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(54) ADDITIVES TO REDUCE METAL PICK-UP IN FUELS

(57) The present invention relates to fuel additives, fuel additive compositions and fuel compositions, as well as a method for fueling an internal combustion engine, providing reduced metal pick-up by fuels where the compositions of the present invention contain a hydrocarbon substituted with at least two carboxy functionalities in the form of acids or at least one carboxy functionality in the form of an anhydride.

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Description

BACKGROUND OF THE INVENTION

[0001] The present invention relates to fuel additives, fuel additive compositions and fuel compositions as well as a method for fueling an internal combustion engine, providing reduced oxidative metal pick-up in fuels.

[0002] In the past there has been some uncertainty regarding the impact of pick-up, or solubilization, of certain oxidative metals by fuel on engine performance. Such matters have generally been evaluated from a corrosion control standpoint. However, there is growing evidence that metal pick-up, for example zinc pick-up, is an issue that can impact engine performance.

[0003] Trace levels of dissolved or soluble metals, such as zinc (Zn) and copper (Cu), in fuels, such as diesel fuel, have been shown to increase injector fouling. Trace metals like these can enter the fuel distribution system through contamination, or through the pick-up (dissolution) of metal, by the fuel, from metals parts that make up part of the fuel distribution system with which the fuel comes into contact. For example, diesel fuel may pick up zinc from galvanized steel surfaces in fuel tanks, resulting in elevated zinc levels in fuels, which may lead to the accelerated injector fouling, discussed above. Zinc, and other metals, may also be picked up by the fuel by contacting such metal-containing surfaces in the vehicle fuel injection system.

[0004] There is a need for fuel additives and fuel compositions that effectively reduce the amount of metal pick-up, and more specifically, zinc pick-up while minimizing the impact on additive and fuel composition costs and complexity.

SUMMARY OF THE INVENTION

[0005] Fuel additives, fuel additive compositions and fuel compositions have been discovered which reduce the amount of metal pick-up seen in fuel compositions. The present invention provides for such compositions as well as a method of reducing contaminant metal pick-up, such as zinc pick-up, in fuel compositions.

[0006] In accordance with the present invention it has been discovered that adding an additive, comprising a hydrocarbon substituted with at least two carboxy functionalities in the form of acids or at least one carboxy functionality in the form an anhydride, to a fuel composition results in the reduction of the amount of oxidative metals pick-up in the fuel composition.

[0007] In some embodiments the substituted hydrocarbon additive is a hydrocarbyl substituted acylating agent with at least two carboxy functionalities in the form of acids or anhydrides.

[0008] In some embodiments, the substituted hydrocarbon additive and/or hydrocarbyl substituted acylating agent has di-acid functionality. In other embodiments the additive is a succinic acylating agent. In still other embodiments, which may be used in combination with one or more of the embodiments described herein, the hydrocarbyl group of the additive is derived from polyisobutylene.

[0009] The metal, for which pick-up is being reduced, include group IV transition metals. In some embodiments, the metal is V, Cr, Mn, Fe, Co, Ni, Cu, Zn, or combinations thereof. In some embodiments, the metal may be selected from the group consisting of copper, zinc, iron, or combinations thereof. In some embodiments, the oxidative metal is zinc. In other embodiments, the oxidative metal, for which the tendency of fuel composition to pick up is being reduced, may be any of the metals, or groups of metals, described above except iron.

[0010] The present invention also provides for the described method wherein the substituted hydrocarbon additive may be: (a) a hydrocarbyl substituted succinic anhydride; (b) a hydrolyzed hydrocarbyl substituted succinic anhydride; or (c) combinations thereof.

[0011] In some embodiments the fuel being treated in the method is susceptible to pick up of oxidative metals to a level greater than 0.5 ppm when left in contact for an extended period of time with solid materials containing said metal.

[0012] The method of the present invention may also result in the reduction of injector deposits in an engine in which the fuel composition of the method is applied.

[0013] The present invention also provides a fuel composition comprising: (a) a fuel; (b) an additive comprising the substituted hydrocarbon additive describe herein; and (c) optional additional performance additives. The present invention also provides a fuel additive composition comprising: (a) an optional solvent; (b) the substituted hydrocarbon additive described herein; and (c) optional additional performance additives.

DETAILED DESCRIPTION OF THE INVENTION

[0014] Various preferred features and embodiments will be described below by way of non-limiting illustration.

Field of the Invention

[0015] The present invention involves a fuel additive, a fuel additive composition, a fuel composition and a method for fueling an internal combustion engine. The invention provides a method of reducing metal-pick, and in some embodiments zinc pick-up, in a fuel composition, in some embodiment during the operation of an internal combustion engine.

[0016] The composition of the present invention may be used in fuel compositions to reduce their tendency to pick-up metals from surfaces with which they come into contact. The additive compositions of the present invention may also provide comparable and/or improved detergency, specifically improved engine deposit control when they are used in fuel compositions. These characteristics allow for improved engine performance, including but not limited to reductions in injector fouling, reduced deposit-caused engine power losses, reduced deposit-caused fuel economy losses and reduced deposit-caused engine emissions.

The Substituted Hydrocarbon Additive

[0017] The substituted hydrocarbon additive of the present invention comprises a hydrocarbon substituted with at least two carboxy functionalities in the form of acids or at least one carboxy functionality in the form an anhydride. In some embodiments the additive is a hydrocarbon substituted with at least two carboxy functionalities in the form of acids or anhydrides. In other embodiments the additive is a hydrocarbyl-substituted succinic acylating agent. In other embodiments the substituted hydrocarbon additive is a dimer acid compound. In still other embodiments the substituted hydrocarbon additive of the present invention includes a combination of two or more of the additives described in this section.

[0018] The substituted hydrocarbon additives of the present invention, when used in the compositions and method described herein, reduce the tendency of fuel compositions in which they are used to pick up metals.

[0019] The substituted hydrocarbon additives include dimer acids. Dimer acids are a type of di-acid polymer derived from fatty acids and/or polyolefins, including the ployalkenes described herein, which contain acid functionality. IN some embodiments, the dimer acid used in the present invention is derived from C10 to C20 polyolefins, C12 to C18 polyolefins, and/or C16 to C18 polyolfines.

[0020] The substituted hydrocarbon additives include succinic acids, halides, anhydrides and combination thereof. In some embodiments the agents are acids or anhydrides, and in other embodiments the agents are anhydrides, and in still other embodiments the agents are hydrolyzed anhydrides. The hydrocarbon of the substituted hydrocarbon additive and/or the primary hydrocarbyl group of the hydrocarbyl-substituted succinic acylating agent generally contains an average of at least about 8, or about 30, or about 35 up to about 350, or to about 200, or to about 100 carbon atoms. In one embodiment, the hydrocarbyl group is derived from a polyalkene.

[0021] The polyalkene may be characterized by a Mn (number average molecular weight) of at least about 300. Generally, the polyalkene is characterized by an Mn of about 500, or about 700, or about 800, or even about 900 up to about 5000, or to about 2500, or to about 2000, or even to about 1500. In another embodiment n varies between about 300, or about 500, or about 700 up to about 1200 or to about 1300.

[0022] The polyalkenes include homopolymers and interpolymers of polymerizable olefin monomers of 2 to about 16 or to about 6, or to about 4 carbon atoms. The olefins may be monoolefins such as ethylene, propylene, 1-butene, isobutene, and 1-octene; or a polyolefinic monomer, such as diolefinic monomer, such 1,3-butadiene and isoprene. In one embodiment, the interpolymer is a homopolymer. An example of a polymer is a polybutene. In one instance about 50% of the polybutene is derived from isobutylene. The polyalkenes are prepared by conventional procedures.

[0023] In one embodiment, the hydrocarbyl groups are derived from polyalkenes having an n of at least about 1300, or about 1500, or about 1600 up to about 5000, or to about 3000, or to about 2500, or to about 2000, or to about 1800, and the Mw/Mn is from about 1.5 or about 1.8, or about 2, or to about 2.5 to about 3.6, or to about 3.2. In some embodiments the polyalkene is polyisobutylene with a molecular weight of 800 to 1200. The preparation and use of substituted hydrocarbons and/or substituted succinic acylating agents, wherein the hydrocarbon and/or substituent is derived from such polyalkenes are described in U.S. Patent 4,234,435, the disclosure of which is hereby incorporated by reference.

[0024] In another embodiment, the substituted hydrocarbon and/or succinic acylating agents are prepared by reacting the above described polyalkene with an excess of maleic anhydride to provide substituted succinic acylating agents wherein the number of succinic groups for each equivalent weight of substituent group is at least 1.3, or to about 1.5, or to about 1.7, or to about 1.8. The maximum number generally will not exceed 4.5, or to about 2.5, or to about 2.1, or to about 2.0. The polyalkene here may be any of those described above.

[0025] In another embodiment, the hydrocarbon and/or hydrocarbyl group contains an average from about 8, or about 10, or about 12 up to about 40, or to about 30, or to about 24, or to about 20 carbon atoms. In one embodiment, the hydrocarbyl group contains an average from about 16 to about 18 carbon atoms. In another embodiment, the hydrocarbyl group is tetrapropenyl group. In one embodiment, the hydrocarbyl group is an alkenyl group.

[0026] The hydrocarbon and/or hydrocarbyl group may be derived from one or more olefins having from about 2 to about 40 carbon atoms or oligomers thereof. These olefins are preferably alpha-olefins (sometimes referred to as mono-1-olefins) or isomerized alpha-olefins. Examples of the alpha-olefins include ethylene, propylene, butylene, 1-octene, 1-nonene, 1-decene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 1-henicosene, 1-docosene, 1-tetracosene, etc. Commercially available alpha-olefin fractions that may be used include the C_{15-18} alpha-olefins, C_{12-16} alpha-olefins, C_{14-16} alpha-olefins, C_{14-18} alpha-olefins, C_{16-18} alpha-olefins, C_{16-20} alpha-olefins, C_{22-28} alpha-olefins, etc. In one embodiment, the olefins are C_{16} and C_{16-18} alpha-olefins. Additionally, C_{30}+ alpha-olefin fractions such as those available from Gulf Oil Company under the name Gulftene can be used. In one embodiment, the olefin monomers include ethylene, propylene and 1-butene.

[0027] Isomerized alpha-olefins are alpha-olefins that have been converted to internal olefins. The isomerized alpha-olefins suitable for use herein are usually in the form of mixtures of internal olefins with some alpha-olefins present. The procedures for isomerizing alpha-olefins are well known to those in the art. Briefly these procedures involve contacting alpha-olefin with a cation exchange resin at a temperature in a range of about 80° to about 130°C until the desired degree of isomerization is achieved. These procedures are described for example in U.S. 4,108,889 which is incorporated herein by reference.

[0028] The mono-olefins may be derived from the cracking of paraffin wax. The wax cracking process yields both even and odd number C_{6-20} liquid olefins of which 85% to 90% are straight chain 1-olefins. The balance of the cracked wax olefins is made up of internal olefins, branched olefins, diolefins, aromatics and impurities. Distillation of the C_{6-20} liquid olefins, obtained from the wax cracking process, yields fractions (e.g., C_{15-18} alpha-olefins) which are useful in preparing the succinic acylating agents.

[0029] Other mono-olefins can be derived from the ethylene chain growth process. This process yields even numbered straight-chain 1-olefins from a controlled Ziegler polymerization. Other methods for preparing the mono-olefins include chlorination-dehydrochlorination of paraffin and catalytic dehydrogenation of paraffins.

[0030] The above procedures for the preparation of mono-olefins are well known to those of ordinary skill in the art and are described in detail under the heading "Olefins" in the Encyclopedia of Chemical Technology, Second Edition, Kirk and Othmer, Supplement, Pages 632,657, Interscience Publishers, Div. of John Wiley and Son, 1971, which is hereby incorporated by reference for its relevant disclosures pertaining to methods for preparing mono-olefins.

[0031] Succinic acylating agents are prepared by reacting the above-described olefins, isomerized olefins or oligomers thereof with unsaturated carboxylic acylating agents, such as itaconic, citraconic, or maleic acylating agents at a temperature of about 160°, or about 185°C up to about 240°C, or to about 210°C. Maleic acylating agents are the preferred unsaturated acylating agent. The procedures for preparing the acylating agents are well known to those skilled in the art and have been described for example in U.S. Patent 3,412,111; and Ben et al, "The Ene Reaction of Maleic Anhydride With Alkenes", J.C.S. Perkin II (1977), pages 535-537. These references are incorporated by reference for their disclosure of procedures for making the above acylating agents. In one embodiment, the alkenyl group is derived from oligomers of lower olefins, i.e., olefins containing from 2 to about 6, or about 4 carbon atoms. Examples of these olefins include ethylene, propylene and butylene.

[0032] The olefin, olefin oligomer, or polyalkene may be reacted with the carboxylic reagent such that there is at least one mole of carboxylic reagent for each mole of olefin, olefin oligomer, or polyalkene that reacts. Preferably, an excess of carboxylic reagent is used. In one embodiment, this excess is between about 5% to about 25%. In another embodiment, the excess is greater than 40%, or greater than 50%, and even greater than 70%.

[0033] The conditions, i.e., temperature, agitation, solvents, and the like, for forming the hydrocarbyl-substituted succinic acylating agent, are known to those in the art. Examples of patents describing various procedures for preparing useful acylating agents include U.S. Patents 3,172,892 (Le Suer et al.); 3,215,707 (Rense); 3,219,666 (Norman et al); 3,231,587 (Rense); 3,912,764 (Palmer); 4,110,349 (Cohen); and 4,234,435 (Meinhardt et al); and U.K. 1,440,219. The disclosures of these patents are hereby incorporated by reference.

[0034] In some embodiments the substituted hydrocarbon additives and/or hydrocarbyl substituted succinic acylating agents suitable for use in the present invention contain di-acid functionality. In other embodiments, which may be used alone or in combination with the embodiments described above, the hydrocarbyl group of the hydrocarbyl substituted succinic acylating agent is derived from polyisobutylene and the di-acid functionality of the agent is derived from carboxylic acid groups, such as hydrocarbyl substituted succinic acid.

[0035] In some embodiments the hydrocarbyl substituted acylating agent comprises one or more hydrocarbyl substituted succinic anhydride groups. In some embodiments the hydrocarbyl substituted acylating agent comprises one or more hydrolyzed hydrocarbyl substituted succinic anhydride groups.

[0036] In some embodiments the hydrocarbyl substituents of the acylating agents described above are derived from homopolymers and/or copolymers containing 2 to 10 carbon atoms. In some embodiments the hydrocarbyl substituents of any of the acylating agents described above are derived from polyisobutylene.

[0037] The fuel additives of the present invention can be solids, semi-solids, or liquids (oils) depending on the particular alcohol(s) and/or amine(s) used in preparing them. For use as additives in oleaginous compositions including lubricating and fuel compositions the fuel additives are advantageously soluble and/or stably dispersible in such oleaginous compositions. Thus, for example, compositions intended for use in fuels are typically fuel-soluble and/or stably dispersible in a fuel in which they are to be used. The term "fuel-soluble" as used in this specification and appended claims does not necessarily mean that all the compositions in question are miscible or soluble in all proportions in all fuels. Rather, it is intended to mean that the composition is soluble in a fuel (hydrocarbon, non-hydrocarbon, mixtures, etc) in which it is intended to function to an extent which permits the solution to exhibit one or more of the desired properties. Similarly, it is not necessary that such "solutions" be true solutions in the strict physical or chemical sense. They may instead be micro-emulsions or colloidal dispersions which, for the purpose of this invention, exhibit properties sufficiently close to those of true solutions to be, for practical purposes, interchangeable with them within the context of this invention.

[0038] As previously indicated, the anti-metal pick-up additives of this invention are useful as additives for fuels, in which they may also function as detergents. The fuel additives of the present invention can be present in fuel compositions at 1 to 10,000 ppm (where ppm is calculated on a weight:weight basis). In additional embodiments, the fuel additive is present in fuel compositions in ranges with lower limits of 1, 3, 5, 10, 50, 100, 150 and 200 ppm and upper limits of 10,000, 7,500, 5,000, and 2,500 where any upper limit may be combined with any lower limit to provide a range for the fuel additive present in the fuel compositions.

[0039] It is contemplated that the additives of the present invention may form salts or other complexes and/or derivatives, when interacting with other components of the compositions in which they are used. Such forms of these additives are also part of the present invention and are include in the embodiment described herein. Some of the succinic acylating agents of the present invention and the processes for making them are disclosed in U.S. Pat. Nos. 5,739,356; 5,777,142; 5,786,490; 5,856,524; 6,020,500; and 6,114,547 which are hereby incorporated by reference. Other methods of making the hydrocarbyl substituted acylating agent can be found in U.S. Pat. Nos. 5,912,213; 5,851,966; and 5,885,944 which are hereby incorporated by reference. In some embodiments the succinic acylating agents of the present invention are prepared by the thermal process and/or chlorine free process only, as described in EP0355895 hereby incorporated by reference.

The Fuel Additive Compositions

[0040] The fuel additive composition of the present invention comprises the fuel additive described above and further comprises a solvent and/or one or more additional performance additives. These additive compositions, also known as additive concentrates and/or concentrates, may be used to prepare fuel compositions by adding the additive composition to an non-additized fuel.

[0041] The solvents suitable for use in the present invention include hydrocarbon solvents that provide for the additive composition's compatibility and/or homogeneity and to facilitate their handling and transfer and may include a fuel as described below. The solvent can be an aliphatic hydrocarbon, an aromatic hydrocarbon, an oxygen-containing composition, or a mixture thereof. In some embodiments the flash point of the solvent is generally about 25°C or higher. In some embodiments the hydrocarbon solvent is an aromatic naphtha having a flash point above 62°C or an aromatic naphtha having a flash point of 40°C or a kerosene with a 16% aromatic content having a flash point above 62°C.

[0042] Aliphatic hydrocarbons include various naphtha and kerosene boiling point fractions that have a majority of aliphatic components. Aromatic hydrocarbons include benzene, toluene, xylenes and various naphtha and kerosene boiling point fractions that have a majority of aromatic components. Alcohols are usually aliphatic alcohols having about 2 to 10 carbon atoms and include ethanol, 1-propanol, isopropyl alcohol, 1-butanol, isobutyl alcohol, amyl alcohol, and 2-methyl-1-butanol.

[0043] The oxygen containing composition can include an alcohol, a ketone, an ester of a carboxylic acid, a glycol and/or a polyglycol, or a mixture thereof. The solvent in an embodiment of the invention will be substantially free of to free of sulphur having a sulphur content in several instances that is below 50 ppm, 25 ppm, below 18 ppm, below 10 ppm, below 8 ppm, below 4 ppm, or below 2 ppm. The solvent can be present in the additive concentrate composition at 0 to 99 percent by weight, and in other instances at 3 to 80 percent by weight, or 10 to 70 percent by weight. The friction modifier of the present invention and the additional performance additives taken separately or in combination can be present in the additive concentrate composition at 0.01 to 100 percent by weight, and in other instances can be present at 0.01 to 95 percent by weight, at 0.01 to 90 percent by weight, or at 0.1 to 80 percent by weight.

[0044] As allowed for by the ranges above, in one embodiment, the additive concentrate may comprise the fuel additive of the present invention and be substantially free of any additional solvent. In these embodiments the additive concentrate containing the fuel additive of the present invention is neat, in that it does not contain any additional solvent added to improve the material handling characteristics of the concentrate, such as its viscosity.

[0045] In several embodiments of the invention the fuel composition, fuel additive concentrate, and/or the fuel additive itself are substantially free of or free of at least one member selected from the group consisting of sulphur, phosphorus, sulfated ash, and combinations thereof, and in other embodiments the fuel composition contains less than 50 ppm, 20 ppm, less than 15 ppm, less than 10 ppm, or less than 1 ppm of any one or all of these members.

[0046] In an embodiment of the invention the additive concentrate composition, or a fuel composition containing the fuel additive of the present invention, may be prepared by admixing or mixing the components of the composition at ambient to elevated temperatures usually up to 60°C until the composition is homogeneous.

[0047] The additional performance additives which may be included in the additive compositions of the present invention are described below.

The Fuel

[0048] The fuel composition of the present invention comprises the fuel additive described above and a liquid fuel, and is useful in fueling an internal combustion engine, A fuel may also be a component of the additive compositions described above.

[0049] It is generally accepted in the industry that many types of commercial fuel, particularly market diesel fuels and/or biofuels, have the capacity to pick up, or solubilize, some level of oxidative metal when placed in direct contact with susceptible metal surfaces. There is also evidence that most if not all fuels, particularly market diesel fuels have some tendency to pick up metals. It has also been recognized that many fuel additives may increase the tendency of the fuel to pick up oxidative metals in the fuel and fuel additive compositions in which they are used. The present invention reduces the propensity to pick up oxidative metals in such fuel and fuel additive compositions.

[0050] In some embodiments, the fuels suitable for use in the present invention include any commercially available fuels, and in some embodiments any commercially available diesel fuels and/or biofuels. In other embodiments, the fuels suitable for use in the present invention include any commercially available fuels which are susceptible to metal pick up, and in some embodiments any commercially available diesel fuels and/or biofuels susceptible to metal pick up.

[0051] In still other embodiments, the fuels suitable for use in the present invention are any fuels, or any diesel fuels and/or biofuels, which are susceptible to pick up of oxidative metals to a level greater than 0.5 ppm when left in contact for an extended period of time with solid materials containing said metal. In some embodiments the exposure time involved is greater than 72 hours, greater than 48 hours, or greater than 24 hours.

[0052] The present invention includes fuel compositions and fuel additive concentrate compositions which may contain fuel. The fuel used in these compositions may or may not exhibit a propensity to pick up oxidative metal, and may in fact be any of the fuels described in this application or combinations thereof. The fuel used in these compositions need not be the same fuel to which the additive of the present invention may be added in the methods described herein. That is, the additive of the present invention may be present in a composition that also comprises a fuel. This fuel may or may not exhibit a propensity to pick up oxidative metal. The additive-containing composition may then be added to a fuel and/or fuel additive composition. The identity of the fuel present in this composition is independent of the identity of the optional fuel component in the additive containing composition. The oxidative metal pick-up propensity of the fuel and/or fuel additive composition may be a result of the properties of the fuel and/or the properties of one or more of the additives present in the fuel and /or additive composition. The addition of the additive-containing compositions, as described in the method and compositions of the present invention result in a reduction of the oxidative metal pick-up propensity of the fuel and/or fuel additive compositions.

[0053] The description that follows of the types of fuels suitable for use in the present invention refer to the fuel that may be present in the additive containing compositions of the present invention as well as the fuel and/or fuel additive compositions to which the additive containing compositions may be added.

[0054] Fuels suitable for use in the present invention are not overly limited. Generally, suitable fuels are normally liquid at ambient conditions e.g., room temperature (20 to 30°C). The liquid fuel can be a hydrocarbon fuel, a non-hydrocarbon fuel, or a mixture thereof.

[0055] The hydrocarbon fuel can be a petroleum distillate, including a gasoline as defined by ASTM specification D4814, or a diesel fuel, as defined by ASTM specification D975. In one embodiment the liquid fuel is a gasoline, and in another embodiment the liquid fuel is a non-leaded gasoline. In another embodiment the liquid fuel is a diesel fuel. The hydrocarbon fuel can be a hydrocarbon prepared by a gas to liquid process to include for example hydrocarbons prepared by a process such as the Fischer-Tropsch process. In some embodiments, the fuel used in the present invention is a diesel fuel, a biodiesel fuel, or combinations thereof.

[0056] The non-hydrocarbon fuel can be an oxygen containing composition, often referred to as an oxygenate, which includes an alcohol, an ether, a ketone, an ester of a carboxylic acid, a nitroalkane, or a mixture thereof. The non-hydrocarbon fuel can include for example methanol, ethanol, methyl t-butyl ether, methyl ethyl ketone, transesterified oils and/or fats from plants and animals such as rapeseed methyl ester and soybean methyl ester, and nitromethane.

[0057] Mixtures of hydrocarbon and non-hydrocarbon fuels can include, for example, gasoline and methanol and/or ethanol, diesel fuel and ethanol, and diesel fuel and a transesterified plant oil such as rapeseed methyl ester and other bio-derived fuels. In one embodiment the liquid fuel is an emulsion of water in a hydrocarbon fuel, a non-hydrocarbon fuel, or a mixture thereof. In several embodiments of this invention the liquid fuel can have a sulphur content on a weight basis that is 5000 ppm or less, 1000 ppm or less, 300 ppm or less, 200 ppm or less, 30 ppm or less, or 10 ppm or less.

[0058] The liquid fuel of the invention is present in a fuel composition in a major amount that is generally greater than

95% by weight, and in other embodiments is present at greater than 97% by weight, greater than 99.5% by weight, or greater than 99.9% by weight.

Additional Performance Additives

[0059] The additive compositions and fuel compositions of the present invention can further comprise one or more additional performance additives. Additional performance additives can be added to a fuel composition depending on several factors to include the type of internal combustion engine and the type of fuel being used in that engine, the quality of the fuel, and the service conditions under which the engine is being operated.

[0060] In some embodiments, the additional performance additives described herein may increase the tendency of a fuel composition to pick-up metals such as zinc. The use of the present invention in such situations can reduce and/or eliminate this impact of the additional additives.

[0061] The additional performance additives can include: an antioxidant such as a hindered phenol or derivative thereof and/or a diarylamine or derivative thereof; a corrosion inhibitor; and/or a detergent/dispersant additive, other than the fuel additive of the present invention, such as a polyetheramine or nitrogen containing detergent, including but not limited to PIB amine dispersants, quaternary salt dispersants, and succinimide dispersants including derivates of succinimide dispersants such as quaternary ammonium salts thereof.

[0062] The additional performance additives may also include: a cold flow improver such as an esterified copolymer of maleic anhydride and styrene and/or a copolymer of ethylene and vinyl acetate; a foam inhibitor and/or antifoam agent such as a silicone fluid; a demulsifier such as a polyalkoxylated alcohol; a lubricity agent such as a fatty carboxylic acid; a metal deactivator such as an aromatic triazole or derivative thereof, including but not limited to benzotriazole; and/or a valve seat recession additive such as an alkali metal sulfosuccinate salt.

[0063] Suitable antifoams also include organic silicones such as polydimethyl siloxane, polyethylsiloxane, polydiethylsiloxane, polyacrylates and polymethacrylates, trimethyl-triflouro-propylmethyl siloxane and the like.

[0064] The additional additives may also include a biocide; an antistatic agent, a deicer, a fluidizer such as a mineral oil and/or a poly(alpha-olefin) and/or a polyether, and a combustion improver such as an octane or cetane improver.

[0065] The additional performance additives, which may be present in the fuel additive compositions and fuel compositions of the present invention, also include di-ester, di-amide, ester-amide, and ester-imide friction modifiers prepared by reacting a dicarboxylic acid (such as tartaric acid) and/or a tricarboxylic acid (such as citric acid), with an amine and/or alcohol, optionally in the presence of a known esterification catalyst. These friction modifiers, often derived from tartaric acid, citric acid, or derivatives thereof, may be derived from amines and/or alcohols that are branched so that the friction modifier itself has significant amounts of branched hydrocarbyl groups present within it structure. Examples of a suitable branched alcohols used to prepare these friction modifiers include 2-ethylhexanol, isotridecanol, Guerbet alcohols, or mixtures thereof.

[0066] The additional performance additives may comprise a high TBN nitrogen containing dispersant, such as a succinimide dispersant, that is the condensation product of a hydrocarbyl-substituted succinic anhydride with a poly(alkyleneamine). Succnimide dispersants are very well known in the art of lubricant formulation. Such molecules are commonly derived from reaction of an alkenyl acylating agent with a polyamine, and a wide variety of linkages between the two moieties is possible including a simple imide structure as well as a variety of amides and quaternary ammonium salts. Succinimide dispersants are more fully described in U.S. Patents 4,234,435 and 3,172,892. Such materials may also contain ester linkages or ester functionality.

[0067] Another class of nitrogen-containing dispersant is the Mannich bases. These are materials which are formed by the condensation of a higher molecular weight, alkyl substituted phenol, an alkylene polyamine, and an aldehyde such as formaldehyde. Such materials are described in more detail in U.S. Patent 3,634,515.

[0068] Other nitrogen-containing dispersants include polymeric dispersant additives, which are generally hydrocarbon-based polymers which contain nintrogen-containing polar functionality to impart dispersancy characteristics to the polymer.

[0069] An amine is typically employed in preparing the high TBN nitrogen-containing dispersant. One or more poly(alkyleneamine)s may be used, and these may comprise one or more poly(ethyleneamine)s having 3 to 5 ethylene units and 4 to 6 nitrogens. Such materials include triethylenetetramine (TETA), tetraethylenepentamine (TEPA), and pentaethylenehexamine (PEHA). Such materials are typically commercially available as mixtures of various isomers containing a range number of ethylene units and nitrogen atoms, as well as a variety of isomeric structures, including various cyclic structures. The poly(alkyleneamine) may likewise comprise relatively higher molecular weight amines known in the industry as ethylene amine still bottoms.

[0070] The additional performance additives may comprise a quaternary salt comprising the reaction product of: (i) at least one compound selected from the group consisting of: (a) the condensation product of a hydrocarbyl-substituted acylating agent and a compound having an oxygen or nitrogen atom capable of condensing with said acylating agent and said condensation product further having a tertiary amino group; (b) a polyalkene-substituted amine having at least one tertiary amino group; and (c) a Mannich reaction product having a tertiary amino group, said Mannich reaction product being prepared from the reaction of a hydrocarbyl-subsituted phenol, an aldehyde, and an amine; and (ii) a quaternizing agent suitable for converting the tertiary amino group of compound (i) to a quaternary nitrogen, wherein the quaternizing agent is selected from the group consisting of dialkyl sulfates, benzyl halides, hydrocarbyl substituted carbonates; hydrocarbyl epoxides in combination with an acid or mixtures thereof.

[0071] In one embodiment the quaternary salt comprises the reaction product of (i) at least one compound selected from the group consisting of: a polyalkene-substituted amine having at least one tertiary amino group and/or a Mannich reaction product having a tertiary amino group; and (ii) a quaternizing agent.

[0072] In another embodiment the quaternary salt comprises the reaction product of (i) the reaction product of a succinic anhydride and an amine; and (ii) a quaternizing agent. In such embodiments, the succinic anhydride may be derived from polyisobutylene and an anhydride, where the polyisobutylene has a number average molecular weight of about 800 to about 1600. In some embodiments the succinic anhydride is chlorine free.

[0073] In some embodiments, the hydrocarbyl substituted acylating agent of component (i)(a) described above is the reaction product of a long chain hydrocarbon, generally a polyolefin substituted with a monounsaturated carboxylic acid reactant such as (1) monounsaturated C_4 to C_{10} dicarboxylic acid such as fumaric acid, itaconic acid, maleic acid.; (2) derivatives of (1) such as anhydrides or C_1 to C_5 alcohol derived mono- or di-esters of (1); (3) monounsaturated C_3 to C_{10} monocarboxylic acid such as acrylic acid and methacrylic acid.; or (iv4 derivatives of (3) such as C_1 to C_5 alcohol derived esters of (3) with any compound containing an olefinic bond represented by the general formula:

$$(R^1)(R^1)C{=}C(R^1)(CH(R^1)(R^1)) \qquad (I)$$

wherein each R^1 is independently hydrogen or a hydrocarbyl group.

[0074] Olefin polymers for reaction with the monounsaturated carboxylic acids can include polymers comprising a major molar amount of C_2 to C_{20}, e.g. C_2 to C_5 monoolefin. Such olefins include ethylene, propylene, butylene, isobutylene, pentene, octene-1, or styrene. The polymers can be homopolymers such as polyisobutylene, as well as copolymers of two or more of such olefins such as copolymers of; ethylene and propylene; butylene and isobutylene; propylene and isobutylene. Other copolymers include those in which a minor molar amount of the copolymer monomers e.g., 1 to 10 mole % is a C_4 to C_{18} diolefin, e.g., a copolymer of isobutylene and butadiene; or a copolymer of ethylene, propylene and 1,4-hexadiene.

[0075] In one embodiment, at least one R of formula (I) is derived from polybutene, that is, polymers of C_4 olefins, including 1-butene, 2-butene and isobutylene. C_4 polymers can include polyisobutylene. In another embodiment, at least one R of formula (I) is derived from ethylene-alpha olefin polymers, including ethylene-propylene-diene polymers. Ethylene-alpha olefin copolymers and ethylene-lower olefin-diene terpolymers are described in numerous patent documents, including European patent publication EP0279863 and the following United States patents: 3,598,738; 4,026,809; 4,032,700; 4,137,185; 4,156,061; 4,320,019; 4,357,250; 4,658,078; 4,668,834; 4,937,299; 5,324,800 each of which are incorporated herein by reference for relevant disclosures of these ethylene based polymers.

[0076] In another embodiment, the olefinic bonds of formula (I) are predominantly vinylidene groups, represented by the following formulas:

$$-(H)C{=}C(R^2)(R^2) \qquad (II)$$

wherein R^2 is a hydrocarbyl group, and in some embodiments both R^2 groups are methyl groups, and

$$-(H)(R^3)C(C(CH_3){=}CH2) \qquad (III)$$

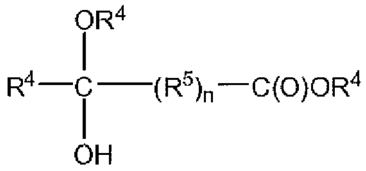
wherein R^3 is a hydrocarbyl group.

[0077] In one embodiment, the vinylidene content of formula (I) can comprise at least about 30 mole % vinylidene groups, at least about 50 mole % vinylidene groups, or at least about 70 mole % vinylidene groups. Such material and methods for preparing them are described in U.S. Pat. Nos. 5,071,919; 5,137,978; 5,137,980; 5,286,823, 5,408,018, 6,562,913, 6,683,138, 7,037,999 and U.S. Publication Nos. 20040176552A1, 20050137363 and 20060079652A1, which are expressly incorporated herein by reference, such products are commercially available by BASF, under the tradename GLISSOPAL® and by Texas Petrochemicals LP, under the tradename TPC 1105™ and TPC 595™.

[0078] Methods of making hydrocarbyl substituted acylating agents from the reaction of the monounsaturated carboxylic acid reactant and the compound of formula (I) are well know in the art and disclosed in the following patents: U.S. Pat. Nos. 3,361,673 and 3,401,118 to cause a thermal "ene" reaction to take place; U.S. Pat. Nos. 3,087,436; 3,172,892; 3,272,746, 3,215,707; 3,231,587; 3,912,764; 4,110,349; 4,234,435; 6,077,909; 6,165,235 and are hereby incorporated by reference.

[0079] In another embodiment, the hydrocarbyl substituted acylating agent can be made from the reaction of at least one carboxylic reactant represented by the following formulas: and

$$(R^4C(O)(R^5)_nC(O))R^4 \qquad (IV)$$

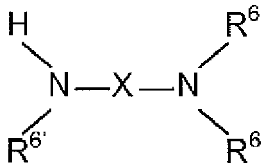


(V)

wherein each R^4 is independently H or a hydrocarbyl group, and each R^5 is a divalent hydrocarbylene group and n is 0 or 1 with any compound containing an olefin bond as represented by formula (I). Compounds and the processes for making these compounds are disclosed in U.S. Pat. Nos. 5,739,356; 5,777,142; 5,786,490; 5,856,524; 6,020,500; and 6,114,547 which are hereby incorporated by reference.

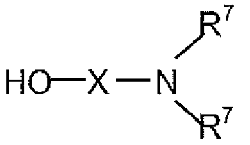
[0080] Other methods of making the hydrocarbyl substituted acylating agent can be found in the following reference, U.S. Pat. Nos. 5,912,213; 5,851,966; and 5,885,944 which are hereby incorporated by reference.

[0081] The compound having an oxygen or nitrogen atom capable of condensing with the acylating agent and further having a tertiary amino group can be represented by the following formulas:



(VI)

wherein X is a alkylene group containing about 1 to about 4 carbon atoms; and wherein each R^6 is independently a hydrocarbyl group, and $R^{6'}$ can be hydrogen or a hydrocarbyl group.



(VII)

wherein X is a alkylene group containing about 1 to about 4 carbon atoms; and wherein each R^7 is independently a hydrocarbyl group.

[0082] Examples of the nitrogen or oxygen contain compounds capable of condensing with the acylating agent and further having a tertiary amino group can include but are not limited to: ethylenediamine, 1,2-propylenediamine, 1,3-propylene diamine, the isomeric butylenediamines, pentanediamines, hexanediamines, heptanediamines, diethylenetriamine, dipropylenetriamine, dibutylenetriamine, triethylenetetraamine, tetraethylenepentaamine, pentaethylenehexaamine, hexamethylenetetramine, and bis(hexamethylene) triamine, the diaminobenzenes, the diaminopyridines or mixtures thereof. In addition, nitrogen or oxygen contain compounds which may be alkylated to contain a tertiary amino group may also used. Examples of the nitrogen or oxygen contain compounds capable of condensing with the acylating agent after being alkylated to having a tertiary amino group can include but are not limited to: dimethylaminopropylamine, N,N-dimethyl-aminopropylamine, N,N-diethylaminopropylamine, N,N-dimethyl-aminoethylamine or mixtures thereof. The nitrogen or oxygen containing compounds capable of condensing with the acylating agent and further having a tertiary amino group can further include aminoalkyl substituted heterocyclic compounds such as 1-(3-aminopropyl)imidazole and 4-(3-aminopropyl)morpholine, 1-(2-aminoethyl)piperidine, 3,3-diamino-N-methyldipropylamine, 3’3-aminobis(N,N-dimethylpropylamine). Another type of nitrogen or oxygen containing compounds capable of condensing with the acylating agent and having a tertiary amino group include alkanolamines including but not limited to triethanolamine, N,N-dimethylaminopropanol, N,N-diethylaminopropanol, N,N-diethylaminobutanol, N,N,N-tris(hydroxyothyl)amine, or mixtures thereof.

[0083] Examples of quaternary ammonium salt and methods for preparing the same are described in the following patents, which are hereby incorporated by reference, US 4,253,980, US 3,778,371, US 4,171,959, US 4,326,973, US 4,338,206, and US 5,254,138.

[0084] The additional performance additives can each be added directly to the additive and/or the fuel compositions of the present invention, but they are generally mixed with the fuel additive to form an additive composition, or concentrate, which is then mixed with fuel to result in a fuel composition. The additive concentrate compositions are described in more detail above.

[0085] In some embodiments, these additional performance additives described above may be the cause and/or a contributing factor to the propensity of a fuel to pick up oxidative metal in the fuel compositions in which they are used. In other embodiments, the additives described above may have no impact on the metal pick-up properties of the fuel composition in which they are used. In either case, the additive compositions and methods of the present invention can counter the potential effect of these additives and reduce the tendency of fuel compositions to pick-up metals, whether that tendency is caused, exacerbated by, or not significantly changes by, the additional performance additives described above.

Industrial Application

[0086] In one embodiment the invention is useful for a liquid fuel and/or for the operation of an internal combustion engine, including either compression ignition engines or spark ignited engines. The internal combustion engine includes 2-stroke or 4-stroke engines fuelled with gasoline, diesel, a natural gas, a mixed gasoline/alcohol or any of the fuels described in the sections above. The compression ignition engines include both light duty and heavy duty diesel engines. The spark ignited engines include port and direct injection gasoline engines.

[0087] In other embodiments the invention is useful in additive compositions in that the fuel additive and methods described above reduce metal pick-up in fuel compositions, thus preventing elevated levels of metals, such as zinc, in the fuel.

[0088] In still other embodiments the additive compositions of the present invention may be used in a lubricating composition such that the additives are present in the lubricating system of the engine. The additives may also enter the combustion chamber of the engine during operation of the engine by the transfer of small amounts of the additive containing lubricating composition to the combustion chamber due to a phenomenon referred to as "blow by" where the lubricating composition, and in this case the additive composition, pass around the piston heads inside the cylinder, moving from the lubricating system of the engine into the combustion chamber.

[0089] In some embodiments the methods and/or compositions of the present invention provide a reduction in metal pick-up of at least 5%, at least 20% or even at least 50%. In some of these embodiments the reduction is in regards to the 7 day and/or 14 day result of the test procedure used in the examples below. In other embodiments the methods and/or compositions of the present invention ensure the metal level of a fuel composition does not rise above 10 ppm, 5 ppm, 1 ppm. 0.5 ppm, 0.3 ppm or even 0.1 ppm of metal content. In some of these embodiments the reduction is in regards to the 7 day and/or 14 day result of the test procedure used in the examples below. In some embodiments, the methods and/or compositions of the present invention, when evaluated at 7 days by the test described in the examples below, provide a reduction in metal levels of at least 30%, or at least 80% and/or ensure metal levels to not rise above 1 ppm. In some embodiments, the methods and/or compositions of the present invention, when evaluated at 14 days by the test described in the examples below, provide a reduction in metal levels of at least 40%, or at least 80% and/or ensure metal levels to not rise above 8 ppm, or even 1 ppm.

[0090] The present invention includes the use of the substituted hydrocarbon and/or hydrocarbyl substituted acylating agents described herein as additives in fuel compositions, as well as the additive itself and the fuel and fuel additive compositions containing said additive. The additives of the present invention may be delivered to the fuel compositions and/or fuel additive compositions in any of the means known in the art and the timing of the additive is not limited. In other words, the additive of the present invention may be added to a fuel composition before, during, or after the production and/or blending of the fuel and/or additive composition. The additive of the invention may be added to fuel and/or additive composition before, during, or after the addition of other performance additives which may be used in the compositions. The additive of the invention may be added as a top treat to fuel and/or additive compositions or be incorporated into the production and/or distribution of the fuel and/or additive compositions in which it is used.

[0091] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include: hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form a ring); substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy); hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms include sulfur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, preferably no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

[0092] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. For instance, metal ions (of, e.g., a detergent) can migrate to other acidic or anionic sites of other molecules. In addition the acylating agents and/or substituted hydrocarbon additives of the present invention may form salts or other complexes and/or derivatives, when interacting with other components of the compositions in which they are used. The products formed thereby, including the products formed upon employing the composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses the composition prepared by admixing the components described above.

EXAMPLES

[0093] The invention will be further illustrated by the following examples, which sets forth particularly advantageous embodiments. While the examples are provided to illustrate the present invention, they are not intended to limit it.

[0094] Example Set 1 - Fuel treated with a succinimide dispersant. An EU certification diesel fuel, known as RF-06, is treated with 200 ppm of a commercially available succinimide dispersant. Seven 500 ML graduated cylinder are prepared for testing by placing in each a 4 cm section of a Goodfellow Zn rod ZN007902, having a length of 200 mm and a diameter of 2.0 mm. The weight of each rod section is recorded and an amount of fuel is added to each cylinder so that the combined mixture of fuel composition and zinc rod is 1 % by weight zinc. Each cylinder is charged with a slightly different amount of fuel to ensure the zinc content of each sample is the same. One of the seven samples (1-1) is kept as a baseline. The other seven samples (1-2 to 1-7) are each independently treated at 200 ppm with an additional additive, as shown the in the table below.

Table 1 - Additional Additives Added to Test Samples

Sample	*Additional Additive (at 200 ppm in the Fuel)*
1-1	None - Baseline
1-2	~1000 MW Hydrolyzed PIBSA - Hydrolyzed polyisobutylene succinic anhydride wherein the polyisobutylene has a number average molecular weight of about 1000.
1-3	~550 MW PIBSA - Polyisobutylene succinic anhydride wherein the polyisobutylene has a number average molecular weight of about 550.
1-4	Pentasize 68F - A commercially available succinic anhydride derived from C16-C18 polyolefin.
1-5	Dimer Acid (hydrogenated) - A commercially available acid product containing two carboxyl groups, purchased from Aldrich under catalog ID 432369-1L.
1-6	~1000 MW PIBSA - Polyisobutylene succinic anhydride wherein the polyisobutylene has a number average molecular weight of about 1000, which is not hydrolyzed
1-7	~1000 MW Mono Esterified PIBSA - Esterified polyisobutylene succinic anhydride wherein the polyisobutylene has a number average molecular weight of about 1000, which is not hydrolyzed, and which is esterified with 1 equiv of n-butanol.

[0095] The containers are stored at ambient conditions in a dark test location for 14 days. Each sample is tested at the 7 day mark and the 14 day mark by Inductively Coupled Plasma (ICP) analysis to determine zinc content. The results of Example Set 1 are summarized in the table below.

Table 2 - Results from Example Set 1.

Sample	Additional Additive (at 200 ppm in the Fuel)	Zinc Level (ppm) at 7 Days	Zinc Level (ppm) at 14 Days
1-1	None - Baseline	0.6	1.3
1-2	~1000 MW Hydrolyzed PIBSA	0.1	0.1

(continued)

Sample	Additional Additive (at 200 ppm in the Fuel)	Zinc Level (ppm) at 7 Days	Zinc Level (ppm) at 14 Days
1-3	~550 MW PIBSA	0.1	0.1
1-4	Pentasize 68F	0.0	0.1
1-5	Dimer Acid (hydrogenated)		
1-6	~1000 MW PIBSA	0.1	0.1
1-7	~1000 MW Mono Esterified PIBSA	0.4	0.8

[0096] Example Set 2 - Biodiesel. Example set 1 is repeated except that the succinimide dispersant treated diesel fuel is replaced with B100, a commercially available biodiesel fuel. In addition, each additional additive in samples 2-2 to 2-7 are present in the fuel composition at 500 ppm. Samples 2-1 to 2-7 are tested in the same manner described above and the results are summarized in the table below.

Table 3 - Results from Example Set 2.

Sample	Additional Additive (at 500 ppm in the B100)	Zinc Level (ppm) at 7 Days	Zinc Level (ppm) at 14 Days
2-1	None - Baseline	1.5	1.7
2-2	~1000 MW Hydrolyzed PIBSA	0.2	0.3
2-3	~550 MW PIBSA	0.3	0.3
2-4	Pentasize 68F	0.2	0.2
2-5	Dimer Acid (hydrogenated)	0.5	0.8
2-6	~1000 MW PIBSA		
2-7	~1000 MW Mono Esterified PIBSA	3.0	3.8

[0097] Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." Unless otherwise indicates all percent values and ppm values herein are weight percent values and/or calculated on a weight basis. Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent, which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements. As used herein, the expression "consisting essentially of" permits the inclusion of substances that do not materially affect the basic and novel characteristics of the composition under consideration.

[0098] In addition, all the embodiments described above have been contemplated as to their use, both alone and in combination, with all of the other embodiments described above, and these combinations are considered to be part of the present invention. The specific embodiments of amines and alcohols described above have been contemplated in combination with the specific embodiments of the carboxylic acids useful in the present invention.

[0099] Various preferred features and embodiments of the present invention will now be described with reference to the following numbered paragraphs (paras).

1. A method of reducing the amount of oxidative metals pick-up in a fuel composition wherein the method comprises: adding to the fuel composition an additive comprising a hydrocarbon substituted with at least two carboxy functionalities in the form of acids or at least one carboxy functionality in the form an anhydride.

2. The method of para 1 wherein the substituted hydrocarbon is a hydrocarbyl substituted acylating agent has diacid functionality.

3. The method of para 1 wherein the substituted hydrocarbon is a succinic acylating agent.

4. The method of any of the paras 1 to 3 wherein the oxidative metal, for which pick-up is being reduced, is selected from the group consisting of copper, zinc, iron, or combinations thereof.

5. The method of any of the paras 1 to 4 wherein the hydrocarbyl group of the substituted hydrocarbon comprises polyisobutylene.

6. The method of any of the paras 1 to 5 wherein the substituted hydrocarbon agent is selected from the group consisting of:

(a) hydrocarbyl substituted succinic anhydrides;
(b) hydrolyzed hydrocarbyl substituted succinic anhydrides;
(c) combinations thereof.

7. The method of para 1 wherein the fuel composition further comprises: a demulsifier, an antifoam agent, cold flow agent, a dispersant/detergent additive, or combinations thereof; and
wherein the fuel is susceptible to pick up of oxidative metals to a level greater than 0.5 ppm when left in contact for an extended period of time with solid materials containing said metal.

8. The method of para 7 wherein the dispersant/detergent additive comprises: succinimide dispersants, quaternary ammonium salts, or combinations thereof.

9. The method of any of the paras 1 to 8 wherein the fuel composition comprises diesel fuel, biodiesel or combinations thereof.

10. The method of any of the paras 1 to 9 wherein the fuel composition is a fuel additive composition.

11. The method of any of the paras 1 to 10 wherein the method also results in the reduction of injector deposits in an engine in which the fuel composition of the method is applied.

12. A fuel composition comprising:

(a) a fuel;
(b) an additive comprising a hydrocarbon substituted with at least two carboxy functionalities in the form of acids or at least one carboxy functionality in the form an anhydride; and
(c) optional additional performance additives.

13. A fuel additive composition comprising:

(a) an optional solvent;
(b) an additive comprising a hydrocarbon substituted with at least two carboxy functionalities in the form of acids or at least one carboxy functionality in the form an anhydride; and
(c) optional additional performance additives.

14. The use of a fuel additive comprising a hydrocarbon substituted with at least two carboxy functionalities in the form of acids or at least one carboxy functionality in the form an anhydride in a fuel composition to reduce the amount of oxidative metal pick-up by saidfuel composition; wherein the use optionally also reduces injector deposit formation in an engine in which the additive containing fuel composition is used.

Claims

1. Use of an additive comprising a hydrocarbon substituted with at least two carboxy functionalities in the form of acids or at least one carboxy functionality in the form an anhydride for reducing the amount of oxidative metals pick-up in a fuel composition to which the additive has been added.

2. The use of claim 1 wherein the substituted hydrocarbon is a hydrocarbyl substituted acylating agent has di-acid functionality.

3. The use of claim 1 wherein the substituted hydrocarbon is a succinic acylating agent.

4. The use of any of the claims 1 to 3 wherein the oxidative metal, for which pick-up is being reduced, is selected from the group consisting of copper, zinc, iron, or combinations thereof.

5. The use of any of the claims 1 to 4 wherein the hydrocarbyl group of the substituted hydrocarbon comprises polyisobutylene.

6. The use of any of the claims 1 to 5 wherein the substituted hydrocarbon agent is selected from the group consisting of:

   (a) hydrocarbyl substituted succinic anhydrides;
   (b) hydrolyzed hydrocarbyl substituted succinic anhydrides;
   (c) combinations thereof.

7. The use of claim 1 wherein the fuel composition further comprises a detergent/dispersant additive which is a quaternary salt comprising the reaction product of:

   (i) at least one compound selected from the group consisting of:

      (a) the condensation product of a hydrocarbyl-substituted acylating agent and a compound having an oxygen or nitrogen atom capable of condensing with said acylating agent and said condensation product further having a tertiary amino group;
      (b) a polyalkene-substituted amine having at least one tertiary amino group; and
      (c) a Mannich reaction product having a tertiary amino group, said Mannich reaction product being prepared from the reaction of a hydrocarbyl-substituted phenol, an aldehyde, and an amine; and

   (ii) a quaternizing agent suitable for converting the tertiary amino group of compound (i) to a quaternary nitrogen, wherein the quaternizing agent is selected from the group consisting of dialkyl sulfates, benzyl halides, hydrocarbyl substituted carbonates; hydrocarbyl epoxides in combination with an acid or mixtures thereof.

8. The use of claim 1 wherein the fuel composition further comprises:

   a demulsifier, an antifoam agent, cold flow agent, a dispersant/detergent additive, or combinations thereof; and wherein the fuel is susceptible to pick up of oxidative metals to a level greater than 0.5 ppm when left in contact for an extended period of time with solid materials containing said metal.

9. The use of claim 7 or claim 8 wherein the dispersant/detergent additive comprises: succinimide dispersants, quaternary ammonium salts, or combinations thereof.

10. The use of claim 9 wherein the dispersant is a quaternary ammonium salt of a succinimide dispersant.

11. The use of any of the claims 1 to 10 wherein the fuel composition comprises diesel fuel, biodiesel or combinations thereof.

12. The use of any of the claims 1 to 11 wherein the fuel composition is a fuel additive composition.

13. The use of any of the claims 1 to 12 wherein the use also results in the reduction of injector deposits in an engine in which the fuel composition of the use is applied.

14. The use of a fuel additive comprising a hydrocarbon substituted with at least two carboxy functionalities in the form of acids or at least one carboxy functionality in the form an anhydride in a fuel composition to reduce the amount of oxidative metal pick-up by said fuel composition; wherein the use optionally also reduces injector deposit formation in an engine in which the additive containing fuel composition is used.

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EUROPEAN SEARCH REPORT

Application Number
EP 18 21 1764

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	GB 1 439 899 A (WESTVACO CORP) 16 June 1976 (1976-06-16) * page 1, line 10 - line 41; claims 1-3,7-10; example 1; table 1 * * page 1, line 64 - line 72 * * page 1, line 80 - page 2, line 3 * * page 2, line 23 - line 43 * * page 3, line 3 - line 41 * * page 3, line 60 * -----	1-14	INV. C10L1/188 C10L1/198 C10L10/04 C10L1/14 C10L10/00 ADD. C10L1/222 C10L1/2383
X	US 4 440 545 A (WEIDIG CHARLES F [US]) 3 April 1984 (1984-04-03) * column 1, line 6 - column 2, line 5; claims 1,5; example 1; table I * * column 4, line 49 - column 6, line 31 * -----	1-7,9, 12-14	
X	US 3 447 918 A (AMICK JAMES W) 3 June 1969 (1969-06-03) * the whole document * -----	1-7,9, 12-14	
X	US 3 282 836 A (MILLER JAMES R ET AL) 1 November 1966 (1966-11-01) * column 1, line 11 - line 55; claims 1-8,11,12; examples I-III; table I * * column 2, line 46 - line 48 * * column 2, line 71 - column 3, line 4 * -----	1-6,9, 12,14	**TECHNICAL FIELDS SEARCHED (IPC)** C10L
X	US 4 531 948 A (KNAPP GORDON G [US]) 30 July 1985 (1985-07-30) * column 1, line 60 - column 2, line 44; claims 1-7; table 1 * * column 3, line 23 - line 68 * ----- -/--	1-4,6-8, 12-14	

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	22 February 2019	Bacon, Alan

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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EUROPEAN SEARCH REPORT

Application Number
EP 18 21 1764

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2 334 158 A (VON FUCHS GEORGE HUGO ET AL) 9 November 1943 (1943-11-09) * column 1, line 1 - line 9; claims 1,2,5,9,10 * * column 1, line 50 - column 2, line 11 * * column 3, line 40 - column 4, line 24 * -----	1-3,6,9, 12,14	
X	WO 2004/024850 A1 (OCTEL STARREON LLC [US]; ASS OCTEL [GB]; MACMILLAN JOHN ALEXANDER [US]) 25 March 2004 (2004-03-25) * page 1, line 1 - line 19; claims 1-12,15-18,25-27 * * page 4, line 17 - line 30 * * page 5, line 4 - line 12 * * page 6, line 10 - line 13 * * page 12 - page 15 * -----	1-7,9, 12-14	
X	WO 2007/062304 A2 (NOVUS INT INC [US]; ABOU-NEMEH IBRAHIM [US]) 31 May 2007 (2007-05-31) * paragraphs [0003], [0004], [0043], [0056], [0058], [0059]; claims 1,3,4,15-18,34,35,49,50 * -----	1-3,6-9, 12-14	TECHNICAL FIELDS SEARCHED (IPC)
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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	22 February 2019	Bacon, Alan

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