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(54) Fuel additives comprising a colloidal metal compound.

(57) An additive composition comprises at least one colloidal metal compound or metallic species and a stabilising component, wherein the stabilising component comprises the product obtainable by the condensation reaction between:

(i) at least one aldehyde or ketone or reactive equivalent thereof, and

(ii) at least one compound comprising one or more aromatic moieties bearing at least one hydroxyl group and at least one further substituent chosen from a hydrocarbyl group, -COOR^1 or COR^1, wherein R^1 represents hydrogen or a hydrocarbyl group.

The composition may further include at least one lubricity enhancer.

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Description

[0001] This invention relates to additive compositions and fuel compositions containing colloidal species and to the use of stabilising components to stabilise such compositions.

[0002] Additive and fuel compositions may contain metal compounds and/or metallic species. As is known in the art, such species can be effective as catalysts to aid the regeneration of diesel particulate filters, as combustion improvers to reduce the soot ignition temperature. The species may be added to a base fuel or stored in a separate on-board tank to be dosed into an engine when required. Colloidal materials are preferred, as the species are required to remain in suspension, either in a carrier liquid or in the fuel. When a separate tank and dosing system is used, the metallic species may be required to remain in stable suspension for long periods, for example, up to several years if the tank is fitted to a vehicle. Even when added to a base fuel, although the species do not need to remain in stable suspension for such long periods, problems can arise, particularly during fuel storage.

[0003] It has been observed that colloidal metal compounds and metallic species are often unstable in additive and fuel compositions, a problem which is exacerbated at both low and high ambient temperatures. Compositions become hazy or cloudy after short periods and precipitates are formed as phase separation occurs. It has also been observed that the presence of some lubricity enhancers and also fatty acid methyl esters (FAME) further de-stabilises the colloidal suspensions.

[0004] The present invention addresses this problem by using a stabilising component to stabilise colloidal metal compounds and metallic species in additive and fuel compositions.

[0005] Accordingly, in a first aspect, there is provided an additive composition comprising at least one colloidal metal compound or metallic species and a stabilising component, wherein the stabilising component comprises the product obtainable by the condensation reaction between:

(i) at least one aldehyde or ketone or reactive equivalent thereof, and

(ii) at least one compound comprising one or more aromatic moieties bearing at least one hydroxyl group and at least one further substituent chosen from a hydrocarbyl group, -COOR^1 or COR^1, wherein R^1 represents hydrogen or a hydrocarbyl group.

[0006] In an embodiment, the composition further comprises at least one lubricity enhancer. This may for example, comprise a carboxylic acid or ester thereof.

[0007] Preferably, the additive composition is substantially free from sulphur-containing compounds. Preferably, the additive composition is substantially free from phosphorus-containing compounds. More preferably, the additive composition is substantially free from both sulphur-containing compounds and phosphorus-containing compounds.

[0008] In a second aspect, there is provided a fuel composition comprising a major amount of a fuel and a minor amount of an additive composition as defined in the first aspect.

[0009] Preferably, the fuel comprises a middle distillate fuel oil.

[0010] In a third aspect, there is provided the use of a stabilising component as defined with reference to the first aspect to stabilise an additive composition comprising a colloidal metal compound or metallic species.

[0011] In a fourth aspect, there is provided the use of a stabilising component as defined with reference to the first aspect to stabilise a fuel composition comprising a colloidal metal compound or metallic species.

[0012] In a fifth aspect, there is provided a method for improving the stability of a fuel additive composition or of a fuel composition, wherein the fuel additive composition or fuel composition comprises a colloidal metal compound or metallic species and optionally, at least one lubricity enhancer; the method comprising the addition of a stabilising component as defined with reference to the first aspect.

[0013] The addition of stabilising components according to the invention provides additive compositions and fuel compositions containing colloidal species with excellent stability across a broad temperature range. Stability in storage and use, particularly at extremes of temperature, especially at high temperatures, and also in the presence of de-stabilising lubricity enhancers is improved. The onset of haze appearance and cloudiness and also of phase separation is retarded.

Stabilising component

[0014] Reactant (i) comprises one or more aldehydes or ketones or reactive equivalents thereof. By "reactive equivalent" is meant a material which generates an aldehyde under the conditions of the condensation reaction or a material which undergoes the required condensation reaction to produce moieties equivalent to those produced by an aldehyde. Typical reactive equivalents include oligomers or polymers of the aldehyde, acetals, or aldehyde solutions.

[0015] The aldehyde may be a mono- or di- aldehyde and may contain further functional groups, such as -COOH groups capable of post-reaction in the product. The aldehyde preferably contains 1-6 carbon atoms, more preferably

1-4 carbon atoms. The aldehyde is preferably aliphatic, such as an alkyl or alkenyl. The aldehyde (i) may comprise a mixture of different aldehydes.

[0016] Preferred reactants (i) are formaldehyde, acetaldehyde, propionaldehyde, the butyraldehydes and substituted analogues or reactive equivalents thereof and glyoxylic acid (or pyruvic acid). Formaldehyde is particularly preferred.

[0017] The or each aromatic moiety may consist exclusively of carbon and hydrogen or may comprise carbon, hydrogen and one or more hetero atoms. It will be understood that, to be capable of undergoing the condensation reaction with reactant (i), reactant (ii) comprises at least one hydrogen capable of being replaced during the reaction so as to allow formation of a carbon-carbon bond between the aldehyde (i) and the reactant (ii). This hydrogen is preferably bonded to at least one aromatic moiety in the reactant (ii).

[0018] Preferred aromatic moieties are selected from the following:

(a) A single ring nucleus such as a benzene ring, and

(b) A multi-ring aromatic nucleus. Such multi-ring nuclei can be of the fused type (e.g. naphthalene, anthracene, indolyl etc.) or they can be of the bridged type, wherein individual aromatic rings are linked through bridging links to each other. Such bridging linkages can be chosen from the group consisting of carbon-carbon single bonds, ether linkages, methylene linkages, lower alkylene linkages, di(lower alkyl) methylene linkages, lower alkylene ether linkages, and mixtures of such bridging linkages.

[0019] When linkages are present in the aromatic nuclei, there are usually no more than five such linkages per nucleus; generally however the aromatic nuclei are single ring nuclei or fused ring nuclei of up to four rings.

[0020] Most preferably, the aromatic moiety is a benzene or substituted benzene nucleus.

[0021] The term, "hydrocarbyl" as used in this specification refers to a group having a carbon atom directly attached to the rest of the molecule and having a hydrocarbon or predominantly hydrocarbon character. Examples include hydrocarbon groups, including aliphatic (e.g. alkyl or alkenyl), alicyclic (e.g. cycloalkyl or cycloalkenyl), aromatic, and alicyclic substituted aromatic, and aromatic substituted aliphatic and alicyclic groups. Aliphatic groups are advantageously saturated and can be linear or branched, preferably branched. These groups may contain non-hydrocarbon substituents provided their presence does not alter the predominantly hydrocarbon character of the group. Examples include keto, hydroxy, nitro, cyano, alkoxy and acyl.

[0022] Examples of substituted hydrocarbyl groups include 2-hydroxyethyl, 3-hydroxypropyl, 4-hydroxybutyl, 2-keto-propyl, ethoxyethyl, and propoxypropyl. The groups may also or alternatively contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms include, for example, nitrogen, and, preferably, oxygen. Preferably, the hydrocarbyl groups are aliphatic groups, such as alkenyl or alkyl group, which may be straight chain or preferably branched.

[0023] Preferably, the hydrocarbyl groups contain 4 - 40 carbon atoms, more preferably 6 -24 carbon atoms, such as 6 -18 carbon atoms.

[0024] Preferably, the further substituent on the one or more aromatic moieties is in the para-position relative to the hydroxyl group. Meta-substituted species are also envisaged although less preferred. Species with more than one further substituent are also included. In such species, the substituents may be the same or different.

[0025] Synthetic methods for preparing compounds suitable as reactant (ii) are known in the art. For example, they may be formed by the Friedel-Crafts reaction, in the presence of a suitable catalyst.

[0026] The subsequent condensation reaction of (ii) with (i) is generally conducted in the temperature range of about 30° to about 200°C, preferably about 80°C to about 150°C. The reaction is generally accompanied by the production of water which is drawn from the reaction mixture, thus driving the reaction to completion. This can be accomplished by conventional techniques such as azeotropic distillation, vacuum distillation and so forth.

[0027] The times for the reaction and the intermediates formed thereby generally takes place in a period of time which is not critical and ranges from about 0.25 to about 48 hours, usually from about 1-8 hours.

[0028] A substantially inert, normally liquid organic solvent/diluent is often used in this reaction to lower viscosity but its use is not absolutely necessary. Often excesses of one or more reactants can be used for this purpose. Useful organic solvent/diluents include lower alkanols, such as butyl and amyl alcohols; aromatic hydrocarbons such as benzene, toluene, xylene and higher alkyl benzenes; aliphatic hydrocarbons such as decane, dodecane; naphthenes and alkyl naphthenes; kerosene; mineral oil; etc. and mixtures of two or more of any such conventional solvent/diluents. As will be apparent, a "substantially inert" solvent/diluent is one which does not react with the reactants or products in any significant amount and, preferably, not at all.

[0029] The reaction of aldehyde (i) with (ii) is usually catalyzed by a base or an acid; preferably with an acidic catalyst such as an inorganic acid for example, hydrochloric acid or sulphuric acid, or an organic acid such as p-toluenesulphonic acid. Suitable basic catalysts include alkali metal hydroxides and tetramethyl ammonium hydroxide. Up to one mole of catalyst for each mole of aldehyde present can be used, normally about 0.1 - 5 mole % of catalyst per mole of (ii) is used.

[0030] It is usually preferable to neutralize a basic catalyst with a low molecular weight organic or inorganic acid before proceeding further. However, such neutralization is not necessary. Useful acids for accomplishing such neutralizations include the lower alkanoic acids, such as formic acid and acetic acid, and inorganic acids such as sulfuric, hydrochloric, phosphoric, nitric acid and the like.

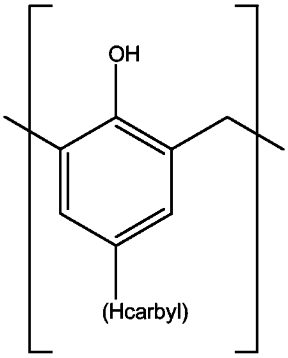
[0031] It is believed that the compositions of this invention contain bridges derived from the organic residue of the aldehyde linking the organic residues of the aromatic compound. Thus, when (i) is formaldehyde, methylene bridges are formed. The invention, however, is in no way intended to be limited by reference to such bridges. The formation of bridges may lead to linear or cyclic macromolecules containing units of (ii).

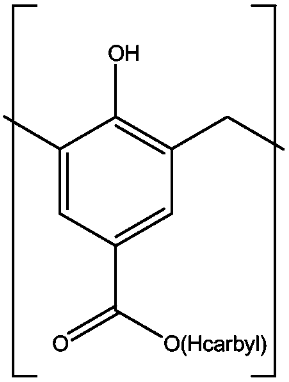
[0032] An example of the condensation product was prepared by heating a stirred mixture of 40g para-substituted, branched-nonylphenol, 5.75g of 95% paraformaldehyde and 0.1g p-toluene sulphonic acid monohydrate in 50 ml xylene to 80-85°C for two hours, followed by reflux at 150-155°C for six hours, the water of reaction being continuously removed via a Dean and Stark receiver. The product had an Mn of 2050 and an Mw of 2940.

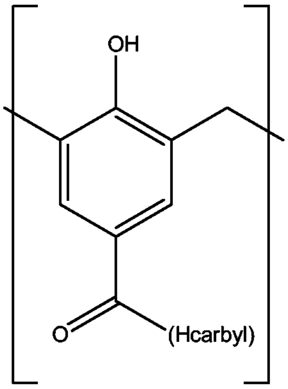
[0033] Typically the product of the condensation reaction has a number-average molecular weight (Mn), as measured by GPC against polystyrene standards, in the range of 500 to 10,000, preferably 500 to 5,000, more preferably 500 to 2,500. The molecular weight distribution (Mw/Mn - wherein both Mn and Mw are measured by GPC) is advantageously in the range of 1 to 2, more preferably 1 to 1.5, such as 1.3 to 1.4.

[0034] Preferably, the product is formed from a reactant (ii) which comprises at least one aliphatic hydrocarbyl-substituted phenol, such as branched chain C_9 or C_{12} alkyl phenol.

[0035] In a particularly preferred embodiment, the stabilising component comprises an alkyl-phenol formaldehyde condensate, such as nonyl-phenol formaldehyde condensate or a hydroxybenzoate formaldehyde condensate, such as that based on the isodecyl ester or a 2-ethylhexyl/n-octyl mixed ester. Representative are materials based on the repeat unit shown in the structures below.







where (Hcarbyl) represents a hydrocarbyl group as defined hereinabove.

Colloidal metal compound or metallic species

[0036] Typically, the colloidal metal compound or metallic species will be in the form of a nanoparticulate. The term 'nanoparticulate' refers to particles whose dimensions are conveniently expressed in nanometres (1 nm = 10^{-9} m). Such particles are usually defined by way of a particle size distribution using d_m notation, where m refers to the percentage of a sample of particles whose dimensions are less than or equal to the stated size. For example d_{90} = 10 nm corresponds to a sample of particles, 90% of which have dimension less than or equal to 10 nm. Such particle sizes and distributions may be determined using transmission electron microscopy, or by other sizing techniques such as light scattering.

[0037] In the present invention, the colloidal species preferably have a d_{90} value of less than 50 nm, more preferably less than 20 nm, even more preferably less than 10 nm, for example less than 5 nm.

[0038] Many types of metal compound and metallic species are suitable for use in the present invention. These may comprise a bound surface layer of a surface active agent. Examples of surface active agents include fatty acids and branched-chain fatty acids or derivatives such as isostearic acid or neodecanoic acid. Some examples of suitable species are those described in EP 0261002, EP 0575189, US 5,449,387 and US 6,136,048.

[0039] Preferably, the colloidal species is a metal oxide species. Particularly preferred are iron oxides, cerium oxide, doped iron oxides and doped cerium oxide. A doped species is one where an amount of the metal of the metal oxide is replaced by one or more further metals. A preferred example is cerium-doped iron oxide, where some of the iron is replaced by cerium. An alternative preferred example is iron-doped cerium oxide. Generally in a doped species, the dopant will be in the minority, for example a cerium-doped iron oxide may contain from 1% or less up to 30% or more by weight of cerium. However, it is also intended that the definition of doped species includes those species where no metal is in the majority.

[0040] More generally, oxides of metals such as the rare earth metals, the transition metals (Groups IIA to IIB of the Periodic Table) and oxides of elements in groups IIIB and IVB of the Periodic Table may be used, both singly or as doped species. In addition to cerium and iron, preferred metals also include manganese, calcium and magnesium.

[0041] As an alternative to metal oxides, other compounds of the metals mentioned above may be used. In particular, metal hydroxides and metal carbonates may be used. As before, these may be compounds of single elements or doped species.

[0042] As a further alternative to metal oxide species, elemental species of the elements mentioned above may be used. As before, these may be single elements or doped species. In this context, a doped species may be more correctly described as an alloy or intermetallic species.

[0043] The present invention also contemplates the use of more than one type of colloidal species. For example, two or more metal oxide species may be used, as may two or more elemental species, two hydroxides, two carbonates, or any mixture thereof.

[0044] Methods for the preparation of the colloidal species and the range of suitable materials will be known to those skilled in the art.

Lubricity enhancer

[0045] Suitable lubricity enhancers include monohydric or polyhydric alcohol esters of C_2-C_{50} carboxylic acids such as glycerol monooleate, esters of polybasic acids with C_1-C_5 monohydric alcohols, esters of dimerized carboxylic acids, reaction products of polycarboxylic acids and epoxides such as 1,2-epoxyethane and 1,2-epoxypropane and lubricity additives derived from fatty acids such as vegetable oil fatty acid methyl esters, as well as fatty acid amides of monoethanolamine and diethanolamine.

[0046] Advantageously the carboxylic acid maybe a polycarboxylic acid, preferably a dicarboxylic acid, preferably having between 9 and 42 carbon atoms, more especially between 12 and 42 carbon atoms, between the carbonyl groups, the alcohol advantageously having from 2 to 8 carbon atoms and from 2 to 6 hydroxy groups.

[0047] Advantageously, the ester has a molecular weight of at most 950, preferably of at most 800. The dicarboxylic acid may be saturated or unsaturated; advantageously it is an optionally hydrogenated "dimer" acid, preferably a dimer of oleic or, especially linoleic acid, or a mixture thereof. The alcohol is advantageously a glycol, more advantageously an alkane or oxaalkane glycol, preferably ethylene glycol. The ester may be a partial ester of the polyhydric alcohol and may contain a free hydroxy group or groups; however, advantageously any acid groups not esterified by the glycol are capped by a monohydric alcohol, for example, methanol. It is within the scope of the invention to use two or more lubricity enhancers.

[0048] Another preferred lubricity enhancer is a mixture of esters comprising:

(d) an ester of an unsaturated monocarboxylic acid and a polyhydric alcohol, and
(e) an ester of an unsaturated monocarboxylic acid and a polyhydric alcohol having at least three hydroxy groups,

the esters (d) and (e) being different.

[0049] The term 'polyhydric alcohol' is used herein to describe a compound having more than one hydroxy-group. It is preferred that (d) is the ester of a polyhydric alcohol having at least three hydroxy groups.

[0050] Examples of polyhydric alcohols having at least three hydroxy groups are those having 3 to 10, preferably 3 to 6, more preferably 3 to 4 hydroxy groups and having 2 to 90, preferably 2 to 30, more preferably 2 to 12 and most preferably 3 to 4 carbon atoms in the molecule. Such alcohols may be aliphatic, saturated or unsaturated, and straight chain or branched, or cyclic derivatives thereof.

[0051] Advantageously, both (d) and (e) are esters of trihydric alcohols, especially glycerol or trimethylol propane. Other suitable polyhydric alcohols include pentaerythritol, sorbitol, mannitol, inositol, glucose and fructose.

[0052] The unsaturated monocarboxylic acids from which the esters are derived may have an alkenyl, cyclo alkenyl or aromatic hydrocarbyl group attached to the carboxylic acid group. The hydrocarbyl group may be interrupted by one or more hetero atoms such as O or N.

[0053] It is preferred that (d) and (e) are both esters of alkenyl monocarboxylic acids, the alkenyl groups preferably having 10 to 36, for example 10 to 22, more preferably 18-22, especially 18 to 20 carbon atoms. The alkenyl group may be mono- or poly-unsaturated. It is particularly preferred that (d) is an ester of a mono-unsaturated alkenyl monocarboxylic acid, and that (e) is an ester of a poly-unsaturated alkenyl monocarboxylic acid. The poly-unsaturated acid is preferably di- or tri- unsaturated. Such acids may be derived from natural materials, for example vegetable or animal extracts. Examples of naturally derived acids include tall oil fatty acid with differing levels of rosin acid, and acids obtainable from rapeseed oil, coriander oil, soyabean oil, cottonseed oil, sunflower oil, castor oil, olive oil, peanut oil, maize oil, almond oil, palm kernel oil, coconut oil, mustard seed oil, beef tallow, hoof oil and fish oils. Recycled oils may also be used.

[0054] Especially-preferred mono-unsaturated acids are oleic and elaidic acid. Especially preferred poly-unsaturated acids are linoleic and linolenic acid.

[0055] The esters may be partial or complete esters, i.e. some or all of the hydroxy groups of each polyhydric alcohol may be esterified. It is preferred that at least one of (d) or (e) is a partial ester, particularly a monoester. Especially good performance is obtained where (d) and (e) are both monoesters.

[0056] The esters may be prepared by methods well known in the art, for example by condensation reactions. If desired, the alcohols may be reacted with acid derivatives such as anhydrides or acyl chlorides in order to facilitate the reaction and improve yields.

[0057] The esters (d) and (e) may be separately prepared and then mixed together, or may be prepared together from a mixture of starting materials. In particular, commercially-available mixtures of suitable acids may be reacted with a selected alcohol such as glycerol to form a mixed ester product. Particularly-preferred commercial acid mixtures are those comprising oleic and linoleic acids. In such mixtures, minor proportions of other acids, or acid polymerisation products, may be present but these should not exceed 15%, more preferably not more than 10%, and most preferably not more than 5% by weight of the total acid mixture.

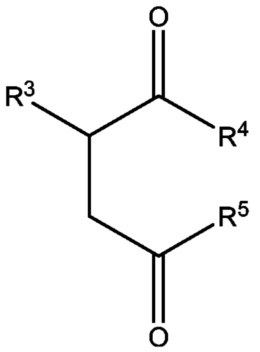
[0058] Similarly, mixtures of esters may be prepared by reacting a single acid with a mixture of alcohols.

[0059] A highly-preferred ester mixture is that obtained by reacting a mixture of oleic and linoleic acids with glycerol, the mixture comprising predominantly (d) glycerol monooleate and (e) glycerol monolinoleate, preferably in approximately equal proportions by weight.

[0060] Further examples are lubricity enhancers prepared by combining the aforesaid esters of C_2-C_{50} carboxylic acids with an ashless dispersant comprising an acylated nitrogen compound having a hydrocarbyl substituent of at least 10 carbon atoms made by reacting an acylating agent with an amino compound, such as the reaction products of polyisobutenyl (C_{80}-$C5_{00}$) succinic anhydride with ethylene polyamines having 3 to 7 amino nitrogen atoms.

[0061] As an alternative to the above described esters, or in combination therewith, the lubricity enhancer may comprise one or more carboxylic acids of the types disclosed in relation to the ester lubricity enhancers. Such acids may be mono- or polycarboxylic, saturated or unsaturated, straight or branched chain and may be generalised by the formula $R^{11}(COOH)_x$ where x is 1-4 and R^{11} is a C_2 to C_{50} hydrocarbyl. Examples are capric, lauric, myristic, palmitic, oleic, elaidic, palmitoleic, petaoselic, ricinoleic, linoleic, linolenic, eicosanic, tall oil fatty, rape seed oil, sunflower oil and dehydrated castor oil fatty acids, and rosin acids and isomers and mixtures thereof. The polycarboxylic acid may be a dimer acid such as that formed by dimerization of unsaturated fatty acids such as linoleic or oleic acid

[0062] Another example of lubricity enhancer chemistry are compounds of the following formula, described in WO 97/45507 and WO 02/02720:



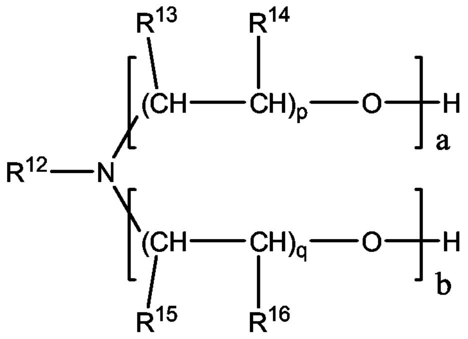
Where R^3 is a C_{10-32} alkenyl group and R^4 and R^5 are $(-OCH_2CH_2)_nOH$, $(-OCH_2CHCH_3)_nOH$, or $-OCH_2CHOHCH_2OH$ in which n = 1-10.

[0063] Other lubricity additives are combinations of the aforesaid esters with ethylene-unsaturated ester copolymers having, in addition to units derived from ethylene, units of the formula

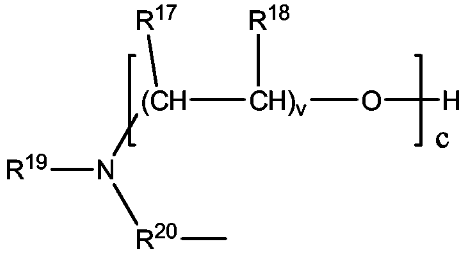
$$-CR^6R^7-CHR^8-$$

wherein R^6 represents hydrogen or methyl; R^7 represents $COOR^9$, wherein R^9 represents an alkyl group having from 1 to 9 carbon atoms which is straight chain or, if it contains 2 or more carbon atoms, branched, or R^7 represents $OOCR^{10}$, wherein R^{10} represents R^9 or H; and R^8 represents H or $COOR^9$. Examples are ethylene-vinyl acetate and ethylene-vinyl propionate and other copolymers where there is present 5-40% of the vinyl ester

Other lubricity enhancers are hydroxy amines of the formula:



where R^{12} is an alkenyl radical having one or more double bonds or an alkyl radical and containing from 4 to 50 carbon atoms, or a radical of the formula:



where each of R^{13}, R^{14}, R^{15}, R^{16}, R^{17} and R^{18} is independently hydrogen or a lower alkyl radical; R^{19} is an alkenyl radical having one or more double bonds or an alkyl radical and containing from 4 to 50 carbon atoms; R^{20} is an alkylene radical containing from 2 to 35, e.g. 2 to 6, carbon atoms; each of p, q and v is an integer between 1 and 4; and each of a, b and c may be 0, providing that at least one of a, b or c is an integer between 1 and 75.

[0064] Other lubricity additives are ester, amine and amine salt derivatives of salicylic acid and alkylated salicylic acids.

[0065] Some lubricity enhancers are described for example, in EP 0807 676, WO94/17160 and WO99/15607.

Fuel

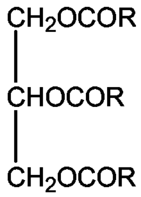
[0066] Preferably, the fuel comprises a fuel oil.

[0067] The fuel oil may be a hydrocarbon fuel such as a petroleum-based fuel oil for example kerosene or distillate fuel oil, suitably a middle distillate fuel oil, i.e. a fuel oil obtained in refining crude oil as the fraction between the lighter kerosene and jet fuels fraction and the heavier fuel oil fraction. Such distillate fuel oils generally boil within the range of about 100°C to about 500°C, e.g. 150° to about 400°C, for example, those having a relatively high Final Boiling Point of above 360°C (by ASTM-D86). Middle distillates contain a spread of hydrocarbons boiling over a temperature range. They are also characterised by pour, cloud and CFPP points, as well as their initial boiling point (IBP) and final boiling point (FBP). The fuel oil can comprise atmospheric distillate or vacuum distillate, or cracked gas oil or a blend in any proportion of straight run and thermally and/or catalytically cracked distillates. The most common petroleum distillate fuels are kerosene, jet fuels, diesel fuels, heating oils and heavy fuel oils, diesel fuels and heating oils being preferred. The diesel fuel or heating oil may be a straight atmospheric distillate, or may contain minor amounts, e.g. up to 35 wt %, of vacuum gas oil or cracked gas oils or both.

[0068] Heating oils may be made of a blend of virgin distillate, e.g. gas oil, naphtha, etc. and cracked distillates, e.g. catalytic cycle stock. A representative specification for a diesel fuel includes a minimum flash point of 38°C and a 90% distillation point between 282 and 380°C (see ASTM Designations D-396 and D-975).

[0069] Also, the fuel oil may be of animal or vegetable oil origin (i.e. a 'biofuel'), or a mineral oil as described above in combination with one or more biofuels. Biofuels, being fuels from animal or vegetable sources, are obtained from a renewable source. Within this specification, the term "biofuel" refers to a vegetable or animal oil or both or a derivative thereof. Certain derivatives of vegetable oil, for example of rapeseed oil, e.g. those obtained by saponification and re-esterification with a monohydric alcohol, may be used as a substitute for diesel fuel.

[0070] Vegetable oils are mainly triglycerides of monocarboxylic acids, e.g. acids containing 10-25 carbon atoms and have the following formula:



$$\begin{array}{l} \mathrm{CH_2OCOR} \\ | \\ \mathrm{CHOCOR} \\ | \\ \mathrm{CH_2OCOR} \end{array}$$

where R is an aliphatic radical of 10-25 carbon atoms which may be saturated or unsaturated.

[0071] Generally, such oils contain glycerides of a number of acids, the number and kind varying with the source vegetable of the oil.

[0072] Examples of oils are rapeseed oil, coriander oil, soyabean oil, cottonseed oil, sunflower oil, castor oil, olive oil, peanut oil, maize oil, almond oil, palm kernel oil, coconut oil, mustard seed oil, beef tallow and fish oils. Rapeseed oil, which is a mixture of fatty acids partially esterified with glycerol, is preferred as it is available in large quantities and can be obtained in a simple way by pressing from rapeseed.

[0073] Examples of derivatives thereof are alkyl esters, such as methyl esters, of fatty acids of the vegetable or animal oils. Such esters can be made by transesterification.

[0074] As lower alkyl esters of fatty acids, consideration may be given to the following, for example as commercial mixtures: the ethyl, propyl, butyl and especially methyl esters of fatty acids with 12 to 22 carbon atoms, for example of lauric acid, myristic acid, margaric acid, palmitic acid, palmitoleic acid, stearic acid, oleic acid, elaidic acid, petroselic acid, ricinoleic acid, elaeostearic acid, linoleic acid, linolenic acid, eicosanoic acid, gadoleic acid, docosanoic acid or erucic acid, which have an iodine number from 50 to 150, especially 90 to 125. Mixtures with particularly advantageous properties are those which contain mainly, i.e. to at least 50 wt % methyl esters of fatty acids with 16 to 22 carbon atoms and 1, 2 or 3 double bonds. The preferred lower alkyl esters of fatty acids are the methyl esters of oleic acid, linoleic acid, linolenic acid and erucic acid.

[0075] Commercial mixtures of the stated kind are obtained for example by cleavage and esterification of natural fats and oils by their transesterification with lower aliphatic alcohols. For production of lower alkyl esters of fatty acids it is advantageous to start from fats and oils with high iodine number, such as, for example, sunflower oil, rapeseed oil, coriander oil, castor oil, soyabean oil, cottonseed oil, peanut oil or beef tallow. Lower alkyl esters of fatty acids based on a new variety of rapeseed oil, the fatty acid component of which is derived to more than 80 wt % from unsaturated fatty acids with 18 carbon atoms, are preferred.

[0076] Other examples of fuel oils include jet-fuels; Fischer-Tropsch fuels; and diesel/alcohol or diesel/water emulsions or solutions. Fischer-Tropsch fuels, also known as FT fuels, include those described as gas-to-liquid fuels and coal conversion fuels. To make such fuels, syngas ($CO + H_2$) is first generated and then converted to normal paraffins by a Fischer-Tropsch process. The normal paraffins may then be modified by processes such as catalytic cracking/reforming or isomerisation, hydrocracking and hydroisomerisation to yield a variety of hydrocarbons such as isoparaffins, cyclo-paraffins and aromatic compounds. The resulting FT fuel can be used as such or in combination with other fuel components and fuel types such as those mentioned in this specification. WO-A- 0104239; WO-A- 0015740; WO-A-0151593; WO-A- 9734969; and WO-155282 describe examples of diesel/water emulsions. WO-A- 0031216; WO-A- 9817745; and WO-A- 024 8294 describe examples of diesel-ethanol emulsions/mixtures.

[0077] Preferably, the fuel oil has a sulphur content of at most 0.2% by weight, especially of at most 0.05% by weight. Fuels with even lower levels of sulphur are also suitable such as, fuels with less than 50ppm sulphur by weight, preferably less than 20 ppm, for example 10ppm or less.

Carrier liquid

[0078] The additive composition will normally comprise a carrier liquid which is convenient as a means for incorporating the additive into bulk oil such as distillate fuel, which incorporation may be done by methods known in the art. The additive composition may also contain other additives as required. Examples of carrier liquids are organic solvents including hydrocarbon solvents, for example petroleum fractions such as naphtha, kerosene, diesel and heater oil; aromatic hydrocarbons such as aromatic fractions, e.g. those sold under the 'SOLVESSO' tradename; alcohols such as 2-ethyl hexanol, isodecanol and tridecyl alcohol and/or esters; and paraffinic hydrocarbons such as hexane and pentane and isoparaffins, e.g. those sold under the 'ISOPAR' and 'CIPAR' tradenames. The carrier liquid must, of course, be selected having regard to its compatibility with the additive and with the oil.

[0079] Preferably, the colloidal species comprises from 1 to 100 ppm, more preferably from 1 to 50 ppm, suitably from 1 to 20 ppm, especially from 1 to 10 ppm by weight of the fuel composition.

[0080] Preferably, the stabilising component comprises from 1 to 500 ppm, more preferably from 1 to 200 ppm, suitably from 1 to 125 ppm, for example from 1 to 100 ppm, or from 1 to 50 ppm, or from 1 to 10 ppm by weight of the fuel composition.

[0081] When present, preferably, the lubricity enhancer comprises from 1 to 500 ppm, more preferably from 50 to 300 ppm, suitably from 150 to 200 ppm, by weight of the fuel composition.

[0082] The total amount of colloidal species, stabilising component and, when, present, lubricity enhancer, in the additive composition is preferably as high as possible. This minimises the amount of additive needed. The proportion of each constituent in the additive composition is preferably such that, when added to a fuel composition, the above defined ranges are achieved. Typically, the ratio of the amount of colloidal species to the amount of stabilising component in the additive composition will be in the range from 1:100 to 1:1.

[0083] Other aspects of the present invention relate to the use of the stabiliser component. From the foregoing description, it will be clear that the stabilising component may be added to an additive composition containing a colloidal species, the additive composition then being added to a fuel. Alternatively, the stabilising component may be added directly to the fuel, either prior to or after the addition of a colloidal species. As is known in the art, additive compositions may contain additional components including lubricity enhancers, detergents, cold flow improvers, corrosion inhibitors and antistatic additives.

[0084] The invention will now be described by way of example only.

Improvement of the phase stability of a colloidal metal oxide species.

Example 1

[0085] The results of a static storage stability experiment in Class 1 diesel fuel at 80°C are given in Table 1.

Table 1

Sample	Metal oxide colloid (ppm)	APFC (ppm)	HBFCa (ppm)	HBFCb (ppm)	Phase separation stability (days)
8275067A	10	-	-	-	4
8275067AC	10	200	-	-	7
8275067AE	10	-	200	-	9
8275067AG	10	-	-	200	8

[0086] The results show that each of the stabilising components improved the phase stability of the metal oxide colloid in the fuel compared to the fuel without a stabiliser (8275067A).

Example 2

[0087] The results of a static storage stability experiment in Class 1 diesel fuel at 80°C are given in Table 1.

[0088] Table 2 indicates that the colloidal metal oxide species displayed poor phase stability in Class 1 fuel alone, as evidenced by the appearance of a haze after 2 days and full phase separation within 4 days (sample ID 8275113B).

[0089] Addition of two types of lubricity additive chemistry (dimer acid ethoxylate and fatty acid glycerol ester) at commercial treat rates did not improve the stability of the colloid significantly (sample IDs 8275113C and D respectively), compared to the control sample.

[0090] However, addition of small amounts of the substituted phenolic stabilisers (APFC, HBFC) to the mixtures significantly improved the time for the onset of haze (Sample IDs 8275113E through 8275113AF), compared to sample 8275113C. This represents an improvement in the stability of the colloidal metal oxide species towards the presence of the fuel additives.

[0091] Furthermore, in samples (Sample IDs 8275113E through 8275113AF) the stabiliser moieties are able to increase the resistance to phase separation.

Table 2

Sample	Metal oxide colloid (ppm)	LE 1 (ppm)	LE 2 (ppm	APFC (ppm)	HBFCa (ppm)	HBFCb (ppm)	Onset of Haze* (days)	Phase Separation Stability* (Days)	Comment*
8275113B	10						2	4	DPF control
8275113C	10	150					1	5	DPF Control + lubricity enhancer 1
8275113D	10		200				-	2	DPF Control + lubricity enhancer 2
8275113E	10	150		25			4	-	DPF+LE1+ APFC stabiliser
82751131	10	150		125			7	11	
8275113J	10		200	25			2	3	DPF + LE2 + APFC stabiliser
8275113L	10		200	75			-	4	
8275113M	10		200	100			7	8	
8275113N	10		200	125			9	-	
82751130	10	150			25		3	11	DPF + LE 1 + HBFCa stabiliser
8275113Q	10	150			75		7	11	
8275113T	10		200		25		2	3	DPF + LE2 + HBFCa stabiliser
8275113U	10		200		50		-	15	
8275113Y	10	150				25	3	-	DPF + LE 1 + HBFCb stabiliser
8275113AA	10	150				75	4	8	
8275113AE	10		200			50	2	3	DPF + LE 2 + HBFCb stabiliser
8275113AF	10		200			75	4	7	

* onset of haze = first appearance of slight suspended haze (in days); phase separation stability = first appearance of a distinct precipitate (in days).

Table continued

Sample	Metal oxide colloid (ppm)	LE 1 (ppm)	LE 2 (ppm	APFC (ppm)	HBFCa (ppm)	HBFCb (ppm)	Onset of Haze* (days)	Phase Separation Stability* (Days)	Comment*

LE 1 = dimer acid ethoxylate; LE 2 = fatty acid glycerol ester; APFC = alkylphenol formaldehyde condensate; HBFCa = hydroxybenzoate formaldehyde condensate based on the isodecyl ester; HBFCb = hydroxybenzoate formaldehyde condensate based on the 2-ethylhexyl/*n-octyl (3:1) mixed ester.*

Example 3

[0092] In Table 3, it is shown that the colloidal metal oxide species started to form a pronounced haze within 3-4 days in Class 1 fuel at 80°C (sample IDs 8275127A and B).

[0093] Addition of 150 ppm of an ethoxylated dimer acid lubricity improver component to this system caused a complete phase separation within 2 days (sample ID 8275127C).

[0094] Addition of 50 ppm of APFC stabiliser to this system greatly improved the resistance to both onset of haze and phase separation of the metal oxide colloid system in the presence of the lubricity improver.

Table 3

Sample	Metal oxide colloid (ppm)	LE 1 (ppm)	APFC (ppm)	Onset of Haze (days)	Phase Separation Stability (Days)	Comment
8275127A	10			3	4	DPF control
8275127B	10			4	8	
8275127C	10	150		-	2	DPF Control+ lubricity enhancer 1
8275127D	10	150	50	4	10	DPF + LI1 + APFC stabiliser
8275127E	10	150	50	5	10	
8275127F	10	150	50	4	9	

Claims

1. An additive composition, the composition comprising at least one colloidal metal compound or metallic species and a stabilising component, wherein the stabilising component comprises the product obtainable by the condensation reaction between:

   (i) at least one aldehyde or ketone or reactive equivalent thereof, and
   (ii) at least one compound comprising one or more aromatic moieties bearing at least one hydroxyl group and at least one further substituent chosen from a hydrocarbyl group, -COOR^1 or COR^1, wherein R^1 represents hydrogen or a hydrocarbyl group.

2. An additive composition according to claim 1, wherein the stabilising component comprises an alkylphenol formaldehyde condensate or a hydroxybenzoate formaldehyde condensate.

3. An additive composition according to claim 1 or claim 2, wherein the colloidal metal compound comprises at least one metal oxide.

4. An additive composition according to claim 3, wherein the metal oxide is chosen from iron oxide, cerium oxide or cerium-doped iron oxide.

5. An additive composition according to any preceding claim further comprising at least one lubricity enhancer.

6. An additive composition according to claim 5, wherein the at least one lubricity enhancer is a carboxylic acid or ester thereof.

7. An additive composition according to any preceding claim which is substantially free from sulphur-containing compounds.

8. A fuel composition comprising a major amount of a fuel and a minor amount of an additive composition according to any preceding claim.

9. A fuel composition according to claim 8, wherein the fuel comprises a middle distillate fuel oil.

10. The use of a stabilising component as defined in claim 1 to stabilise an additive composition comprising a colloidal metal compound or metallic species.

11. Use according to claim 10, wherein the additive composition further comprises at least one lubricity enhancer.

12. The use of a stabilising component as defined in claim 1 to stabilise a fuel composition comprising a colloidal metal compound or metallic species.

13. Use according to claim 12, wherein the fuel composition further comprises at least one lubricity enhancer.

14. A method for improving the stability of a fuel additive composition or of a fuel composition, wherein the fuel additive composition or fuel composition comprises a colloidal metal compound or metallic species and optionally, at least one lubricity enhancer; the method comprising the addition of a stabilising component as defined in claim 1.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 05 10 4098

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