ASHLESS CONTROLLED RELEASE GELS FOR FUELS

The present invention relates to a control release gel for delivery of additives to fuels where the gel compositions are free of ash producing components, or are substantially free of ash producing components, such that the gel compositions of the present invention do not supply any ash to the fuel compositions with which they are used. Further, the invention provides for the use of such compositions in the operation of an internal combustion engine.
ASHLESS CONTROLLED RELEASE GELS FOR FUELS

FIELD OF THE INVENTION

[0001] The present invention relates to a fuel additive controlled release gel composition that release one or more fuel additives into a fuel composition, wherein the gel composition is substantially ash free to ash free, in that the gel composition and/or the components it delivers to the fuel do not result in any ash production during the operation of the engine that uses the fuel, that is, when the fuel is consumed. Furthermore, the present invention relates to gel compositions, methods of operating engines utilizing such gel compositions, and fuel conditioning devices utilizing such gel compositions, where the gel compositions release additives into a fuel without the addition of metal-containing (i.e. ash producing) components.

BACKGROUND OF THE INVENTION

[0002] It is desirable to keep fuel compositions as ashless as possible, that is free of components that contain materials, such as metals, which may result in the formation of sulfated ash. Because of this need, fuel additives must generally be low ash or ashless. Ashless fuel additives are advantageous because they protect after treatment devices and can also reduce deposit formation in internal combustion engines.

[0003] Fuel additives can degrade over time and/or become less effective due to oxidation, temperature effects, the sometimes chemically harsh environment of the fuel system during the operation of an engine or similar piece of equipment, as well as many other causes. In other cases, a fuel composition could benefit from the addition of a fuel additive during the operation of an engine, where it would be inconvenient and/or impractical and/or not feasible to add such additives to the fuel before it is supplied to the fuel system of an engine and/or before the operation of the engine begins.

[0004] The use of controlled release gel compositions is known as a means to supply additives to functional fluids such as engine oils. The use of ashless controlled release gel compositions is known as a means to supply additives to

[0005] The present invention provides for the controlled release of one or more ashless fuel additives from an ashless fuel additive gel composition to a fuel, allowing for the improved performance of the engine using said fuel, as well as the gel compositions used therein.

SUMMARY OF THE INVENTION

[0006] The present invention provides a fuel additive gel composition comprising: a) a fuel soluble dispersant; b) a fuel soluble acid selected from the group consisting of an acid formed from a polymer containing acidic groups in the backbone, a polyacidic compound, surfactants with acidic groups in the backbone, emulsifiers with acidic groups in the backbone and mixtures thereof; and c) optionally at least one additional fuel additive; wherein the gel composition is substantially free of ash producing components, and wherein the gel composition will release over time one or more of its components into a fuel composition with which it comes into contact.

[0007] The present invention further provides for fuel additive gel compositions wherein the fuel additive gel is at least 50% soluble in the fuel in which it is used, on a weight basis. In other words at least 50% of the gel itself is soluble in the fuel and less than 50% of the gel itself is insoluble in the fuel. Also includes are gel compositions which are substantially ashless and completely ashless, that is gel compositions containing only substantially ashless or ashless components and gel compositions containing only ashless components.

[0008] The present invention further provides a process for operating an internal combustion engine comprising: 1) supplying one or more fuel additive gel compositions to the fuel system of the internal combustion engine, where the fuel additive gel composition may be any of the embodiments described herein; and 2) contacting the fuel and the fuel additive gel composition during the operation of the internal combustion engine which results in a controlled release of at least one of the additives in the fuel additive gel composition to a fuel; and 3) supplying said fuel to an engine during the engine's operation.
The present invention also provides a fuel conditioning device comprising a fuel additive gel composition and a means for containing said gel composition; wherein the fuel additive gel composition may be any of the embodiments described herein; and wherein the fuel conditioning device may be placed inside and/or connected to the fuel system of an internal combustion engine. The fuel conditioning device allows for the contacting of the fuel in the fuel system with the fuel additive gel composition, during the operation of the engine as the fuel is supplied to the engine.

**DETAILED DESCRIPTION OF THE INVENTION**

The present invention provides a fuel additive gel composition that control releases one or more of its components into a fuel. The components of the gel composition are substantially ashless and/or ashless so that the gel compositions of the present invention do not supply and/or cause any ash formation in the engines that use the fuel compositions involved.

The controlled release gel comprises: a) a fuel soluble dispersant; b) a fuel soluble acid selected from the group consisting of an acid formed from a polymer containing acidic groups in the backbone, a polyacidic compound, surfactants with acidic groups in the backbone, emulsifiers with acidic groups in the backbone and mixtures thereof; and c) optionally at least one additional fuel additive.

The additive composition is in the form of a gel. The composition is a mixture of an ashless dispersant and an acid when combined form a gel. The controlled release gel is substantially free of ash producing components and in another embodiment has the absence of ash producing components.

Gels are materials that comprise mixtures of two or more substances and which exist in a semi-solid state more like a solid than a liquid. A gel exists in a semi-solid state more like a solid than a liquid, see Parker, Dictionary of Scientific and Technical Terms, Fifth Edition, McGraw Hill, © 1994. See, also, Larson, "The Structure and rheology of Complex Fluids", Chapter 5, Oxford University Press, New York, New York, © 1999, each which is incorporated herein by reference. The rheological properties of a gel can be measured by small amplitude oscillatory shear testing. This technique measures the structural character of the gel and produces a term called the storage modulus which represents storage of elastic energy and the
loss modulus which represents the viscous dissipation of that energy. The ratio of the loss modulus/storage modulus, which is called the loss tangent, or "tan delta", is $\geq 1$ for materials that are liquid-like and $\leq 1$ for materials that are solid-like. The additive gels have tan delta values in one embodiment of about $\leq 1$ or $\leq 0.95$, in another embodiment of about $\leq 0.75$ and in another embodiment of about $\leq 0.5$ or $\leq 0.3$.

[0014] Gel compositions can also be evaluated by using a cone penetrometer, according to ASTM D 217. The cone penetrometer (cone pen) value obtained is one measurement of the stiffness and/or firmness of a gel. In one embodiment the fuel additive gel compositions of the present invention have a cone pen value of 300 or less, 200 or less, or from 30 to 200, or from 40 to 165.

[0015] The fuel additive gel compositions of the present invention comprise at least two additives that when combined, form a gel. In some embodiments the fuel additive gel is formed by combining a substantially ashless dispersant and a substantially ashless acid to form a gel. In one embodiment, the additive gel does not contain any ash containing detergents including, but not limited to, over based metal sulfonated detergents. In one embodiment, the gel is formed by combining an acid and an ashless succinimide dispersant. In one embodiment, the ratio of the ashless dispersant to the acid is from about 1:100 to about 100:1, in another embodiment from about 1:50 to about 50:1, or from 10:1 to about 1:10 or from 5:1 to about 1:5.

[0016] The Fuel Soluble Dispersant. Suitable fuel soluble dispersant includes additives that may generally be referred to as dispersants or detergents. Often dispersant additives are referred to as detergents when used in fuel applications. In the present invention, the fuel soluble dispersant includes both additives generally referred to as dispersants and well as fuel additives generally referred to as detergents. The dispersant component of the present invention may include Mannich dispersants, polymeric dispersants, carboxylic dispersants, amine dispersants, and combinations and mixtures thereof. Suitable dispersants are substantially ashless to completely ashless, where ashless refers to the lack of any ash producing components or groups. In one embodiment the dispersant is polyisobutylene succinimide dispersant.
Suitable dispersants are also soluble in the fuel composition with which the gel composition is to be used. In some embodiments the dispersant is soluble in one or more of the fuels described herein. In some embodiments the dispersant is soluble in gasoline, diesel fuel, biofuels, or combinations thereof. The term "fuel soluble" as used herein, is described in more detail below.

Ashless type dispersants are characterized by a polar group attached to a relatively high molecular weight hydrocarbon chain. Typical ashless dispersants include N-substituted long chain alkenyl succinimides, having a variety of chemical structures including typically:

\[
\begin{align*}
R^1 & \quad [R_2NH]_x - C_2H_4 - NH_3 \\
& \quad \text{and/or}
\end{align*}
\]

wherein each R¹ is independently an alkyl group, frequently a polyisobutylene group, with a molecular weight of 500-5000, and R² are alkenylene groups, commonly ethylene (C₂H₄) groups. Succinimide dispersants are more fully described in U.S. Patent 4,234,435 which is incorporated herein by reference. The dispersants described in this patent are particularly effective for producing a gel in accordance with the present invention.

In some embodiments the ashless dispersant component is an ashless dispersant such as a polyisobutylene succinimide and the like. Polyisobutylene succinimide ashless dispersants are commercially available products which are typically made by reacting together polyisobutylene having a number average molecular weight ("Mn") of about 300 to 10,000 with maleic anhydride to form polyisobutylene succinic anhydride ("PIBSA") and then reacting the product so obtained with a polyamine typically containing 1 to 10 ethylene amino groups per molecule. The dispersant so obtained is typically formed from a mixture of different compounds and can be characterized by a variety of different variables including the
degree of its amine substitution (i.e., the ratio of the equivalents of amino groups to carboxylic groups, or the N:CO ratio), its maleic anhydride conversion level (i.e., its molar ratio of anhydride to PIB within the structure of the PIBSA, as defined in U.S. Patent 4,234,435, incorporated herein by reference), the Mn of its PIB group, and its mode of preparation (thermal assisted succination vs. Cb-assisted succination). Analogous compounds made with other polyamines (e.g. polypropenyl) can also be used. Ashless dispersants of this type are described, for example, in U.S. Patent 4,234,435, which is incorporated herein by reference.

[0020] Normally, the N:CO ratio of these polyisobutylene succinimide ashless dispersants will be about 0.6 to 1.6 more typically about 0.7 to 1.4 or even 0.7 to 1.2. In addition or alternatively, the maleic anhydride conversion level of these polyisobutylene succinimide ashless dispersants will normally be at least about 1.3, more typically at least 1.5 or even 1.6 or above. In addition or alternatively, the Mn of the polyisobutylene segments of these polyisobutylene succinimide ashless dispersants are normally ≥ about 350, more typically at least 1200, at least about 1500 or even 1800 or above. In addition or alternatively, these polyisobutylene succinimide ashless dispersants are also made using Cb-assisted succination rather than thermal assisted succination, since this produces PIBSAs of higher conversion than thermally produced PIBSAs (the latter known as DA or direct addition PIBSAs).

[0021] The Mannich dispersant are the reaction products of alkyl phenols in which the alkyl group contains at least about 30 carbon atoms with aldehydes (especially formaldehyde) and amines (especially polyalkylene polyamines). Mannich bases having the following general structures (including a variety of different isomers and the like) are especially interesting.

\[ \text{OH} \quad \text{CH}_2\text{-NH} \left[ R_2\text{-NH} \right]_x \text{-R}_2\text{-NH-CH}_2 \quad \text{OH} \]

and/or
Another class of ashless dispersants is nitrogen containing carboxylic dispersants. Examples of these "carboxylic dispersants" are described in Patent U.S. Patent 3,219,666.

Amine dispersants are reaction products of relatively high molecular weight aliphatic halides and amines, preferably polyalkylene polyamines. Examples thereof are described, in U.S. Patent 3,565,804.

Polymeric dispersants are interpolymers of oil-solubilizing monomers such as decyl methacrylate, vinyl decyl ether and high molecular weight olefins with monomers containing polar substituents, e.g., amino alkyl acrylates or acrylamides and poly-(oxyethylene)-substituted acrylates. Examples of polymer dispersants thereof are disclosed in the following U.S. Patents: 3,329,658 and 3,702,300.

Dispersants can also be post-treated by reaction with any of a variety of agents. Among these are urea, thiourea, dimercaptothiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, and phosphorus compounds.

The ashless dispersants described herein may be used alone or in combination. The dispersant component may be present in a range from about 0.001 wt % to about 99.5 wt %, 0.01% to 50%, or 0.05% to 25%. In other embodiments the dispersant may be present in the range from about 1 wt% to about 70 wt% gel, or from about 5 wt% to about 50 wt% total weight of the gel.

The Acid Component. The acid component may include a polymer containing acidic groups in the backbone, for example, polymers derived from styrene and maleic anhydride, polymers derived from acrylates including acrylic acid, acrylic acid esters, methacrylic acid and its esters, polymers derived from high molecular weight (Cn wherein n ≤ 12) esters and acids, polymers derived from esterified maleic anhydride styrene copolymers, polymers derived from maleic anhydride and alpha olefins which may also partially esterified, polymers derived from MAA-grafted esterified ethylene propylene diene monomer copolymer; surfactants with acidic groups in the backbone; emulsifiers with acidic groups in the
backbone; polyacidic compounds, for example, polyacidic surfactants and/or polyacidic dispersants; functionalized derivatives of each component listed herein and mixtures thereof.

[0028] In one embodiment, the acid is formed from the polymerization of styrene and maleic anhydride. In one embodiment, the copolymer is partially esterified with one or more C₆ to C₃₂ alcohol or mixture of alcohols and in another embodiment C₈ to C₃₈ alcohols. The equivalent ratio of alcohol to acid groups is from about 0.1 wt% to about 0.99 wt% and in another embodiment about 0.45 wt% to about 0.95 wt%. In one embodiment, the polyacidic surfactants include a maleinated OCP (olefin copolymer of ethylene and propylene). In another embodiment the acid is a maleinated copolymer of an alpha-olefin and/or a copolymer of a maleinated alpha olefin. In another embodiment, the polyacidic surfactants include polyisobutylene disuccan, from the reaction of polyisobutylene and maleic anhydride. In one embodiment, the polyacidic dispersants include a succinimide resulting from reaction of <1 equivalent of an ethylene diamine polyamine with the maleinated OCP. In another embodiment, the polyacidic dispersants include a succinimide resulting from reaction of <1 equivalent of an ethylene diamine polyamine with polyisobutylene disuccan. The TAN is ≥ 1, in another embodiment the TAN is ≥ 3 (e.g. KOH/g and the oil blend viscosity at about 10% oil is 75 cSt at IOOC and in another embodiment IocSt at 100°C. In one embodiment, the acid must have residual acid groups with a total acid number ≥ 1 and in another embodiment ≥ 3.

[0029] Suitable acids are also soluble in the fuel composition with which the gel composition is to be used. In some embodiments the acid is soluble in one or more of the fuels described herein. In some embodiments the acid is soluble in gasoline, diesel fuel, biofuels, or combinations thereof. The term "fuel soluble" as used herein, is described in more detail below.

[0030] The acids can be used alone or in combination. The acid component may be present in a range from about 0.01 wt % to about 99.5 wt%, 0.1% to 75%, or 1% to 50%. In other embodiments the acid component is present from about 0.1 wt% to about 90 wt%, or about 1 wt% to about 80 wt%.
[0031] **Optional Additional Fuel Additives.** Typically, the fuel additive gel composition further contains at least one additional additive for controlled release into the fuel. These additional additive may include viscosity modifiers, friction modifiers, ashless detergents, cloud point depressants, pour point depressants, demulsifiers, flow improvers, antistatic agents, ashless dispersants other than those described in component (a), ashless antioxidants, antifoams, corrosion/rust inhibitors, extreme pressure/antiwear agents, seal swell agents, lubricity aids, antimisting agents, and mixtures thereof; resulting in a controlled release gel that over time releases the optional additional additives into the fuel when the fuel additive gel composition is contacted with the fuel. The optional additional additive component may be present in a range from about 0 wt% to about 95 wt %, 30% to 95%, or 40% to 95% of the total weight of the gel.

[0032] Additional performance additives can be added to a fuel composition, via the gel compositions of the present invention, and these additive may be selected depending on several factors, which 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.

[0033] 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.

[0034] 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 a benzotriazole; and/or a valve seat recession additive such as an alkali metal sulfosuccinate salt.
[0035] Suitable antifoams also include organic silicones such as polydimethyl siloxane, polyethylsiloxane, polyacrylates and polyacrylamides, trimethyl-trifluoro-propylmethyl siloxane and the like.

[0036] 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.

[0037] 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 its structure. Examples of a suitable branched alcohols used to prepare these friction modifiers include 2-ethylhexanol, isotridecanol, Guerbet alcohols, or mixtures thereof.

[0038] The additional performance additives may comprise one or more of the dispersants described above, with the understanding that such a dispersant, present as an additional fuel additive, would be different from the one or more dispersants that make up the component described above.

[0039] 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-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 an alkylphenol agent for example dialkyl sulfates,
benzyl halides, hydrocarbyl substituted carbonates; hydrocarbyl epoxides in combination with an acid or mixtures thereof.


[0041] Suitable antifoams include organic silicones such as poly dimethyl siloxane, poly ethyl siloxane, polydiethyl siloxane, polyacrylates and polymethacrylates, trimethyl-trifluoro-propylmethyl siloxane and the like.

[0042] Suitable anti-misting agents include very high (>100,000Mn) polyolefms such as 1.5 Mn polyisobutylene (for example the material of the trades name Vistanex®), or polymers containing 2-(N-acrylamido), 2-methyl propane sulfonic acid (also known as AMPS®), or derivatives thereof, and the like.

[0043] Suitable corrosion inhibitors include alkylated succinic acids and anhydrides derivatives thereof, organo phosphonates and the like.

[0044] Ashless metal deactivators include derivatives of benzotriazoles such as tolyltriazole, N,N-bis(heptyl)-ar-methyl 1H-benzotriazole- 1-methanamine, N,N-bis(nonyl)-ar-methyl 1H-Benzotriazole- 1-methanamine, N,N-bis(decyl)ar-methyl 1H-Benzotriazole- 1-methanamine, N,N-(undecyl)ar-methyl 1H-benzotriazole- 1-methanamine, N,N-bis(dodecyl)ar-methyl 1H-Benzotriazole- 1-methanamine N,N-bis(2-ethylhexyl)-ar-methyl 1H-Benzotriazole- 1-methanamine and mixtures thereof. In one embodiment the metal deactivator is N,N-bis(l-ethylhexyl)ar-methyl 1H-benzotriazole-1-methanamine; 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles;2-alkyldithiobenzothiazoles; 2-N,N-dialkyldithiocarbamoyl)benzothiazoles;2,5-bis(alkyl-dithio)-1,3,4-thiadiazoles such as 2,5-bis(tert-octyldithio)-1,3,4-thiadiazole 2,5-bis(tert-nonylldithio)-1,3,4-thiadiazole, 2,5-bis(tert-decyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-dodecyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-dodecyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-tridecyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-tetradecyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-octadecyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-nonadecyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-eicosyldithio)-1,3,4-thiadiazole and mixtures thereof; 2,5-bis(N,N-
dialkyldithiocarbamoyl)-1,3,4-thiadiazoles; 2-alkydithio-5-mercapto thiadiazoles; and the like.

Demulsifiers include polyethylene and polypropylene oxide copolymers and the like. The demulsifiers may be used alone or in combination.

Lubricity aids include glycerol monooleate, sorbitan monooleate and the like. Lubricity additives also include additives with an acid functionality as well as the ester and amide derivatives thereof, where suitable agents often contain from 8 to 50 carbon atoms. The lubricity additives may be used alone or in combination. Flow improvers include ethylene vinyl acetate copolymers and the like.

Cloud point depressants and pour point depressants include alkylphenols and derivatives thereof, ethylene vinyl acetate copolymers, fumarate vinyl acetate copolymers, and the like.

Seal swell agents include organo sulfur compounds such as thiophene, 3-(decyloxy)tetrahydro-l, 1-dioxide, phthalates and the like.

Optionally, other components can be added to the fuel additive gel compositions, including fuels, base stock oils, inert carriers, dyes, bacteriostatic agents, solid particulate additives, and the like so long as these components do not prevent gel formation and/or have an undesired effect on the gel.

The Fuel. The fuels with which the fuel additive gel compositions of the present invention may be used are not overly limited, so long as the components of the gel composition are sufficiently fuel soluble. In some embodiments all components of the gel composition must be at least somewhat fuel soluble. In other embodiments all gel components must be substantially fuel soluble. In other embodiments, the gel composition itself must be at least somewhat, or substantially fuel soluble. In still other embodiments, both the components of and resulting gel composition must be at least somewhat, or substantially fuel soluble. In some embodiments the fuel additive gel of the present invention is at least 50% soluble in the fuel in which it is used, on a weight basis.

The term "fuel soluble" as used herein and in the claims does not necessarily mean that all the compositions and/or components 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.

[0052] Suitable fuels are those which are useful in fueling an internal combustion engine. 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.

[0053] Fuels suitable for use with the present invention are not overly limited. Generally, suitable fuels are normally liquid at ambient conditions e.g., room temperature (20 to 30°F). The liquid fuel can be a hydrocarbon fuel, a non-hydrocarbon fuel (non-petroleum based fuel), or a mixture thereof.

[0054] 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.

[0055] 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 and/or non-esterified oils and/or fats from plants and animals such as rapeseed methyl ester and soybean methyl ester and/or vegetable oil, and nitromethane.

[0056] 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. Biodiesel fuel may also be used, including the various blends of biodiesel, including but not limited blends ranging from B100 and B99.9, to B20 and B2. 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.

[0057] 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.

[0058] Industrial Application. In one embodiment the invention provides a method for operating an internal combustion engine. The fuel additive gel composition may be delivered to the fuel from within a fuel filter or a fuel line canister, or any other means by which the gel is brought into contact with the fuel, including embodiments where the fuel is contacted with the fuel additive gel in a storage tank and is then supplied to the fuel system of the internal combustion engine it will be fueling. In other embodiments the fuel is contacted with the fuel additive gel within the fuel system of the internal combustion engine. Any container/delivery device within the fuel system may be used.

[0059] The fuel additive gel composition may be positioned within the fuel system, anywhere the gel will be in contact with the fuel including, but not limited to, the fuel tank, the fuel filter, the fuel line, the tank cap, a fuel bypass loop, a canister and/or housing and/or pocket and/or packet that is placed inside the fuel system. The fuel additive gel composition may be contained within a fuel condition device that is placed inside and/or attached to the fuel system of the engine (such as a fuel filter that contains the gel composition and/or a fuel tank cap that contains some amount of fuel composition). The gel composition may be present in one or more locations in the fuel system and different formulations of the gel composition may be used at each location.

[0060] In one embodiment, the gel is positioned anywhere in a fuel filter. The filter is a desirable location to place the gel because the gel and/or spent gel can
easily be removed, and then replaced with a new and/or recycled gel at the same
time the fuel filter is replaced.

[0061] The gel needs to be in contact with the fuel, in one embodiment the gel is
in contact with the fuel in the range of about 100% to about 1%, about 75% to about
25%, of the fuel system, on a volume basis and/or a fuel flow rate basis. In another
embodiment the gel is in contact with the fuel in the range of about 50% of the fuel
system on a volume and/or fuel flow rate basis.

[0062] The release rate of the fuel additive components from the gel to the fuel
is determined primarily by the gel formulation. The release rate is also dependent on
the form of the gel and/or the mode of addition. The gel may be positioned in a
location desirable for the specified and desirable dissolution rate of the specified
additives. The gel's formulation may be composed of one or more components that
selectively dissolve completely into the fuel, or partially such that a portion of the
components remains till the end of its service life, or combinations thereof.

[0063] The gel is added to the fuel system by any known method depending on
the desired form of the gel, the desired speed of addition, the desired release rate, the
desired mode of operation and/or any of the combinations of the above. In one
embodiment the additive composition is a gel and is added to the fuel system by
means of an injector pump, or a container in the fuel filter, or an in-line canister
installed on the fuel line between the fuel tank and the engine. In one embodiment
the gel is added to the fuel system by means of an addition device such as an auger
system.

[0064] In one embodiment the properties imparted by the fuel additives
delivered to the fuel include dispersancy, antioxidance, corrosion inhibition, wear
prevention, scuffing prevention, pitting prevention including micro and macro
pitting, friction modifying properties including increased and/or decreased friction
coefficients, detergency, pour point control using viscosity modifiers, foam control
or mixtures thereof.

[0065] 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 sulfoxyl); 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.

[0066] 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. 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.

**SPECIFIC EMBODIMENTS**

[0067] 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.

[0068] Various ashless fuel additive gel compositions are prepared by mixing the components listed for each example in the table below, where the values in the
table are PBW. Each mixture is held at 100 degrees C for at least 1 hour, but no more than 8 hours, to allow the mixture to cure and form a gel.
Table 1 - Gel Composition Formulations of Examples in PBW.

<table>
<thead>
<tr>
<th>Component</th>
<th>Ex 1</th>
<th>Ex 2</th>
<th>Ex 3</th>
<th>Ex 4</th>
<th>Ex 5</th>
<th>Ex 6</th>
<th>Ex 7</th>
<th>Ex 8</th>
<th>Ex 9</th>
<th>Ex 10</th>
<th>Ex 11</th>
<th>Ex 12</th>
<th>Ex 13</th>
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<td>20</td>
<td>25</td>
<td>30</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOFA²</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>52.5</td>
<td>55</td>
<td>57.5</td>
<td>60</td>
<td>65</td>
<td>70</td>
<td>62.5</td>
<td>50</td>
<td>40</td>
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<tr>
<td>Ethomeen T/12³</td>
<td>12.5</td>
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<td>25</td>
<td>30</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>MSC Copoly⁴</td>
<td>62.5</td>
<td>50</td>
<td>40</td>
<td>32</td>
<td>38</td>
<td>36</td>
<td>34</td>
<td>32</td>
<td>28</td>
<td>24</td>
<td>30</td>
<td>40</td>
<td>48</td>
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<td>Dispersant³</td>
<td>12.5</td>
<td>10</td>
<td>10</td>
<td>8</td>
<td>9.5</td>
<td>9</td>
<td>8.5</td>
<td>8</td>
<td>7</td>
<td>6</td>
<td>7.5</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>% Actives⁶</td>
<td>25</td>
<td>40</td>
<td>50</td>
<td>60</td>
<td>52.5</td>
<td>55</td>
<td>57.5</td>
<td>60</td>
<td>65</td>
<td>70</td>
<td>62.5</td>
<td>50</td>
<td>40</td>
</tr>
<tr>
<td>Cone Pen⁷</td>
<td>42</td>
<td>50</td>
<td>65</td>
<td>85</td>
<td>71.5</td>
<td>79.5</td>
<td>91.5</td>
<td>61</td>
<td>75</td>
<td>120</td>
<td>165</td>
<td>105</td>
<td>65</td>
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</tbody>
</table>

1 - Glycerol Oleate is also known as Glycerol Monooleate.
2 - TOFA is Tall Oil Fatty Acid.
3 - Ethomeen T/12 is a commercially available surfactant available from Akzo Nobel.
4 - MSC Copolymer is a maleic anhydride/styrene copolymer partially esterified with a mixture of C16-18 alcohols, containing 40% mineral oil.
5 - The Dispersant is an ashless dispersant made from 2000 number average molecular weight DA PIBSA and Methylene tetraamine.
6 - The percent actives is the percent by weight of the gel composition that is not part of the gel matrix, that is the percent of the additives present which do not interact to form a gel but rather are contained within the gel and are released to the fuel during use of the composition.
7 - Cone penetrometer values are measured by ASTM D217 using a A pen and reported in tenths of millimeters, unadjusted for scale. Cone penetrometer values cannot be obtained for liquids.

[0069] Two comparative examples are prepared, using the same components as described above, but these examples do not form gel compositions, even after being cured for up to either hours at 100 degrees C. The compositions are viscous liquids.

Table 2 - Gel Composition Formulations of Comparative Examples in PBW.

<table>
<thead>
<tr>
<th>Component</th>
<th>Comp Ex1</th>
<th>Comp Ex2</th>
</tr>
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<tbody>
<tr>
<td>Glycerol Oleate¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOFA²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethomeen T/12³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MSC Copoly⁴</td>
<td>16</td>
<td>8</td>
</tr>
<tr>
<td>Dispersant³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>% Actives⁶</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cone Pen⁷</td>
<td>LIQUID</td>
<td>LIQUID</td>
</tr>
</tbody>
</table>

See footnotes for Table 1.

[0070] Examples 1 and 2 are tested to evaluate their overall solubility in fuel, by adding 1.3 grams of the gel composition to a 50 gram sample of a standard gasoline. The samples are held at 23 degrees C and stirred overnight. After the test, the following results were observed: 72% of Example 1 had dissolved into the fuel (considering the formulation, this means all 25% of the actives had been delivered to
the fuel as well as 63% of the gel matrix material); 62% of Example 2 had dissolved into the fuel (all 40% of the actives and 36% of the gel matrix material).

[0071] Examples 2, 3, 4, 9, 10 and 11 are also tested to evaluate their solubility in fuel. A small amount of the gel composition of each of the listed Examples is added to a measured amount of standard diesel fuel, forming a fuel sample that has a 1% by weight gel treatment for Examples 2, 3 and 4; and a 0.33% by weight gel treatment for Examples 9, 10 and 11. Each sample is stirred and held at 23 degrees C for 3 days. At the end of the test, all samples showed more than 50% of the gel sample had dissolved into the fuel composition and 100% of the gel had dissolves in the samples treated with Examples 4, 9 and 10.

[0072] Examples 9, 10, 11 and 12 are tested to evaluate their impact on HFRR test results. The samples are evaluated in the HFRR test for diesel fuel, ASTM D6079. Startex Chemical Diesel Fuel A was used in all testing, including a baseline run. Each fuel sample for the testing is prepared by treating the diesel fuel with 0.3 percent the gel composition of the Example. All fuel samples were prepared by mixing the fuel and gel for 3 days at 23 degrees C. In the case of the fuel sample using Example 12, the fuel is mixed with the gel during a vehicle release test. The results of the HFRR testing are summarized in the table below:

<table>
<thead>
<tr>
<th>Test Parameter</th>
<th>Baseline Diesel Fuel</th>
<th>Fuel treated w/ Example 9</th>
<th>Fuel treated w/ Example 10</th>
<th>Fuel treated w/ Example 11</th>
<th>Fuel treated w/ Example 12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg Film Thickness$^1$</td>
<td>33%</td>
<td>92%</td>
<td>89%</td>
<td>93%</td>
<td>92%</td>
</tr>
<tr>
<td>COF$^2$</td>
<td>0.322</td>
<td>0.123</td>
<td>0.132</td>
<td>0.144</td>
<td>0.193</td>
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<tr>
<td>Wear Scar$^3$</td>
<td>543</td>
<td>315</td>
<td>327</td>
<td>258</td>
<td>334</td>
</tr>
</tbody>
</table>

1 - The average film thickness is a measure of the contact resistance between the ball and the disc, determined by the HFRR software.
2 - The COF is the coefficient of friction calculated as a function of friction force/applied load.
3 - The wear scar is the diameter of the wear scar found on the ball at the end of the test, reported in microns.

[0073] The results show that the gel compositions of the present invention, when added to fuel, increase the average film thickness, reduce the coefficient of friction and reduce the wear scar, as measured by HFRR testing. The gel compositions of the present invention provide this benefit by being fuel soluble and also without adding any ash producing materials to the fuel composition.
Although only a few embodiments of the present invention have been described above, it should be appreciated that many modifications can be made without departing from the spirit and scope of the invention. All such modifications are intended to be included within the scope of the present invention, which is to be limited only by the following claims.

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.

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.
We claim:

1. A fuel additive gel composition comprising:
   a) a fuel soluble dispersant;
   b) a fuel soluble acid selected from the group consisting of an acid formed from a polymer containing acidic groups in the backbone, a polyacidic compound, surfactants with acidic groups in the backbone, emulsifiers with acidic groups in the backbone and mixtures thereof; and
   c) optionally at least one additional fuel additive;
   wherein the gel composition is substantially free of ash producing components, and wherein the gel composition will release over time one or more of its components into a fuel composition with which it comes into contact.

2. The fuel additive gel composition of claim 1 wherein the fuel additive gel is at least 50% soluble in the fuel in which it is used, on a weight basis.

3. The fuel additive gel compositions of any of the claims 1 to 2 wherein the fuel additive gel composition contains completely ashless components and wherein the weight ratio of the dispersant to the acid is about 0.01:1 to about 100:1; and wherein the gel has a tan delta value of ≤ 1.

4. The composition of any of the claims 1 to 2 wherein the dispersant is present in a range from about 0.001 wt % to about 99.5 wt %, preferably 0.01% to 50% and more preferably 0.05% to 25%; and wherein the acid is present in a range from about 0.01 wt % to about 99.5 wt%, preferably 0.1% to 75% and more preferably 1% to 50%; and wherein the optional additional additive is present in a range from about 0 wt % to about 95 wt %, preferably 30% to 95% and more preferably 40% to 95% of the total weight of the gel.

5. The composition of any of the claims 1 to 4 wherein the dispersant component comprises one or more dispersants selected from the group consisting of
Mannich dispersants, polymeric dispersants, carboxylic dispersants, amine dispersants, polyisobutylene succinimide dispersants and combinations thereof; wherein the dispersant component is fuel soluble and is substantially free of ash forming components.

6. The composition of any of the claims 1 to 5 wherein the acid component comprises an acid derived from a polymer selected from the group consisting of: polymers derived from the polymerization of styrene and maleic anhydride; polymers derived from acrylic acid; polymers derived from acrylic acid esters; polymers derived from methacrylic acid; polymers derived from methacrylic acid esters; polymers derived from high molecular weight esters and acids; partially esterified maleic anhydride styrene copolymers; polymers derived from maleic anhydride and alpha olefins and partially esterified versions thereof, polymers derived from esterified maleic anhydride grafted ethylene propylene diene monomer copolymers; a polyacidic compound; surfactants with acidic groups in the backbone; emulsifiers with acidic groups in the backbone; and combinations thereof.

7. The composition of any of the claims 1 to 6 wherein the acid component comprises an acid selected from the group consisting of: an acid formed from the polymerization of styrene and maleic anhydride; an acid formed from the partial esterification of such a copolymer with one or more C$_6$ to C$_{32}$ alcohols or a mixture of such alcohols; and combinations thereof.

8. The composition of any of the claims 1 to 7 wherein the acid has a residual acid group with a total acid number > 1, preferably 2-100, more preferably 5-50

9. The composition of any of the claims 1 to 8 further comprising one or more additional fuel additive selected from the group consisting of viscosity modifiers, friction modifiers, detergents, cloud point depressants, pour point depressants, demulsifiers, flow improvers, antistatic agents, other dispersants, antioxidants, antifoams, corrosion/rust inhibitors, extreme pressure/antiwear agents, seal swell agents, lubricity agent, antimisting agents, and mixtures thereof;
and wherein at least one fuel additive is controlled released over time into a fuel when the gel is in contact with the fuel.

10. The composition of claim 9 wherein the additional fuel additive is a friction modifier and/or a lubricity agent.

11. A process for operating an internal combustion engine comprising:
   I. supplying one or more fuel additive gel compositions to the fuel system of the internal combustion engine, where the fuel additive gel composition comprises:
      a) a fuel soluble dispersant;
      b) a fuel soluble acid selected from the group consisting of an acid formed from a polymer containing acidic groups in the backbone, a polyacidic compound, surfactants with acidic groups in the backbone, emulsifiers with acidic groups in the backbone and mixtures thereof; and
      c) optionally at least one additional fuel additive;
      wherein the gel composition is substantially free of ash producing components;
   II. contacting the fuel and the fuel additive gel composition during the operation of the internal combustion engine;
      resulting in a controlled release of at least one of the additives in the fuel additive gel composition into a fuel, where the release is substantially free of the addition of ash into the fuel; and
   III. supplying said fuel to an engine during the engine's operation.

12. The process of claim 11 wherein the fuel additive gel composition is at least 50% soluble in the fuel in which it is used, on a weight basis.

13. The process of any of the claims 11 to 12 wherein the release rate of the additive components from the gel composition to the fuel is determined by the fuel; additive gel composition formulation; and wherein the gel formulation comprises one or more additives that only partially dissolve into the fuel over time.
14. A fuel conditioning device comprising a fuel additive gel composition and a means for containing said gel composition; wherein the fuel additive gel composition comprises:

a) a fuel soluble dispersant;

b) a fuel soluble acid selected from the group consisting of an acid formed from a polymer containing acidic groups in the backbone, a polyacidic compound, surfactants with acidic groups in the backbone, emulsifiers with acidic groups in the backbone and mixtures thereof; and

c) optionally at least one additional fuel additive;

wherein the gel composition is substantially free of ash producing components;

and wherein the fuel conditioning device may be placed inside and/or connected to the fuel system of an internal combustion engine; and wherein the fuel conditioning device allows for the contacting of the fuel in the fuel system with the fuel additive gel composition, during the operation of the engine as the fuel is supplied to the engine.

15. The fuel conditioning device of claim 14 wherein the fuel additive gel composition is at least 50% soluble in the fuel in which it is used, on a weight basis.
INTERNATIONAL SEARCH REPORT

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

CIOL

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X


Further documents are listed in the continuation of Box C

See patent family annex

Date of the actual completion of the international search

29 July 2010

Date of mailing of the international search report

04/08/2010

Name and mailing address of the ISA/

European Patent Office, P B 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel (+31-70) 340-2040, Fax (+31-70) 340-3016

Authorized officer

Bork, Ana-Maria
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