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MacDuff et al.(10) **Pub. No.: US 2011/0162260 A1**(43) **Pub. Date: Jul. 7, 2011**(54) **ALCOHOL FUEL SOLUBLE ADDITIVE FOR
REMOVING DEPOSITS IN FUELING
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C10L 1/185 (2006.01)(52) **U.S. Cl. 44/385; 44/434; 44/436; 44/447**(57) **ABSTRACT**

The present invention provides a fuel additive composition comprising (a) an alkoxylate detergent, (b) a fatty acid or derivative thereof, or mixtures thereof wherein the additive composition is soluble in the fuel where the fuel is a blend of hydrocarbonaceous and nonhydrocarbonaceous fuel with a nonhydrocarbonaceous fuel content of at least 50 percent by weight. Additionally, the present invention further provides for a fuel composition comprising such an additive composition and such a fuel. The present invention also provides for a method of operating an engine and a method of reducing deposits in a fuel system by using such an additive composition and fuel blend.

ALCOHOL FUEL SOLUBLE ADDITIVE FOR REMOVING DEPOSITS IN FUELING SYSTEMS

BACKGROUND OF THE INVENTION

[0001] The present invention relates to a fuel additive concentrate, the fuel additive concentrate in an alcohol fuel, and a method for fueling an internal combustion engine, providing improved deposit control and removal of deposits, where those deposits are polymeric residues that are insoluble in the alcohol fuel.

[0002] Governments around the world are implementing the use of nonhydrocarbonaceous fuels for economic and environmental reasons. Oxygenates such as ethanol, butanol, isopropanol, methanol, methyl tert-butyl ether (MTBE) and ethyl tert-butyl ether (ETBE) in particular are gaining ground as alcohol and ether fuels of choice as they present renewable and/or environmentally friendly alternatives to petroleum based fuels such as gasoline or diesel fuel. Additionally, fuels made from alcohol feedstocks benefit the agricultural sector and therefore, have the backing of political and pricing support. These factors in combination with rises in crude oil, desire for energy independence, and fears of global warming explain the recent growth in the alcohol fuel market. Brazil has a long history of using fuel alcohol, particularly ethanol.

[0003] Alcohol fuels and alcohol blended fuels can have unique effects on engine hardware and lubricant resulting in the tendency for increased engine deposits formation, accelerated lubricant oxidation, increased wear of vital engine components, and a loss of fuel economy. Some issues have been addressed through the development of new vehicle technology, while other issues will require new inventive additives technology.

[0004] Specifically, conventional polyisobutylene (PIB) based gasoline detergents can precipitate out of alcohol fuels in a fuel system leading to problems such as fuel filter plugging and the formation of deposits in the fuel induction system. PIB detergents may be introduced into alcohol fuels or alcohol blended fuels at several points along the supply chain. One example of potential introduction is during the blending of alcohol fuels, such as E85, at a terminal. Gasoline containing high doses of PIB detergent could be inadvertently blended with the fuel or be present as a residue in fuel handling equipment leading to contamination. Another example of when gasoline, and the PIB detergents they often contain, may be introduced into alcohol fuels, is during the fueling of a flexible fuel vehicle (FFV). Such vehicles are becoming more common in the market. A consumer with a FFV could have a partial tank of PIB detergent dosed gasoline, which he or she then re-fills with an alcohol fuel such as E85, or vice versa. The result of these and other examples is the same: a significant amount of PIB detergent in an alcohol fuel or alcohol fuel blended with gasoline, which may lead to fuel system problems such as the formation of persistent deposits of a soft, sludge-like, hard or rubbery texture. Alcohol fuels alone are not capable of removing these deposits, creating a need for a means to prevent these deposits and/or remove these deposits from the engine.

SUMMARY OF THE INVENTION

[0005] It has been discovered that alcohol fuels which are additized with an alkoxylate detergent and/or a fatty acid or derivative thereof can remove deposits in fuel systems created

by PIB detergents and also change the composition of the deposits, such that the deposits are more easily removed.

[0006] The present invention solves the problems associated with alcohol fuels' tendencies for engine deposits formation and lack of ability to remove such deposits by providing fuel additives for alcohol fuels and fuel compositions that improve the alcohol fuels' ability to remove and prevent such deposits and the problems related to them.

[0007] The present invention provides a fuel composition comprising: (A) a fuel where the fuel is a liquid at room temperature comprising a blend of hydrocarbonaceous and nonhydrocarbonaceous fuel having a nonhydrocarbonaceous fuel content of at least 50 percent by weight; and (B) an additive component comprising: (i) a alkoxylate detergent; (ii) a fatty acid or derivative thereof; or (iii) combination thereof. The additive component must be soluble in the fuel blend. The present invention also includes additive concentrates containing the additive component described herein as well as the additive component itself. In some embodiments the additive compositions, additive concentrate compositions and/or fuel compositions of the present invention further comprise and antioxidant.

[0008] In some embodiments of the present invention the alkoxylate detergent comprises (a) a polyether; (b) a polyetheramine; or (c) a mixture thereof.

[0009] The present invention also provides a method of operating an internal combustion engine using the additive compositions and/or fuel compositions derived herein. The present invention further provides a method for reducing the formation of deposits and for removing deposits in engines and/or fuel systems where the deposits result from the use of hydrocarbonaceous-fuel-soluble additives and derivatives thereof in a fuel blend of hydrocarbonaceous and nonhydrocarbonaceous in such engines and/or fuel systems.

DETAILED DESCRIPTION OF THE INVENTION

[0010] Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0011] The fuel additive concentrates, fuel compositions and methods of the present invention promote engine cleanliness and deposit removal, which enables optimal engine operation. In particular, the additives, concentrates, compositions and methods of the present invention promote the prevention and/or removal of engine deposits caused by the presence of PIB-based additives in alcohol fuels and alcohol blended fuels, which enables optimal engine operation.

The Fuel

[0012] The fuel composition of the present invention may comprise a fuel additive component and/or concentrate, as described above. Suitable fuels are liquid at room temperature and are useful in fueling an engine. The fuel is normally a liquid at ambient conditions e.g., room temperature (20 to 30° C.). The fuel may be a nonhydrocarbonaceous fuel (hydrocarbon fuel), a nonhydrocarbonaceous fuel, or a mixture thereof.

[0013] The hydrocarbon fuel may be a petroleum distillate to include a gasoline as defined by ASTM specification D4814 or a diesel fuel as defined by ASTM specification D975. In one embodiment of the invention, the fuel is a gasoline, and in other embodiment, the fuel is a nonleaded gasoline. In another embodiment of this invention, the fuel is a diesel fuel. The hydrocarbon fuel may 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.

[0014] The nonhydrocarbonaceous fuel is a fuel obtained from processes other than fuel streams obtained through the refining of fossil fuels. The nonhydrocarbonaceous fuel can be obtained from fermentation processes using bio-feed stocks, such as, corn, cellulose; sugar cane; or other agricultural or natural plant sources. The nonhydrocarbonaceous fuel can be obtained synthetically from hydrocarbonaceous or nonhydrocarbonaceous ingredients. The nonhydrocarbonaceous fuel can be an oxygen containing composition, often referred to as an oxygenate, which can include an alcohol, an ether, a ketone, an ester of a carboxylic acid, a nitroalkane such as nitromethane, or a mixture thereof. The nonhydrocarbonaceous fuel can include, for example, methanol, ethanol, propanol, butanol, 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. In such embodiments the fuel most also be a different material than the fatty acid component of component B(ii) described below.

[0015] The nonhydrocarbonaceous fuel can be alcohol fuel, such as, punctilious alcohol or anhydrous alcohol or hydrous alcohol, such as, AlCool™. The nonhydrocarbonaceous fuel can be denatured ethanol (that is a blend of ethanol with a denaturant). The nonhydrocarbonaceous fuel can be denatured ethanol as defined by ASTM specification D4806. In several embodiments of this invention, the denatured ethanol can have a denaturant content on a weight basis that is 10 percent by weight, or 7 percent by weight, or 5 percent by weight, or 3 percent by weight, or 1 percent by weight, or less than 1 percent by weight or 0 percent by weight. In several embodiments the denaturant can be hydrocarbonaceous or nonhydrocarbonaceous. In one embodiment, the hydrocarbonaceous denaturant can be natural gasoline, refined gasoline, kerosene, diesel fuel, benzene or toluene. The hydrocarbonaceous denaturant can be a petroleum distillate to include a gasoline as defined by ASTM specification D4814 or a diesel fuel as defined by ASTM specification D975. In another embodiment the nonhydrocarbonaceous denaturant can be diethyl phthalate, isopropanol, phenylethyl alcohol, musk ketone, menthol, or benzyl salicylate. In several embodiments of this invention, the fuel can have an oxygenate content on a weight basis that is 15 percent by weight, or 25 percent by weight, or 50 percent by weight, or 65 percent by weight, or 70 percent by weight, or 75 percent by weight, or 85 percent by weight, or 90 percent by weight.

[0016] In an embodiment of the invention, the fuel can be an emulsion of water in a hydrocarbon fuel, a nonhydrocarbonaceous fuel, or a mixture thereof. In several embodiments of this invention, the fuel can have a water content that is up to and including 20 percent by weight, 10 percent by weight, or 5 percent by weight. In additional embodiments, the fuel of the present invention can have a water content of 20, 10, 7, 5, 3 or 1 percent by weight. In yet another embodiment, the fuel of the present invention may have a water content of less than 1 percent by weight.

[0017] In several embodiments of this invention, the fuel can have a sulfur 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. In another embodiment, the fuel can have a sulfur content on a weight basis of 1 to 100

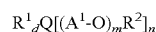
ppm. In one embodiment, the fuel contains 0 ppm to 1000 ppm, or 0 to 500 ppm, or 0 to 100 ppm, or 0 to 50 ppm, or 0 to 25 ppm, or 0 to 10 ppm, or 0 to 5 ppm of alkali metals, alkaline earth metals, transition metals or mixtures thereof. In another embodiment, the fuel contains 1 to 10 ppm by weight of alkali metals, alkaline earth metals, transition metals or mixtures thereof. It is well known in the art that a fuel containing alkali metals, alkaline earth metals, transition metals or mixtures thereof have a greater tendency to form deposits and therefore foul or plug injectors.

[0018] Suitable fuels for use in the present invention include blends of hydrocarbonaceous fuel and nonhydrocarbonaceous fuel. In one embodiment of the present of the invention the fuel is such a blend where the hydrocarbonaceous fuel comprises gasoline and the nonhydrocarbonaceous fuel comprises methanol, ethanol, butanol, or mixtures thereof. Fuel blends suitable for use in this invention include blends with a nonhydrocarbonaceous fuel content of 1 to 99 percent by weight, 20 to 95 percent by weight, 40 to 95 percent by weight, 50 to 90 percent by weight or 60 to 90 percent by weight. In one set of embodiments, the fuel blend may contain at least 35 percent by weight, at least 55 percent by weight, at least 75 percent by weight, or at least 85 percent by weight nonhydrocarbonaceous fuel. In one embodiment, the fuel blend is E85 or a similar commercial fuel.

[0019] The fuel of the invention can be present in a fuel composition in a major amount that is generally greater than 50 percent by weight, and in other embodiments is present at greater than 90 percent by weight, greater than 95 percent by weight, greater than 99.5 percent by weight, or greater than 99.8 percent by weight.

The Additive Component

[0020] In one embodiment the additive component of the present invention may comprise an alkoxyate, which may also be referred to as an alkoxyate detergent. The alkoxyates of the present invention may be represented by the formula:



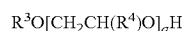
wherein, R^1 is H, $TC(O)-$, or a C_{1-36} hydrocarbyl group, wherein T is a C_{1-36} fatty acid hydrocarbyl mixture in tallow fatty acid or a fatty acid free of rosin acid; R^2 is H, $-(CH_2)_3NH_2$, $-W-NH_2$, $WC(O)-$, or mixtures thereof, wherein W is a C_{1-36} hydrocarbyl group; A^1 is a hydrocarbyl group including but not limited to $-CH_2CH(Y)-$, $-CH(Y)CH_2-$, and mixtures thereof where Y is H, $-CH_3$, $-CH_2CH_3$, or some other hydrocarbyl group; m is an integer from 1 to 50; n is an integer 1 to 3; Q can be O or N; provided that if Q is N then d can be an integer from 0 to 2 and n is the integer 3-d; if Q is O then d can be an integer 0 to 1 and n is the integer 2-d.

[0021] In one embodiment the alkoxyate of the present invention can be a (i) a polyether, (ii) a polyetheramine, or (iii) mixtures thereof. In another embodiment of the present invention the alkoxyate can be a (i) polyether containing two or more ester terminal groups or one or more ester groups and one or more terminal ether groups; or (ii) a polyetheramine comprising a polyether containing one or more ester groups and one or more terminal amino groups; or (iii) mixtures thereof. In yet another embodiment the alkoxyate of the present invention can be a polyether or polyetheramine, or mixture thereof, derived from propylene oxide or butylene oxide, or a mixture thereof.

[0022] Examples of the alkoxyate can include: C₁₂₋₁₅ alcohol initiated polypropyleneoxide (22-24) ether amine, Bayer ACTACLEAR ND21-A™ (C₁₂₋₁₅ alcohol initiated polypropyleneoxide (22-24) ether-ol), tall oil fatty acid initiated polypropyleneoxide (22-24) ester-ol, butanol initiated polypropyleneoxide (23-25) ether-tallow fatty acid ester, glycerol dioleate initiated polypropyleneoxide (23-25) ether-ol, propylene glycol initiated polypropyleneoxide (33-34) ether tallow fatty acid ester, tallow fatty acid initiated polypropyleneoxide (22-24) ester-ol and C₁₂₋₁₅ alcohol initiated polypropyleneoxide (22-24) ether tallow fatty acid ester.

[0023] These alkoxyates can be made from the reaction of a fatty acid such as tall oil fatty acids (TOFA) that is, the mixture of fatty acids predominately oleic and linoleic and contains residual rosin acids or tallow acid that is, the mixture of fatty acids predominately stearic, palmitic and oleic with an alcohol terminated polyether such as polypropylene glycol in the presence of an acidic catalyst, usually methanesulphonic acid. These alkoxyates can also be made from the reaction of glycerol dioleate and propylene oxide in the presence of catalyst.

[0024] Polyethers—The alkoxyate of the present invention may be a polyether wherein the polyether can be represented by the formula:



where R³ is a hydrocarbyl group, R⁴ is selected from the group consisting of hydrogen, hydrocarbyl groups of 1 to 16 carbon atoms, and mixtures thereof, and q is a number from 2 to 50.

[0025] Polyethers of present invention can include compounds having two or more consecutive ether groups. The polyethers of this invention can include polyoxyalkylenes having a sufficient number of repeating oxyalkylene units to render the polyoxyalkylene soluble in a normally liquid fuel, such as, in hydrocarbons boiling in a gasoline or diesel fuel range and blends of hydrocarbon fuel with non-hydrocarbon fuel such as alcohol. Generally, polyoxyalkylenes having at least 5 oxyalkylene units are suitable for use in the present invention.

[0026] The polyethers of the present invention can be prepared by condensing an alcohol or alkylphenol with an alkylene oxide, mixture of alkylene oxides or with several alkylene oxides in sequential fashion in a 1:1-50 mole ratio of hydric compound to alkylene oxide to form a polyether. U.S. Pat. Nos. 5,112,364 and 5,264,006 provide reaction conditions for preparing a polyether.

[0027] The alcohols can be monohydric or polyhydric, linear or branched, saturated or unsaturated and having 1 to 50 carbon atoms, or from 8 to 30 carbon atoms, or from 10 to 16 carbon atoms. Branched alcohols of the present invention can include Guerbet alcohols, as described in U.S. Pat. No. 5,264,006, which generally contain between 12 and 40 carbon atoms and can be represented by the formula:



where each R⁵ is an independent hydrocarbyl group. In one embodiment, the alkyl group of the alkylphenols can be 1 to 50 carbon atoms, or 2 to 24 carbon atoms, or 10 to 20 carbon atoms.

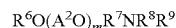
[0028] In one embodiment, the alkylene oxides include 1,2-epoxyalkanes having 2 to 18 carbon atoms, or 2 to 6 carbon atoms. In yet another embodiment, the alkylene oxides can be ethylene oxide, propylene oxide and butylene oxide. Especially useful is propylene oxide, butylene oxide,

or a mixture thereof. The number of alkylene oxide units in the polyether intermediate can be 1-50, or 12-30, or 16-28.

[0029] A commercial example of a polyether is the Lyon-dell ND® series. Other suitable polyethers are also available from Dow Chemicals, Huntsman, and ICI.

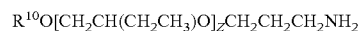
[0030] Polyetheramines—The alkoxyate of the present invention may be a polyetheramine wherein the polyetheramine can include compounds having two or more consecutive ether groups and at least one primary, secondary or tertiary amine group where the amine nitrogen has some basicity. The polyetheramines of this invention can include poly(oxyalkylene) amines having a sufficient number of repeating oxyalkylene units to render the poly(oxyalkylene)amine soluble in a normally liquid fuel, such as, in hydrocarbons boiling in a gasoline or diesel fuel range and blends of hydrocarbon fuel with non-hydrocarbon fuel. Generally, poly(oxyalkylene) amines having at least 5 oxyalkylene units are suitable for use in the present invention. Poly(oxyalkylene)amines can include: hydrocarbylpoly(oxyalkylene)amines, hydrocarbylpoly(oxyalkylene)polyamines, hydropoly(oxyalkylene)amines, hydropoly(oxyalkylene)polyamines, and derivatives of polyhydric alcohols having at least two poly(oxyalkylene) amine and/or poly(oxyalkylene)polyamine chains on the molecule of the derivative.

[0031] In one embodiment, the poly(oxyalkylene)amine for use in the invention is represented by the formula:



wherein R⁶ is a hydrocarbyl group of 1 to 50 carbon atoms, or 8 to 30 carbon atoms; A² is an alkylene group having 2 to 18 carbon atoms and preferably 2 to 6 carbon atoms; m is a number from 1 to 50; R⁷ is an alkylene group having 2 to 18 carbon atoms or preferably 2 to 6 carbon atoms; and R⁸ and R⁹ are independently hydrogen, a hydrocarbyl group or —[R'N(R'')]_nR''' wherein R' is an alkylene group having 2 to 6 carbon atoms, R'' and R''' are independently hydrogen or a hydrocarbyl group, and n is a number from 1 to 7.

[0032] In another embodiment, the poly(oxyalkylene)amine of the present invention can be represented by the formula:

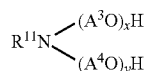


wherein R¹⁰ is an aliphatic group or alkyl-substituted phenyl group of 8 to 30 carbon atoms; and Z is a number from 12 to 30. In yet another embodiment, the poly(oxyalkylene)amine of the present invention can be represented by the formula above wherein R¹⁰ is CH₃CH(CH₃)[CH₂CH(CH₃)]₂CH(CH₃)CH₂CH₂— and Z is a number from 16 to 28. Poly(oxyalkylene)amines of the present invention can have a molecular weight in the range from 300 to 5,000.

[0033] The polyetheramines of the present invention can be prepared by using the polyethers described above as intermediates and converting them to polyetheramines. The polyether intermediates can be converted to polyetheramines by several methods. The polyether intermediate can be converted to a polyetheramine by a reductive amination with ammonia, a primary amine or a polyamine as described in U.S. Pat. Nos. 5,112,364 and 5,752,991. In one embodiment, the polyether intermediate can be converted to a polyetheramine via an addition reaction of the polyether to acrylonitrile to form a nitrile which is then hydrogenated to form the polyetheramine. U.S. Pat. No. 5,264,006 provides reaction conditions for the cyanoethylation of the polyether with acrylonitrile and the subsequent hydrogenation to form the polyetheramine. In yet another embodiment, the polyether intermediate or poly(oxyalkylene) alcohol is converted to the corresponding poly(oxy-

alkylene) chloride via a suitable chlorinating agent followed by displacement of chlorine with ammonia, a primary or secondary amine, or a polyamine as described in U.S. Pat. No. 4,247,301.

[0034] The mixed alkoxylates of the present invention may also include an alkoxylated fatty amine, which can include amines represented by the formula:



wherein R^{11} is a hydrocarbyl group having 4 to 30 carbon atoms, A^3 and A^4 are vicinal alkylene groups, and the sum of x and y is an integer that is at least 1. The hydrocarbyl group is a univalent radical of carbon atoms that is predominantly hydrocarbon in nature, but can have nonhydrocarbonaceous substituent groups and can have heteroatoms. The hydrocarbyl group R^{11} can be an alkyl or alkylene group of 4 to 30 carbon atoms, or 10 to 22 carbon atoms. The vicinal alkylene groups A^3 and A^4 can be the same or different and include: ethylene ($-\text{CH}_2-$), propylene ($-\text{CH}_2\text{CH}_2\text{CH}_2-$) and butylene ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$) having the carbon to nitrogen and carbon to oxygen bonds on adjacent or neighboring carbon atoms. Examples of alkoxylated fatty amines can include: diethoxylated tallowamine, diethoxylated oleylamine, diethoxylated stearylamine, and the diethoxylated amine from soybean oil fatty acids. Alkoxylated fatty amines are commercially available from Akzo under the Ethomeen® series.

[0035] In one embodiment, the alkoxylate detergent can be present in the fuel additive concentrate in an amount from 1 to 99 percent by weight, or 2 to 50 percent by weight, or 5 to 40 percent by weight, or 5 to 30 percent by weight, in yet another embodiment from 8 to 25 percent by weight.

[0036] In one embodiment, the alkoxylate detergent of this invention can be present in a fuel composition on a weight basis from 1 to 10,000 ppm (parts per million), and in other embodiment from 5 to 8,000 ppm, or 10 to 7000 ppm, or 20 to 5000 ppm, or 30 to 2000 ppm, or 50 to 1500, or 40 to 1000 ppm, or 40 to 650 ppm.

[0037] The additive component of this invention may further comprise one or more of the various detergents and other additives described herein. Such additives include Mannichs, succinimides, polyisobutylene amines, glyoxylates, and mixtures thereof.

[0038] Mannich detergents, sometimes referred to as a Mannich base detergents, are a reaction product of a hydrocarbyl-substituted phenol, an aldehyde, and an amine or ammonia. The hydrocarbyl substituent of the hydrocarbyl-substituted phenol can have 10 to 400 carbon atoms, in another instance 30 to 180 carbon atoms, and in a further instance 10 or 40 to 110 carbon atoms. This hydrocarbyl substituent can be derived from an olefin or a polyolefin. Useful olefins include alpha-olefins, such as 1-decene, which are commercially available. Useful polyolefins include, but are not limited to, polyisobutylene having a number average molecular weight of 140 to 5000, in another instance of 400 to 2500, and in a further instance of 140 or 500 to 1500. The polyisobutylene can have a vinylidene double bond content of 5 to 69 percent, in a second instance of 50 to 69 percent, and in a third instance of 50 to 95 percent. The hydrocarbyl-substituted phenol can be prepared by alkylating phenol with

an olefin or polyolefin described above, such as a polyisobutylene or polypropylene, using well-known alkylation methods. Aldehyde used to form the Mannich detergent can have 1 to 10 carbon atoms, and is generally formaldehyde or a reactive equivalent thereof such as formalin or paraformaldehyde. The amine used to form the Mannich detergent can be a monoamine or a polyamine, including alkanolamines having one or more hydroxyl groups, as described in greater detail above. Useful amines include ethanolamine, diethanolamine, methylamine, dimethylamine, ethylenediamine, dimethylaminopropylamine, diethylenetriamine and 2-(2-aminoethylamino) ethanol. The Mannich detergent can be prepared by reacting a hydrocarbyl-substituted phenol, an aldehyde, and an amine as described in U.S. Pat. No. 5,697,988.

[0039] Another type of detergent, which can be used in the present invention, is a succinimide. Succinimide detergents are well known in the field of lubricants and include primarily what are sometimes referred to as “ashless” detergents because they do not contain ash-forming metals and they do not normally contribute any ash forming metals when added to a lubricant. Succinimide detergents are the reaction product of a hydrocarbyl substituted succinic acylating agent and an amine containing at least one hydrogen attached to a nitrogen atom. The term “succinic acylating agent” refers to a hydrocarbon-substituted succinic acid or succinic acid-producing compound (which term also encompasses the acid itself). Such materials typically include hydrocarbyl-substituted succinic acids, anhydrides, esters (including half esters) and halides.

[0040] Yet another type of detergent, which can be used in the present invention, can be a polyisobutylene amine. The amine use to make the the polyisobutylene amine can be a polyamine such as ethylenediamine, 2-(2-aminoethylamino) ethanol, or diethylenetriamine. The polyisobutylene amine of the present invention can be prepared by several known methods generally involving amination of a derivative of a polyolefin to include a chlorinated polyolefin, a hydroformylated polyolefin, and an epoxidized polyolefin. In one embodiment of the invention the polyisobutylene amine is prepared by chlorinating a polyolefin such as a polyisobutylene and then reacting the chlorinated polyolefin with an amine such as a polyamine at elevated temperatures of generally 100 to 150° C. as described in U. S. Pat. No. 5,407,453.

[0041] Yet another type of detergent, which can be used in the present invention, is a glyoxylate. A glyoxylate detergent is a fuel soluble ashless detergent which, in a first embodiment, is the reaction product of an amine having at least one basic nitrogen, i.e. one $>\text{N}-\text{H}$, and a hydrocarbyl substituted acylating agent resulting from the reaction, of a long chain hydrocarbon containing an olefinic bond with at least one carboxylic reactant selected from the group consisting of compounds of the formula (I)



and compounds of the formula (II)



wherein each of R^1 , R^3 and R^4 is independently H or a hydrocarbyl group, R^2 is a divalent hydrocarbylene group having 1 to 3 carbons and n is 0 or 1.

[0042] Compounds and the processes for making these compounds are disclosed in U.S. Pat. Nos. 5,696,060; 5,696,067; 5,739,356; 5,777,142; 5,856,524; 5,786,490; 6,020,500; 6,114,547; 5,840,920 and are incorporated herein by reference.

The Fatty Acids or Derivates Thereof

[0043] In one embodiment the additive component of the present invention may comprise a fatty acid or derivative thereof. Derivatives of the fatty acid useful in present invention include partial and full esters of such acids as well as fatty acid amides and imides. In particular, suitable derivatives include glycerol monoesters including those derived from oleic acid, such as glycerol monooleate. The fatty acids or derivatives thereof of the present invention can have 4 to 30 carbon atoms, or 8 to 26 carbon atoms, or 12 to 22 carbon atoms. Saturated and unsaturated monocarboxylic acids are useful and include capric, lauric, myristic, palmitic, stearic, behenic, oleic, petroselinic, elaidic, palmitoleic, linoleic, linolenic and erucic acid. Typical fatty acids are those derived from natural oil typically containing C6 or C22 fatty acid esters, i.e., glycerol fatty acid esters or triglycerides derived from natural sources, for use herein include, but are not limited to beef tallow oil, lard oil, palm oil, castor oil, cottonseed oil, corn oil, peanut oil, soybean oil, sunflower oil, olive oil, whale oil, coconut oil, palm oil, rape oil, and soya oil.

[0044] These fatty acids may also be tall oil fatty acids (TOFA) or fatty acids derived from tallow that is, the mixture of fatty acids predominately oleic and linoleic, which contain residual rosin acids or tallow acid that is, the mixture of fatty acids predominately stearic, palmitic and oleic.

[0045] In another embodiment of this invention, the fatty acid can be the partial ester of a fatty carboxylic acid. The partial ester of the present invention has at least one free hydroxyl group and is formed by reacting at least one fatty carboxylic acid and at least one polyhydric alcohol.

[0046] The fatty carboxylic acid used to form the partial ester can be saturated or unsaturated aliphatic, can be branched or straight chain, can be a monocarboxylic or polycarboxylic acid, and can be a single acid or mixture of acids. The fatty carboxylic acid can have 4 to 30 carbon atoms, or 8 to 26 carbon atoms, or 12 to 22 carbon atoms. Saturated and unsaturated monocarboxylic acids are useful and include capric, lauric, myristic, palmitic, stearic, behenic, oleic, elaidic, palmitoleic, linoleic, linolenic and erucic acid.

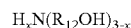
[0047] The polyhydric alcohol used to form the partial ester has two or more hydroxyl groups and includes alkylene glycols, polyalkylene glycols, triols, polyols having more than three hydroxyl groups, and mixtures thereof. Examples of polyhydric alcohols include ethylene glycol, diethylene glycol, neopentyl glycol, glycerol, trimethylol propane, pentaerythritol, and sorbitol.

[0048] The partial esters having at least one free hydroxyl group are commercially available or can be formed by a variety of methods well known in the art. These esters are derived from any of the above described fatty carboxylic acids and polyhydric alcohols or mixtures thereof. Preferred esters are derived from fatty carboxylic acids having 12 to 22 carbon atoms and glycerol, and will usually be mixtures of mono- and diglycerides, such as, a mixture of glycerol monooleate and glycerol dioleate. In one embodiment, the fatty acid of the present invention is glycerol monooleate.

[0049] Another derivative of the fatty carboxylic acid is the amide of the fatty carboxylic acid. In general, these com-

pounds are the reaction product of the natural fatty acid oils containing 6 to 22 carbon atoms and an amine. The fatty carboxylic acid of these amides can be saturated or unsaturated aliphatic, can be branched or straight chain, can be a monocarboxylic or polycarboxylic acid, and can be a single acid or mixture of acids. The fatty carboxylic acid can have 6 to 30 carbon atoms, or 8 to 26 carbon atoms, or 12 to 22 carbon atoms. Saturated and unsaturated monocarboxylic acids are useful and include capric, lauric, myristic, palmitic, stearic, behenic, oleic, petroselinic, elaidic, palmitoleic, linoleic, linolenic and erucic acid.

[0050] The amine can be an alkyl amine having from 2 to 10 carbon atoms, or 4 to 6 carbon atoms. A typical amine can be the alkanol amines. The alkanolamine used in the reaction with the fatty acid can be a primary or secondary amine, which possesses at least one hydroxy group. The alkanolamine corresponds to the general formula:



wherein R_{12} is a lower hydrocarbyl having from two to six carbon atoms and x is 1 or 2. The expression "alkanolamine" is used in its broadest sense to include compounds containing at least one primary or secondary amine and at least one hydroxy group, such as, for example, monoalkanolamines, dialkanolamines, and so forth. It is believed that almost any alkanolamine can be used, although preferred alkanolamines are lower alkanolamines having from two to six carbon atoms. The alkanolamine can possess an O or N functionality, in addition to the one amino group (that group being a primary or secondary amino group), and at least one hydroxy group. Suitable alkanolamines for use herein include: monoethanolamine, diethanolamine, propanolamine, isopropanolamine, dipropanolamine, di-isopropanolamine, butanolamines, aminoethylaminoethanols, e.g., 2-(2-aminoethylamino)ethanol, and the like with diethanolamine being preferred. It is also contemplated that mixtures of two or more alkanolamines can be employed.

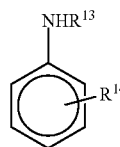
[0051] In one embodiment, the fatty acids or derivatives thereof can be present in the fuel additive concentrate in an amount from 1 to 99 percent by weight, or 2 to 50 percent by weight, or 5 to 40 percent by weight, or 5 to 30 percent by weight, in yet another embodiment from 8 to 25 percent by weight.

[0052] In one embodiment, the fatty acids or derivatives thereof can be present in a fuel composition on a weight basis from 1 to 10,000 ppm (parts per million), and in other embodiment from 5 to 8,000 ppm, or 10 to 7000 ppm, or 20 to 5000 ppm, or 30 to 2000 ppm, or 50 to 1500, or 40 to 1000 ppm, or 40 to 650 ppm.

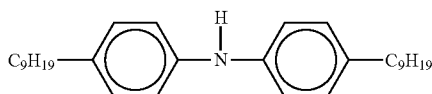
Antioxidant

[0053] In some embodiments, the present invention may also include one or more antioxidants. The antioxidants for use in the present invention are well known and include a variety of chemical types including aromatic amines, derivatized phenylene diamines and hindered phenols.

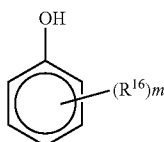
[0054] Aromatic amines are typically of the formula:



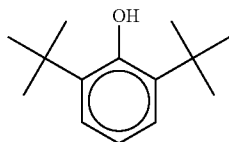
wherein R^{13} is a phenyl group or a phenyl group substituted by R^{15} , and R^{14} and R^{15} are independently a hydrogen or an alkyl group containing 1 to 24 carbon atoms. Preferably R^{13} is a phenyl group substituted by R^{15} and R^{14} and R^{15} are alkyl groups containing from 4 to 20 carbon atoms. In one embodiment, the antioxidant can be an alkylated diphenylamine, such as, nonylated diphenylamine containing typically some of the formula:



[0055] Hindered phenol antioxidants are typically alkyl phenols of the formula:

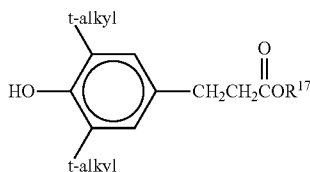


wherein R^{16} is an alkyl group containing 1 to 24 carbon atoms and m is an integer of 1 to 5. In certain embodiments, R^{16} contains 4 to 18 carbon atoms or 4 to 12 carbon atoms. R^{16} may be either straight chained or branched chained, especially branched. Suitable values of m include 1 to 4, such as 1 to 3 or, particularly, 2. In certain well-known embodiments, the phenol is a butyl substituted phenol containing 2 or 3 *t*-butyl groups. When m is 2, the *t*-butyl groups may occupy the 2,6-positions, that is, the phenol is sterically hindered:



The antioxidant can be, and typically is, further substituted at the 4-position with any of a number of substituents, such as hydrocarbyl groups or groups bridging to another hindered phenolic ring.

[0056] Also included among the antioxidants are hindered ester substituted phenols such as those represented by the formula:



wherein *t*-alkyl can be, among others, *t*-butyl, R^{17} is a straight chain or branched chain alkyl group containing 1 to 22 carbon atoms, or 2 to about 22, or 2 to 8, or 4 to 8 carbon atoms. R^3 may be a 2-ethylhexyl group or an *n*-butyl or *n*-octyl group. Hindered ester substituted phenols can be prepared by heating a 2,6-dialkylphenol with an acrylate ester under base catalysis conditions, such as, aqueous KOH.

[0057] In certain embodiment, a mixture of antioxidants are employed, such as, both a phenolic and an aromatic amine antioxidant, or mixtures thereof, or alternatively phenolic, or aromatic amine, or derivatized phenylene diamine antioxidant or mixtures thereof.

[0058] In one embodiment, the amount of antioxidant can be present in the fuel additive concentration in an amount from 1 to 99 percent by weight, or from 1 to 40 percent by weight, or from 2 to 30 percent by weight, or from 2 to 20 percent by weight.

[0059] In one embodiment, the amount of the antioxidant in the fuel composition can be present in an amount from 1 to 1000 ppm, or 1 to 5000, or 2 to 500, or 4 to 200 or 5 to 100 ppm.

Fuel Compositions and Fuel Additive Compositions

[0060] In some embodiments, the present invention is a fuel additive concentrate comprising an alkoxylate detergent, as described above, and/or a fatty acid or derivative thereof, also as described above. In other embodiments, the present invention is a fuel composition wherein the fuel composition comprise a fuel, as described above, and a fuel additive concentrate, also as described above. In any these embodiments may further comprises an antioxidant as described above. In the embodiments where the present invention is a fuel composition, the fuel additive concentrate may be present in the fuel in an amount from 1 to 10000 ppm, in another embodiment 5 to 8000 ppm, in another embodiment 10 to 5000 ppm or 20 to 5000 ppm, in yet another embodiment 100 to 4000 ppm, and in another embodiment 100 to 2000, or 150 to 2000 or 150 to 1000 ppm, all on a weight basis.

[0061] In addition, the fuel additive concentrate compositions and fuel compositions of the present invention may contain other additives that are well known to those of skill in the art. These can include corrosion inhibitors, dyes, bacteriostatic agents, auxiliary, gum inhibitors, marking agents, metal deactivators, detergents, demulsifiers, or mixtures thereof.

INDUSTRIAL APPLICATIONS

[0062] In one embodiment the present invention can be used in an internal combustion engine. The internal combustion engine includes a 2-stroke or 4-stroke engine fueled with alcohol blended fuel. The internal combustion engine includes a direct injection or spark ignited engine.

[0063] In one embodiment the present invention can be used to reduce the deposition of hydrocarbonaceous-fuel-soluble additives and derivatives in a fuel system and/or engine in which the invention is used. In one embodiment of the present invention, the deposits being reduced are the result of PIB-based detergents and other additives common in gasoline but which themselves and derivatives thereof are insoluble in nonhydrocarbonaceous fuels. The additive compositions of the present invention may be used in fuel compositions and/or in the operation of an internal combustion engine to reduce the amount of such deposits forming, aid in the removal of such deposits once they have already formed, or combinations thereof.

[0064] This use of the compositions of the present may be realized by supplying the additive component of the present invention to a fuel composition, as described above, where said fuel composition is then used in a fuel system and/or in the operation of an internal combustion engine.

[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 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 such 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.

EXAMPLES

[0067] Hot bar testing was used to evaluate the ability of a clean up material, which may be a fuel, to remove deposits left by a build up material, which may also be a fuel. In the examples summarized in the table below, the build up material is PIB-containing E85 and the clean up material is E85 containing various other materials. The test can simulate the build-up of deposits in engines from PIB-containing E85 and evaluate the ability of the clean up material to remove those deposits.

[0068] The hot bar testing equipment consists of a purpose built heated aluminum test bar. The test bar sits on an inclined gradient, heated by an electrical cartridge heater controlled by a Eurotherm controller at the lower end. The temperature along the bar ranges from 290° C. at the lower end to ~110° C. at the unheated top the end. The test bar is brought to temperature and then 50 ml of the build up fluid is dripped at approximately 0.5 ml/min on the top of the unheated and elevated end of the test bar. Once all of the build-up fluid has been dispensed, the test bar is allowed to bake for 30 minutes. After this time the test bar is allowed to cool and the build-up material cold streak is then measured. Next, the test bar is again brought to temperature and 50 ml of the clean up fluid is dispensed in the same manner. Once all of the clean up fluid has been dispensed, the test bar is allowed to bake for 30 minutes. After this time, the clean up material hot streak is measured, then the test bar is allowed to cool and the clean up material cold streak is measured.

[0069] The effectiveness of a clean up material's deposit removing ability is determined the lengths of the hot streak and the cold streak generated by the clean up material. The longer the streak generated by the clean up material, the more soluble the deposits in question are in the clean up material, and therefore, the better the clean up material is at removing said deposits.

[0070] Hot bar testing was completed on a series of fuel samples, where the build up material used in all samples was E85 ethanol additized with a PIB based detergent dosed at 1000 ppm m/m. Various clean-up materials were used, some of which represent the present invention. The table below summarizes the results:

TABLE 1

Hot Bar Test Results			
Example	Clean Up Material	Hot Streak Length (mm)	Cold Streak Length (mm)
1 (comp)	E85	93	92
2 (comp)	E85	100	108
3 (comp)	E85	107	109
4 (comp)	Gasoline	395	395
5	E85, 1000 ppm tall oil fatty acid	175	209
6	E85, 1000 ppm tall oil fatty acid	215	241
7	E85, 3200 ppm C11-C14 polyetheramine	304	332
8	E85, 3200 ppm C12-C15 propoxylated alcohol	285	408
9	E85, 3200 ppm C11-C14 polyetheramine	340	370
10	E85, 2000 ppm tall oil fatty acid	339	387
11	E85, 3200 ppm C12-C15 alkyl ethers	381	408
12	E85, 3200 ppm C12-C15 alkyl ethers	382	408
13	E85, 20000 ppm tall oil fatty acid	415	415

[0071] Comparative example 4, which uses gasoline as the clean up material, is included to show the large extent to which PIB deposits are soluble in gasoline, as represented by the high streak lengths for comparative example 4 compared to the other comparative examples, which used E85 alone, and showed significantly lower streak lengths and so solubility and deposit removal ability.

[0072] Examples 5-13 represent non-limiting embodiments of the present invention, and show significantly increased streak lengths, and so deposit removal abilities, compared to comparative examples 1-3 where E85 was used alone. The results show that the present invention, when employed in a fuel, significantly increases the ability of the fuel to remove deposits.

[0073] 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 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 oil, which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amounts,

ranges, 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.

What is claimed is:

1. A fuel composition comprising:
 - A. a fuel which is a liquid at room temperature comprising a blend of hydrocarbonaceous and nonhydrocarbonaceous fuel having a nonhydrocarbonaceous fuel content of at least 50 percent by weight; and
 - B. an additive component comprising at least one of the following:
 - (i) a alkoxyate detergent; and
 - (ii) a fatty acid or derivative thereof;
 wherein the additive component is soluble in the fuel blend.
2. A fuel composition of claim 1 wherein the alkoxyate detergent comprises (a) a polyether; (b) a polyetheramine; or (c) a mixture thereof.
3. A fuel composition of claim 1 further comprising an antioxidant.
4. The fuel composition of claim 1, wherein the hydrocarbonaceous fuel comprises gasoline and the nonhydrocarbonaceous fuel comprises methanol, ethanol, butanol, or mixtures thereof.
5. A method of fueling an internal combustion engine comprising:
 - I. supplying to the internal combustion engine a fuel composition comprising:
 - A. a fuel which is a liquid at room temperature comprising a blend of hydrocarbonaceous and nonhydrocarbonaceous fuel having a nonhydrocarbonaceous fuel content of at least 50 percent by weight; and
 - B. an additive component comprising at least one of the following:
 - (i) a alkoxyate detergent; and
 - (ii) a fatty acid or derivative thereof;
 wherein the additive component is soluble in the fuel blend.
 6. A method for reducing the deposition of hydrocarbonaceous-fuel-soluble additives and derivatives thereof from a fuel blend of hydrocarbonaceous and nonhydrocarbonaceous in a fuel system, comprising:
 - I. adding to said fuel blend, which is a liquid at room temperature, and which comprises a blend of hydrocarbonaceous and nonhydrocarbonaceous fuel with a nonhydrocarbonaceous fuel content of at least 50 percent by weight, an additive component comprising at least one of the following:
 - (i) a alkoxyate detergent; and
 - (ii) a fatty acid or derivative thereof;
 wherein the additive component is soluble in the fuel blend;
 - II. supplying said fuel blend to a fuel system.

7. An alcohol fuel additive concentrate comprising at least one of the following:

- a alkoxyate detergent; and
- (ii) a fatty acid or derivative thereof;

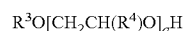
wherein the concentrate is soluble in a fuel which is liquid at room temperature and comprises a blend of hydrocarbonaceous and nonhydrocarbonaceous fuel with a nonhydrocarbonaceous fuel content of at least 50 percent by weight.

8. The additive concentrate of claim 7 wherein the alkoxyate detergent comprises (a) a polyether; (b) a polyetheramine; or (c) a mixture thereof.

9. The concentrate of claim 7 further comprising an antioxidant.

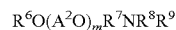
10. The additive concentrate of claim 8 wherein the alkoxyate detergent is derived from ethylene oxide, propylene oxide, butylene oxide or a mixture thereof.

11. The additive concentrate of claim 8 wherein the alkoxyate detergent comprises a polyether represented by the formula:



wherein R^3 is a hydrocarbyl group, R^4 is selected from the group consisting of hydrogen, hydrocarbyl groups of 1 to 16 carbon atoms, and mixtures thereof, and q is a number from 2 to about 50.

12. The fuel additive concentrate of claim 8 wherein the alkoxyate detergent comprises a polyetheramine represented by the formula:



wherein R^6 is a hydrocarbyl group of 1 to 50 carbon atoms, or about 8 to about 30 carbon atoms; A^2 is an alkylene group having 2 to 18 carbon atoms and preferably 2 to 6 carbon atoms; m is a number from 1 to about 50; R^7 is an alkylene group having 2 to 18 carbon atoms or preferably 2 to 6 carbon atoms; and R^8 and R^9 are independently hydrogen, a hydrocarbyl group or $-[R''N(R''')]nR'''$ wherein R' is an alkylene group having 2 to 6 carbon atoms, R'' and R''' are independently hydrogen or a hydrocarbyl group, and n is a number from 1 to 7.

13. The fuel additive concentrate of claim 8 wherein the alkoxyate detergent comprises a polyetheramine represented by the formula:



wherein R^{10} is an aliphatic group or alkyl-substituted phenyl group of about 8 to about 30 carbon atoms; and Z is a number from about 12 to about 30;

and wherein the polyetheramine has a molecular weight in the range from about 300 to about 5,000.

14. The fuel additive concentrate of claim 1 wherein component (B), comprises a tall oil fatty acid with an average of about 4 to 30 carbon atoms.

* * * * *