
+ 0.5% v/v o-toluidine	95.6	1.1
+ 0.1% v/v p-toluidine	94.7	0.2
+ 0.2% v/v p-toluidine	94.5	0.0
+ 0.3% v/v p-toluidine	94.6	0.1
+ 0.4% v/v p-toluidine	94.7	0.2
+ 0.5% v/v p-toluidine	94.7	0.2
+ 0.1% v/v N-Methylaniline	94.9	0.4
+ 0.2% v/v N-Methylaniline	95.1	0.6
+ 0.3% v/v N-Methylaniline	95.3	0.8
+ 0.4% v/v N-Methylaniline	95.7	1.2
+ 0.5% v/v N-Methylaniline	96.0	1.5
+ 0.05g Pb/litre	96.0	1.5
+ 0.10g Pb/litre	97.0	2.5
+ 0.15g Pb/litre	97.6	3.1
+ 9 mg/l Fe (4.5ppm K)	95.5	1.0
+ 18 mg/l Fe (4.5ppm K)	96.0	1.5
Fuel Sample	RON	Δ RON
80% v/v PU50 + 20% v/v FCCS	94.6	--
+0.05g Pb/litre	96.2	1.6
+0.05g Pb/litre + 9 mg Fe/litre	96.5	1.9
+0.05g Pb/litre + 0.2% v/v m-toluidine	96.5	1.9
+0.05g Pb/litre + 0.2% v/v o-toluidine	96.5	1.9
+0.05g Pb/litre + 0.2% v/v N-methylaniline	96.6	2.0
+18 mg Fe/litre	96.0	1.4
+18 mg Fe/litre + 0.2% v/v m-toluidine	96.0	1.4
+18 mg Fe/litre + 0.2% v/v o-toluidine	96.0	1.4
+18 mg Fe/litre + 0.2% v/v N-methylaniline	96.1	1.5
+14.5 mg Fe/litre	95.8	1.2
+14.5 mg Fe/litre + 0.2% v/v m-toluidine	96.0	1.4
+14.5 mg Fe/litre + 0.2% v/v o-toluidine	96.0	1.4
+14.5 mg Fe/litre + 0.2% v/v N-methylaniline	95.9	1.3

Fuel Sample	RON	Δ RON
Fuel Sample	RON	Δ RON
80/20 PU50 FCCS	94.6	--
+ 9 mg Fe/litre	95.3	0.7
+ 9 mg Fe/litre + 9 mg/kg Ca as Ca(HFOD) ₂	95.2	0.6
+ 9 mg Fe/litre + 4.5 mg/kg as Ca(HFOD) ₂	95.1	0.5
+ 9 mg Fe/litre + 18 mg/kg as Ca(HFOD) ₂	95.3	0.7
+ 9 mg Fe/litre + 4.5 mg/kg as Ca(HFOD) ₂	95.2	0.6
+ 9 mg Fe/litre + 9 mg/kg as Mg(TMHD) ₂	95.3	0.7
+ 9 mg Fe/litre + 4.5 mg/kg as Mg(TMHD) ₂	95.5	0.9
+ 9 mg Fe/litre + 18 mg/kg as Mg(TMHD) ₂	95.5	0.9
+ 9 mg Fe/litre + 4.5 mg/kg as Mg(TMHD) ₂	95.4	0.8
Fuel Sample	RON	Δ RON
80/20 PU50 FCCS	94.6	--
+ 18 mg Mn/litre as MMT	96.6	2.0
+ 7 mg Fe/litre	95.5	0.9
+ 7 mg Fe/litre + 0.2% v/v o-toluidine	95.7	1.1
+ 7 mg Fe/litre + 3 mg/kg Potassium	95.4	0.8
+ 7 mg Fe/litre + 3 mg/kg Potassium + 0.2% v/v o-toluidine	95.8	1.2
+ 10 mg Fe/litre	95.5	0.9
+ 10 mg Fe/litre + 0.2% v/v o-toluidine	95.9	1.3
+ 14 mg Fe/litre	95.7	1.1
+ 14 mg Fe/litre + 0.2% v/v o-toluidine	96.0	1.4

Fuel sample	RON	Δ RON	MON	Δ MON
PU50/FCCS Blend	95.3		83.7	
+0.3% v/v N-methyl aniline	96.2	0.9/1.2	84.3	0.6/0.4
+0.225% v/v N-methyl aniline	96.1	0.8/1.1	84.2	0.5/0.3
+12mg Fe/litre and 0.3% v/v N-methyl aniline	96.9	1.6/1.9	85.0	1.3/1.1
+9mg Fe/litre and 0.225% v/v N-methyl aniline	96.5	1.2/1.5	84.8	1.1/0.9
+12mg Fe/litre and 0.3% v/v N-methyl aniline(4.5ppmK)	96.7	1.4/1.7	84.9	1.2/1.0
+9mg Fe/litre and 0.225% v/v N-methyl	96.4	1.1/1.4	84.8	1.1/0.9

Fuel sample	RON	Δ RON	MON	Δ MON
aniline(3.4ppmK)				
+4.5ppm K	95.2	-0.1/0.2	83.8	1.1/0.9
+0.695% v/v xylene	95.3	0.0/0.3	83.8	1.1/0.9
+12mgFe/litre	96.0	0.7/1.0	84.5	0.8/0.6
+0.3% v/v N-methyl aniline (4.5ppm K)	95.8	0.5/0.8	84.4	0.7/0.5
+12mgFe/litre (4.5ppm K)	96.0	0.7/1.0	84.6	0.9/0.7
+12mgFe/litre and 0.3% v/v N-methyl aniline	96.4	1.1/1.4	85.0	1.3/1.1
+12mgFe/litre and 0.3% v/v N-methyl aniline (4.5ppm)	96.1	0.8/1.1	84.9	1.2/1.0
PU50/FCCS Blend	95.0		83.9	
FCC Gasoline	90.8		79.3	
+12mg Fe/litre and 0.3% v/v N-methyl aniline	93.0	2.2	80.1	0.8
+12mg Fe/litre and 0.3% v/v N-methyl aniline(4.5ppmK)	93.4	2.6	81.2	1.9
+12mg Mn/litre and 0.3% v/v N-methyl aniline(4.5ppmK)	93.7	2.9	80.8	1.5
+12mg Mn/litre and 0.3% v/v N-methyl aniline	93.8	3.0	80.1	0.8
+18mgMn/litre(4.5ppmK)	93.5	2.7	81.3	2.0
+18mgMn/litre	93.2	2.5	80.6	1.3
Reformate gasoline	95.7		85.9	
+12mg Fe/litre and 0.3% v/v N-methyl aniline	97.3	1.6	86.6	0.7
+12mg Fe/litre and 0.3% v/v N-methyl aniline(4.5ppmK)	97.6	1.9	87.0	1.1
+12mg Mn/litre and 0.3% v/v N-methyl aniline(4.5ppmK)	97.2	1.5	86.8	0.9
+12mgMn/litre and 0.3% v/v N-methyl aniline	97.2	1.5	86.8	0.9
+18mgMn/litre(4.5ppmK)	96.7	1.0	86.5	0.6
+18mgMn/litre	96.7	1.0	86.4	0.5

All publications mentioned in the above specification are herein incorporated by reference. Various modifications and variations of the described methods and system of the invention will be apparent to those skilled in the art without departing from the scope and spirit of the invention. Although the invention has been described in connection with specific preferred embodiments, it should be understood that the invention as claimed should not be unduly limited to such specific embodiments. Indeed, various modifications of the described modes for carrying out the invention which are obvious to those skilled in chemistry or related fields are intended to be within the scope of the following claims

CLAIMS

1. A fuel additive composition comprising
 - (i) at least one primary antiknock component selected from
 - 5 (a) iron or an iron compound;
 - (b) lead or a lead compound;
 - (c) manganese or manganese compound; and
 - (d) a metal selected from rare earth metals, lithium, nickel, and thallium or a compound comprising a metal selected from rare earth metals, lithium, nickel,
10 and thallium;
 - (ii) at least one secondary antiknock component selected from
 - (a) oxyhydrocarbyl compounds; and
 - (b) nitrohydrocarbyl compounds
 - (iii) at least one of
 - 15 (a) a sulphur passivating agent,
 - (b) a material capable of preventing and/or inhibiting valve seat recession of an internal combustion engine.
2. A fuel additive composition according to claim 1 wherein the primary antiknock
20 component is selected from iron or an iron compound.
3. A fuel additive composition according to claim 1 or 2 wherein the iron and/or iron compound is an iron compound.
- 25 4. A fuel additive composition according to any one of claims 1 to 3 wherein the iron compound is a ferrocene and/or a substituted ferrocene.
5. A fuel additive composition according to any one of claims 1 to 4 wherein the primary antiknock component is selected from lead or a lead compound.
30
6. A fuel additive composition according to any one of claims 1 to 5 wherein the lead and/or lead compound is a lead compound.
7. A fuel additive composition according to any one of claims 1 to 6 wherein the lead
35 compound is a tetraalkyl lead compound.

8. A fuel additive composition according to any one of claims 1 to 7 wherein the lead compound is tetraethyl lead
- 5 9. A fuel additive composition according to any one of claims 1 to 8 wherein the primary antiknock component is selected from manganese or a manganese compound.
10. A fuel additive composition according to any one of claims 1 to 9 wherein the manganese and/or manganese compound is a manganese compound.
- 10 11. A fuel additive composition according to any one of claims 1 to 10 wherein the manganese and/or manganese compound is cyclopentadienyl manganese tricarbonyl.
12. A fuel additive composition according to any one of claims 1 to 11 wherein the
15 manganese and/or manganese compound is methylcyclopentadienyl manganese tricarbonyl.
13. A fuel additive composition according to any one of claims 1 to 12 wherein the primary antiknock component is selected from rare earth metals and rare earth metal
20 compounds.
14. A fuel additive composition according to claim 13 wherein rare earth metal is cerium (Ce).
- 25 15. A fuel additive composition according to any one of claims 1 to 14 wherein the primary antiknock component is selected from lithium or lithium compounds.
16. A fuel additive composition according to any one of claims 1 to 15 wherein the lithium and/or lithium compound is a lithium compound.
- 30 17. A fuel additive composition according to any one of claims 1 to 15 wherein the lithium and/or lithium compound is selected from lithium salts of alkyl and dialkyl amino-alkyl phenols, lithium salt of 2-(di-iso-butylaminomethyl)-4-cresol, lithium salts of 2-dimethylaminomethyl-4-cresol, lithium salt of 2-(dimethylamino-methyl)-5-cresol, and
35 lithium salt of 2-(diethylaminomethyl)-4-cresol

18. A fuel additive composition according to any one of claims 1 to 17 wherein the primary antiknock component is selected from nickel or nickel compounds.
- 5 19. A fuel additive composition according to any one of claims 1 to 18 wherein the primary antiknock component is selected from thallium or thallium compounds.
20. A fuel additive composition according to any one of claims 1 to 19 wherein the at least one secondary antiknock component is an oxyhydrocarbyl compound.
- 10 21. A fuel additive composition according to any one of claims 1 to 20 wherein the at least one secondary antiknock component is a nitrohydrocarbyl compound.
22. A fuel additive composition according to any one of claims 1 to 21 wherein the at
15 least one secondary antiknock component is selected from toluidine, N-methylaniline, aliphatic alcohols, phenols; dihydroxy benzenes, trihydroxy benzenes, polyhydroxy benzenes, catechol, hydroquinone, carboxylic acids, esters, formates, acetates, propionates, benzoates, oxalates, malonates, succinates, carbonates, ethers, cyclic ethers; aliphatic, aldehydes, ketones, amines, aliphatic amines, polyamines; tertiary
20 amines, primary and secondary aromatic amines, 4-methoxy aniline, pyridine, naphthalene, fluorene, chrysene, pyrrole, pyrazole, triazole, tetrazole, pyrimidine, triazine, indazole, benzimidazole, benzotriazole, purine, quinoline, quinoxaline, anthraquinone, diphenyl amines, 4, 4' -dimethyldiphenylamine, aromatic diamines and polyamines; hydrazines; N,N'- diphenyl-N'- di-p-tolylhydrazine, N-nitrosamines; N-
25 nitroso-4-methyldiphenylamine, diaromatic N-nitrosoamines, carbazole, phenoxazine, bridged diphenylamine molecules, benzohydroxamic acid, maleimide, phthalimide, 1,2,3,4-tetrahydroquinoline, oxazoles, thiazoles, furans, benzofurans, azoles, azines and derivatives thereof.
- 30 23. A fuel additive composition according to any one of claims 1 to 22 wherein the at least one secondary antiknock component is selected from toluidine and N-methylaniline.
24. A fuel additive composition according to any one of claims 1 to 23 wherein the sulphur passivating manganese and/or manganese compound is a manganese
35 compound.

25. A fuel additive composition according to any one of claims 1 to 24 wherein the sulphur passivating manganese and/or manganese compound is cyclopentadienyl manganese tricarbonyl.
- 5
26. A fuel additive composition according to any one of claims 1 to 25 wherein the sulphur passivating manganese and/or manganese compound is methylcyclopentadienyl manganese tricarbonyl.
- 10
27. A fuel additive composition according to any one of claims 1 to 26 wherein the s block metal or the s block metal of the s block compound is selected from magnesium and calcium.
28. A fuel additive composition according to any one of claims 1 to 27 wherein the
- 15 sulphur passivating compound is an acetate compound.
29. A fuel additive composition according to any one of claims 1 to 28 wherein the sulphur passivating compound is an alkyl acetate
- 20
30. A fuel additive composition according to any one of claims 1 to 29 wherein the sulphur passivating compound is selected from 2,4-pentane dione and t-butyl acetate.
31. A fuel additive composition according to any one of claims 1 to 30 wherein the material capable of preventing and/or inhibiting valve seat recession of an internal
- 25 combustion engine is selected from phosphorus, phosphorus compounds, potassium and potassium compounds.
32. A fuel additive composition according to any one of claims 1 to 31 wherein the material capable of preventing and/or inhibiting valve seat recession of an internal
- 30 combustion engine is selected from phosphorus compounds and potassium compounds.
33. A fuel additive composition according to any one of claims 1 to 32 wherein the at least one primary antiknock component is iron or an iron compound; and manganese or manganese compound.

34. A fuel additive composition according to any one of claims 1 to 33 wherein the at least one primary antiknock component is iron or an iron compound; and manganese or manganese compound and the composition comprises a material capable of preventing and/or inhibiting valve seat recession of an internal combustion engine.

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35. A fuel composition comprising

(A) a fuel additive composition as defined in any one of claims 1 to 34; and

(B) a fuel.

10 36. A fuel composition according to claim 35 wherein the fuel is gasoline.

37. Use of a composition for the prevention and/or inhibition of combustion knock in an internal combustion engine, wherein the composition is a fuel additive composition as defined in any one of claims 1 to 34.

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38. Use of a composition for the prevention and/or inhibition of spark plug fouling in an internal combustion engine, wherein the composition is a fuel additive composition as defined in any one of claims 1 to 34.

20 39. Use of a composition for the prevention and/or inhibition of catalyst poisoning in an internal combustion engine, wherein the composition is a fuel additive composition as defined in any one of claims 1 to 34.

40. Use of a composition for increasing the octane number of a fuel, wherein the
25 composition is a fuel additive composition as defined in any one of claims 1 to 34.

41. Use according to claim 39 wherein the fuel is gasoline.

42. A process for at least one of

30 (I) the prevention and/or inhibition of combustion knock in an internal combustion engine,

(II) the prevention and/or inhibition of spark plug fouling in an internal combustion engine,

(III) the prevention and/or inhibition of catalyst poisoning in an internal combustion
35 engine,

(IV) increasing the octane number of a fuel,
wherein the process comprises contacting a fuel with a fuel additive composition as defined in any one of claims 1 to 34, prior to combustion of the fuel.

5 43. A fuel additive as substantially hereinbefore described with reference to any one of the Examples.

44. A fuel composition as substantially hereinbefore described with reference to any one of the Examples.

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45. Use as substantially hereinbefore described with reference to any one of the Examples.

15 46. A process as substantially hereinbefore described with reference to any one of the Examples.