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(54) Use of quaternary ammonium salts in gasoline fuel to improve performance

Verwendung von quarternären Ammoniumsalzen in Benzinbrennstoff zur Verbesserung der Brennstoffleistung

Utilisation de sels d’ammonium quaternaire dans l’essence pour améliorer les performances

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WO-A2-2008/027881	**AU-A1- 2011 275 778**
US-A- 4 473 377	**US-A1- 2013 296 210**

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Description

TECHNICAL FIELD:

[0001] The disclosure is directed to use of a gasoline fuel composition that exhibits reduced friction, wear, and/or corrosion. In particular, the disclosure relates to an additive that reduces friction or wear in an engine and thus improves fuel economy and/or reduces the corrosiveness of a fuel in a fuel delivery system of an engine or fuel storage terminal.

BACKGROUND AND SUMMARY:

[0002] Fuel compositions for vehicles are continually being improved to enhance various properties of the fuels in order to accommodate their use in newer, more advanced engines. Accordingly, the fuel compositions contain additives which are directed to certain properties that require improvement. For example, friction modifiers, such as fatty acid amides, are added to fuels to reduce friction and wear in the fuel delivery systems of an engine. Other additives are included in the fuel compositions to reduce the corrosiveness of the fuel compositions and/or improve the electrical conductivity of the fuel compositions. Still other additives are added to fuels to improve the fuel economy of an engine operating on the fuels. Each of the foregoing additives may improve a single property of the fuel composition and, in some instances, may adversely affect other properties of the fuel composition. Accordingly, fuel compositions typically include a complex mixture of additives that are selected to cooperate with each other to improve the fuel composition. Accordingly, there is a need for a fuel additive that is effective to improve multiple characteristics of a fuel.

[0003] US 2013/0296210 A1 discloses the use of quaternized alkylamine nitrogen compounds as a fuel additive for reduction or prevention of deposits in the injection systems of direct injection diesel engines, especially in common rail injection systems, for reduction of the fuel consumption of direct injection diesel engines, especially of diesel engines with common rail injection systems. The quaternized alkylamine nitrogen compounds are also taught to be useful for minimizing power loss in direct injection diesel engines, especially in diesel engines with common rail injection systems; and as an additive for gasoline fuels, especially for operation of DISI engines. An example of a reaction product comprising a quaternized nitrogen compound is N-methyl-N-(2-hydroxypropyl)-N,N-ditallowammonium acetate which is said to be a gasoline fuel additive.

[0004] US 4,473,377 discloses hydrocarbyl ammonium hydrocarbyl carboxylate internal salts and their metal-containing derivatives made by reacting certain amines with certain organic acids to obtain the former and reacting that product with a metal oxide or salt to obtain the latter. These products are said to be useful in lubricants and liquid fuel compositions for a variety of purposes, including reduced friction.

[0005] AU 2011 275 778 A1 discloses acid-free quaternized nitrogen compounds and the production and use thereof as diesel fuel and lubricant additives for reducing deposits in diesel engines. More specifically, the use of said acid-free quaternized nitrogen compounds as (1) fuel additives for reducing or preventing deposits in the injection systems of direct-injection diesel engines, in particular in common rail injection systems, (2) for reducing the fuel consumption of direct-injection diesel engines, in particular of diesel engines having common rail injection systems, and (3) for minimizing the power loss in direct-injection diesel engines, in particular in diesel engines having common rail injection systems, is disclosed.

[0006] WO 2008/027881 A2 discloses a quaternary ammonium salt detergent made from the reaction product of the reaction of: (a) Mannich reaction product having a tertiary amino group, wherein the Mannich reaction product is prepared from the reaction of a hydrocarbyl-substituted phenol, an aldehyde, and amine; and (b) a quaternizing agent suitable for converting the tertiary amino group to a quaternary nitrogen, and the use of such quaternary ammonium salt detergents in a fuel composition to reduce intake valve deposits.

[0007] In addition, since some of the fuel additives are passed into the engine sump during combustion, a fuel additive that is also beneficial to the engine lubricant would be desirable. The properties of an engine oil of lubricating viscosity that a fuel-borne additive might affect include the corrosiveness, friction, and fuel economy of said engine oil.

[0008] In accordance with the disclosure, exemplary embodiments provide use of a fuel composition for reducing wear in a fuel delivery system. The invention is set out in the appended claims.

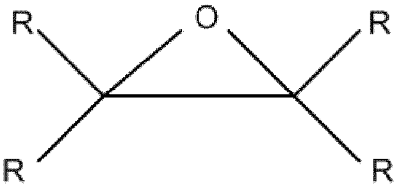
[0009] The fuel composition includes gasoline and from 10 to 500 ppm by weight based on a total weight of the fuel composition, of an alkoxylated quaternary ammonium salt derived from an epoxide, a tertiary amine, and an optional protonating agent.The fuel composition may be essentially free of a quaternary ammonium salt of a hydrocarbyl Mannich compound such that the concentration of the quaternary ammonium salt of a hydrocarbyl Mannich compound in the fuel composition has no measurable effect on injector cleanliness or deposit formation.

[0010] An advantage of the method described herein is that the additive for the fuel composition may not only improve the wear properties of the fuel, but the additive may also be effective to improve fuel economy and the friction properties of the fuel

[0011] In one embodiment, the fuel additive may be derived from an amido amine that is made in the substantial absence of acylating agents such as those disclosed in U.S. Patent No. 8,147,569. An advantage of the fuel additive described herein is that the additive may be used at a much lower concentration than a quaternary ammonium salt derived from an amine that is derived from an acylating agent, yet may provide better friction, and wear performance than conventional quaternary ammonium salts made from amines derived from acylating agents.

[0012] In one embodiment, the additive is derived from a tertiary amine wherein the tertiary amine is an amido amine that is derived from acid having from 1 to 54 carbon atoms. In another embodiment, the additive may be derived from an ether amine such as an alkylether amine.

[0013] In one embodiment, the epoxide is selected from compounds of the formula:



wherein each R is independently selected from H and a C_1 to C_{50} hydrocarbyl group.

[0014] In a further embodiment, the fuel composition contains from 60 to 180 ppm by weight, such as from 70 to 170 ppm by weight, or from 80 to 150 ppm by weight of the alkoxylated quaternary ammonium salt based on a total weight of the fuel composition. Each of the end points of each range disclosed herein can be combined with any of the other end points of the ranges that are disclosed herein.

[0015] In another embodiment, an oil of lubricating viscosity contains from 0.05 to 5.0 wt.%, such as from 0.1 to 1.0 wt.%, or 0.15 to 0.5 wt.% of the alkoxylated quaternary ammoniuim salt based on the total weight of the oil composition.

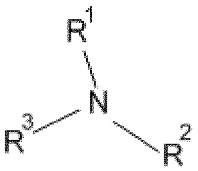
[0016] Additional embodiments and advantages of the disclosure will be set forth in part in the detailed description which follows, and/or can be learned by practice of the disclosure. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the disclosure, as claimed.

BRIEF DESCRIPTION OF THE DRAWING

[0017] FIG. 1 is a depiction of the improvement in torque efficiency for a motorized engine operated at from 500 to 3000 rpm at 115°C when using an engine lubricant containing a friction modifier.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0018] The fuel additive component of the present disclosure may be used in a minor amount 10 to 500 ppm by weight in a major amount (50 wt% or more) of fuel and may be added to the fuel directly or added as a component of an additive concentrate to the fuel. A suitable fuel additive component for improving the operation of internal combustion engines may be made by reacting a tertiary amine of the formula:



wherein each of R^1, R^2, and R^3 is selected from hydrocarbyl groups containing from 1 to 200 carbon atoms, 1 to 100 carbon atoms, or 1 to 50 carbon atoms, optionally, a carboxylic acid or a phenol, and a quaternizing agent to provide an alkoxylated quaternary ammonium salt. In one embodiment at least one and not more than two of R^1, R^2, and R^3 contain 1 to 3 carbon atoms. The reaction may be conducted in the presence of a protonating agent having an acid disassociation constant (pK_a) of less than 13, such as a carboxylic acid or an alkyl phenol. The alkoxylated quaternary ammonium salt may also be derived from an amido amine and a quaternizing agent reacted in the presence of a protonating agent. The protonating agent may be obtained from a carboxylic acid, an alkyl phenol, an amine or an epoxide. In one embodiment, the protonating agent may be obtained from the amido amine derived from a fatty acid wherein the reaction product containing the amido amine has an acid number ranging from 1 to 200 mg KOH/g. Regardless of how the alkoxylated quaternary ammonium salt is made, a feature of the disclosure is that the amine contains at least one tertiary amino group and the amido amine is made in a reaction medium that is substantially devoid of or does not contain an acylating agent.

[0019] As used herein, the term "hydrocarbyl group" or "hydrocarbyl" 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 a molecule and having a predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

(1) 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 an alicyclic radical);
(2) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of the description herein, do not alter the predominantly hydrocarbon substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, amino, alkylamino, and sulfoxy);
(3) hetero-substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this description, 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, or as a further example, no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; in some embodiments, there will be no non-hydrocarbon substituent in the hydrocarbyl group.

[0020] As used herein, the term "major amount" is understood to mean an amount greater than or equal to 50 wt. %, for example from 80 to 98 wt.% relative to the total weight of the composition. Moreover, as used herein, the term "minor amount" is understood to mean an amount less than 50 wt. % relative to the total weight of the composition.

[0021] As used herein the term "substantial absence of an acylating agent" means that the reaction product is made in the absence or substantial absence of a reaction product of a long chain hydrocarbon, generally a polyolefin substituted with a monounsaturated carboxylic acid reactant such as (i) α,β-monounsaturated C_4 to C_{10} dicarboxylic acid such as fumaric acid, itaconic acid, maleic acid; (ii) derivatives of (i) such as anhydrides or C_1 to C_5 alcohol derived mono- or di-esters of (i); (iii) α,β-monounsaturated C_3 to C_{10} monocarboxylic acid such as acrylic acid and methacrylic acid; or (iv) derivatives of (iii) such as C_1 to C_5 alcohol derived esters of (iii) with any compound containing an olefinic bond represented by the general formula:

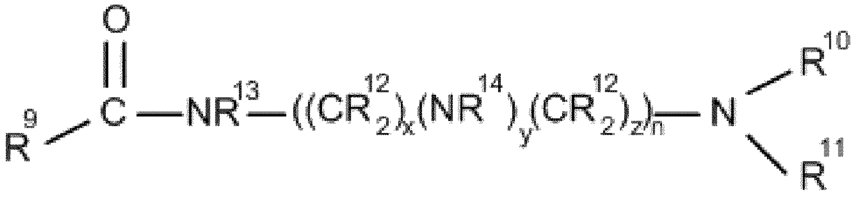
$$(R^4)(R^5)C{=}C(R^6)(CH(R^7)(R^8))$$

wherein each of R^4 and R^5 is, independently, hydrogen or a hydrocarbon based group. Each of R^6, R^7 and R^8 is, independently, hydrogen or a hydrocarbon based group; preferably at least one is a hydrocarbon based group containing at least 20 carbon atoms.

[0022] As used herein, the term, " substantial absence" only allows the presence of a small amount of a component as an impurity.

Amine Compound

[0023] According to the disclosure, any suitable amine or polyamine containing at least one tertiary amino group may be used. In one embodiment, an amine including diamines and polyamines may be reacted with a C_1 to C_{54} carboxylic acid to form an amido amine and the amido amine may be subsequently reacted with a quaternizing agent. Suitable tertiary amido amine compounds may have a hydrocarbyl linkage, such as an ether linkage between the amido group and the amino group or the tertiary amido amine may be a compound of the formula:



$$R^9-C(=O)-NR^{13}-((CR^{12}_2)_x(NR^{14})_y(CR^{12}_2)_z)_n-N(R^{10})(R^{11})$$

wherein each of R^{10}, and R^{11} is selected from hydrocarbyl groups containing from 1 to 50 carbon atoms, each R^9, R^{12}, R^{13} and R^{14} may be independently selected from hydrogen or a hydrocarbyl group, x may range from 1 to 6, y may be 0 or 1, z may be 1 to 6, and n may range from 1 to 6. Each hydrocarbyl group R^9 to R^{14} may be independently selected from linear, branched, substituted, cyclic, saturated, unsaturated hydrocarbyl groups, and may contain one or more hetero atoms. Suitable hydrocarbyl groups may include, but are not limited to alkyl groups, aryl groups, alkylaryl groups, arylalkyl groups, alkoxy groups, aryloxy groups, amino groups, and the like. Particularly suitable hydrocarbyl groups may be linear or branched alkyl groups. A representative example of amine reactants which may be amidized and quaternized to yield compounds disclosed herein include for example, but are not limited to, dimethyl amino propyl amine, and 2-(2-dimethylamino-ethoxy) ethylamine.

[0024] If the amine contains solely primary or secondary amino groups, it may be desirable to alkylate at least one of the primary or secondary amino groups to a tertiary amino group prior to quaternizing the amine. In one embodiment, the primary amines and secondary amines or mixtures therof with tertiary amines may be exhaustively or partially alkylated to a tertiary amine and further alkoxylated to a quaternary salt.

[0025] When the amine has a hydroxyl group, the amine may be converted to an ester amine by reacting the amine with a C_1 to C_{54} carboxylic acid. The acid may be a monoacid, a dimer acid, or a trimer acid. The acid may be selected from the group consisting of formic acid, acetic acid, propionic acid, butyric acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic, arachidic acid, behenic acid, lignoceric acid, cerotic acid, myristoleic acid, palmitoleic acid, sapienic acid, oleic acid, elaidic acid, vaccenic acid, linoleic acid, linoelaidic acid, α-linolenic acid, arachidonic acid, eicosapentaenoic acid, erucic acid, docosahexaenoic acid, and the dimer and trimer acids thereof. When reacted with the amine, the reaction product may be a C_1-C_{54}-alkyl or alkenyl-substituted ester amine such as a C_1-C_{54}-alkyl or alkenyl-substituted ester propyldimethylamine.

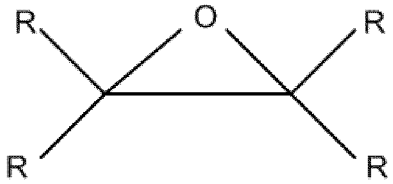
[0026] When the amine is an ether amine, it may be a hydrocarbyl ether amine or a polyamine. For example, the amine may have the formula R^{15}--[O--CH_2--$CH(CH_3)]_y$-$NR^{16}R^{17}$, wherein R^{15} is a hydrocarbyl radical having from 8 to 18 carbon atoms and y is an integer ranging from 1 to 6, and wherein R^{16} and R^{17} are the same as defined for R^1-R^3 above. In one example, R^{16} and R^{17} contain from one to three carbon atoms, such as methyl or ethyl groups.

Protonating Agent

[0027] In one embodiment, a protonating agent may be used to make the quaternary ammonium salt. The protonating agent may have a pKa of less than 13 including carboxylic acids and alkyl phenols. Specific examples of the organic acid are aliphatic, alkenyl or aromatic monocarboxylic acids such as formic acid, acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, undecanic acid, lauric acid, tridecanic acid, myristic acid, pentacanic acid, palmitic acid, heptadecanic acid, stearic acid, nonadecanic acid, arachidic acid, isobutyric acid, isovaleric acid, isocaproic acid, ethylbutyric acid, methyl-valeric acid, isocaprylic acid, propylvaleric acid, ethyl-caproic acid, isocapric acid, tuberculostearic acid, pivalic acid, 2,2-dimethylbutanic acid, 2,2-dimethylpentanic acid, 2,2-dimethylhexanic acid, 2,2-dimethylheptanic acid, 2,2-dimethyloctanic acid, 2-methyl-2-ethylbutanic acid, 2-meth-yl-2-ethylpentanic acid, 2-methyl-2-ethylhexanic acid, 2-methyl-2-propylpentanic acid, 2-methyl-2-propylhexanic acid, 2-methyl-2-propylheptanic acid, acrylic acid, crotonic acid, isocrotonic acid, 3-butenic acid, pentenic acid, hexenic acid, heptenic acid, octenic acid, nonenic acid, decenic acid, undecenic acid, dodecinic acid, tuzuic acid, physteric acid, palmitoleic acid, petroselinic acid, oleic acid, elaidic acid, vaccenic acid, gadoleic acid, methacrylic acid, 3-methylcrotonic acid, tiglic acid, methylpentenic acid, cyclopentacarboxylic acid, cyclohexanecarboxylic acid, phenylacetic acid, chloroacetic acid, glycolic acid, lactic acid, polyalkyl or polyalkenyl succinic ester acid, amide acid, imide acid. Also useful are aliphatic polycarboxylic acids such as citric acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecane diacid, dodecane di-acid, tridecane diacid, tetradecane diacid, pentadecane di-acid, hexadecane diacid, heptadecane diacid, octadecane diacid, noncadecane diacid, eicosane diacid, methylmalonic acid, ethylmalonic acid, propylmalonic acid, butylmalonic acid, pentylmalonic acid, hexylmalonic acid, dimethylmalonic acid, methylethylmalonic acid, diethylmalonic acid, methyl-propylmalonic acid, methylbutylmalonic acid, ethylpropyl-malonic acid, dipropylmalonic acid, ethylbutylmalonic acid, propylbutylmalonic acid, dibutylmalonic acid, methylsuccinic acid, ethylsuccinic acid, 2,2-dimethylsuccinic acid, 2,3--dimethylsuccinic acid, 2-methylglutaric acid, maleic acid, citraconic acid, itaconic acid, methyleneglutaric acid, monomethyl maleate, 1,5-octanedicarboxylic acid, 5,6-decane-dicarboxylic acid, 1,7-decanedicarboxylic acid, 4,6-dimeth-yl-4-nonene-1,2-dicarboxylic acid, 4,6-dimethyl-1,2-nonane-dicarboxylic acid, 1,7-dodecanedicarboxylic acid, 5-ethyl-1,10-decanedicarboxylic acid, 6-methyl-6-dodecene-1,12-di-carboxylic acid, 6-methyl-1,12-dodecanedicarboxylic acid, 6--ethylene-1,12-dodecanedicarboxylic acid, 7-methyl-7-tetra-decene-1,14-dicarboxylic acid, 7-methyl-1,14-tetradecanedi-carboxylic acid, 3-hexyl-4-decene-1,2-dicarboxylic acid, 3-hexyl-1,12-decanedicarboxylic acid, 6-ethylene-9-hexadecene-1,16-dicarboxylic acid, 6-ethyl-1,16-hexadecanedicarboxylic acid, 6-phenyl-1,12-dodecanedicarboxylic acid, 7,12-dimeth-y-7,1-octadecanediene-1,18-dicarboxylic acid, 7,12-dimeth-yl-1,18-octadecanedicarboxylic acid, 6,8-diphenyl-1,14-tetradecanedicarboxylic acid, 1,1-cyclopentanedicarboxylic acid, 1,1-cyclopentanedicarboxylic acid, 1,2-cyclopentanedi-carboxylic acid, 1,1-cyclohexanedicarboxylic acid, 1,2-cyclohexanedicarboxylic acid, 4-cyclohexene-1,2-dicarboxylic acid, 5-nobornene-2,3-dicarboxylic acid, malic acid, glutamic acid, tartaric acid, and polyalkyl or polyalkenyl succinic diacids. Phenols which may be used include, but are not limited to [beta]-naphthol, o-nitrophenol, p-nitrophenol, p--aminophenol, catechol, resorcinol, 4,4'-dihydroxydiphenyl-2,2-propane, C_1-C_{20}-alkyl phenols, and polyalkyl phenols or substituted Mannich bases.

Quaternizing Agent

[0028] A suitable quaternizing agents may be selected from the group consisting of hydrocarbyl epoxides of the formula:



wherein each R is independently selected from H and a C_1 to C_{50} hydrocarbyl group, and polyepoxides. Non-limiting examples of suitable epoxides that may be used as quaternizing agents may be selected from the group consisting of:

1,3-Butadiene diepoxide
Cyclohexene oxide
Cyclopentene oxide
Dicyclopentadiene dioxide
1,2,5,6-Diepoxycyclooctane
1,2,7,8-Diepoxyoctane
1,2-Epoxybutane
cis-2,3-Epoxybutane
3,4-Epoxy-1-butene
3,4-Epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate
1,2-Epoxydodecane
1,2-Epoxyhexadecane
1,2-Epoxyhexane
1,2-Epoxy-5-hexene
1,2-Epoxy-2-methylpropane
exo-2,3 -Epoxynorbornane
1,2-Epoxyoctane
1,2-Epoxypentane
1,2-Epoxy-3-phenoxypropane
(2,3-Epoxypropyl)benzene
N-(2,3-Epoxypropyl)phthalimide
1,2-Epoxytetradecane
exo-3,6-Epoxy-1,2,3,6-tetrahydrophthalic anhydride
3,4-Epoxytetrahydrothiophene-1,1-dioxide
Isophorone oxide
Methyl-1,2-cyclopentene oxide
2-Methyl-2-vinyloxirane
α-Pinene oxide
Ethylene oxide
(±)-propylene oxide
Polyisobutene oxide
cis-Stilbene oxide
Styrene oxide
Glycidol
Glycidol ethers
Tetracyanoethylene oxide
Tris(2,3-epoxypropyl) isocyanurate and combinations of two or more of the foregoing. A particularly suitable epoxide may be selected from ethylene oxide and propylene oxide.

[0029] The alkoxylated quaternary ammonium salts from amido amines may be made in one stage or two stages. The reaction may be carried out by contacting and mixing the amido amine with the olefin oxide in the reaction vessel wherein a carboxylic acid is added to the reaction mixture to provide a protonating agent. The carboxylic acid may be same acid used to make the amido amine or may be selected from any of the above listed fatty acids, formic acid, acetic acid, propionic acid, butyric acid, polymeric acid and mixtures thereof, such a polyolefinic mono-or di-carboxylic acid, polymeric polyacids and mixtures thereof, and the like. When used, the mole ratio of protonating agent per mole of epoxy equivalents added to the reaction mixture may range from 1:1 to 10:1, for example from 1:1 to 5:1, or from 1:1 to 2:1 moles of acid per mole of epoxy equivalents. In one embodiment, the anion of the quaternary ammonium salt is a carboxylate anion.

[0030] The reaction may be carried out at temperature ranging from 30° to 90°C, for example from 45° to 70° C. The reaction may be conducted by reacting any amount of tertiary amino groups to epoxy groups sufficient to provide a quaternary ammonium compound. In one embodiment a mole ratio of tertiary amino groups to epoxy groups may range from 2:1 to 1:2. When the reaction is completed volatiles and unreacted reagents may be removed from the reaction product by heating the reaction product under vacuum. The product may be diluted with mineral oil, diesel fuel, kerosene, alcohol, or an inert hydrocarbon solvent to prevent the product from being too viscous, if necessary.

[0031] One or more additional optional compounds may be present in the fuel compositions of the disclosed embodiments. For example, the fuels may contain conventional quantities of cetane improvers, corrosion inhibitors, cold flow improvers (CFPP additive), pour point depressants, solvents, demulsifiers, lubricity additives, additional friction modifiers, amine stabilizers, combustion improvers, dispersants, antioxidants, heat stabilizers, conductivity improvers, metal deactivators, carrier fluid, marker dyes, organic nitrate ignition accelerators, cyclomatic manganese tricarbonyl compounds, and the like. In some aspects, the compositions described herein may contain 10 weight percent or less, or in other aspects, 5 weight percent or less, based on the total weight of the additive concentrate, of one or more of the above additives. Similarly, the fuels may contain suitable amounts of conventional fuel blending components such as methanol, ethanol, dialkyl ethers, 2-ethylhexanol, and the like.

[0032] In some aspects of the disclosed embodiments, organic nitrate ignition accelerators that include aliphatic or cycloaliphatic nitrates in which the aliphatic or cycloaliphatic group is saturated, and that contain up to 12 carbons may be used. Examples of organic nitrate ignition accelerators that may be used are methyl nitrate, ethyl nitrate, propyl nitrate, isopropyl nitrate, allyl nitrate, butyl nitrate, isobutyl nitrate, sec-butyl nitrate, tert-butyl nitrate, amyl nitrate, isoamyl nitrate, 2-amyl nitrate, 3-amyl nitrate, hexyl nitrate, heptyl nitrate, 2-heptyl nitrate, octyl nitrate, isooctyl nitrate, 2-ethylhexyl nitrate, nonyl nitrate, decyl nitrate, undecyl nitrate, dodecyl nitrate, cyclopentyl nitrate, cyclohexyl nitrate, methylcyclohexyl nitrate, cyclododecyl nitrate, 2-ethoxyethyl nitrate, 2-(2-ethoxyethoxy)ethyl nitrate, tetrahydrofuranyl nitrate, and the like. Mixtures of such materials may also be used.

[0033] Examples of suitable optional metal deactivators useful in the compositions of the present application are disclosed in U.S. Pat. No. 4,482,357 issued Nov. 13, 1984. Such metal deactivators include, for example, salicylidene-o-aminophenol, disalicylidene ethylenediamine, disalicylidene propylenediamine, N,N'-disalicylidene-1,2-diaminopropane, triazole, tolutriazole, and other substituted triazoles.

[0034] In some embodiments of this disclosure, the additives may be employed in amounts sufficient to reduce or inhibit deposit formation in a fuel system or combustion chamber of an engine and/or crankcase. In some aspects, the fuels may contain minor amounts of the above described reaction product that controls or reduces the formation of engine deposits, for example injector deposits in gasoline or diesel engines.

[0035] The additives of the present disclosure, including the alkoxylated quaternary ammonium salt described above, and optional additives used in formulating the fuels used in this invention may be blended into the base fuel individually or in various sub-combinations. In some embodiments, the additive components of the present application may be blended into the fuel concurrently using an additive concentrate, as this takes advantage of the mutual compatibility and convenience afforded by the combination of ingredients when in the form of an additive concentrate. Also, use of a concentrate may reduce blending time and lessen the possibility of blending errors.

[0036] The fuels of the present disclosure may be applicable to the operation of gasoline and diesel engines. The engine include both stationary engines (e.g., engines used in electrical power generation installations, in pumping stations, etc.) and ambulatory engines (e.g., engines used as prime movers in automobiles, trucks, road-grading equipment, military vehicles, etc.). For example, the fuels may include any and all middle distillate fuels, diesel fuels, biorenewable fuels, biodiesel fuel, fatty acid alkyl ester, gas-to-liquid (GTL) fuels, jet fuel, alcohols, ethers, kerosene, low sulfur fuels, synthetic fuels, such as Fischer-Tropsch fuels, liquid petroleum gas, bunker oils, coal to liquid (CTL) fuels, biomass to liquid (BTL) fuels, high asphaltene fuels, fuels derived from coal (natural, cleaned, and petcoke), genetically engineered biofuels and crops and extracts therefrom, and natural gas. "Biorenewable fuels" as used herein is understood to mean any fuel which is derived from resources other than petroleum. Such resources include, but are not limited to, corn, maize, soybeans and other crops; grasses, such as switchgrass, miscanthus, and hybrid grasses; algae, seaweed, vegetable oils; natural fats; and mixtures thereof. In an aspect, the biorenewable fuel can comprise monohydroxy alcohols, such as those comprising from 1 to 5 carbon atoms. Non-limiting examples of suitable monohydroxy alcohols include methanol, ethanol, propanol, n-butanol, isobutanol, t-butyl alcohol, amyl alcohol, and isoamyl alcohol.

[0037] Accordingly, aspects of the present disclosure are directed to methods for reducing wear in a fuel system of an engine. In another aspect, the quaternary ammonium salts described herein or fuel containing the quaternary ammonium salt may be combined with polyhydrocarbyl-succinimides, -Mannich compounds, -acids, -amides, -esters, -amide/acids and -acid/esters.

[0038] In some aspects, the methods comprise injecting a hydrocarbon-based compression ignition fuel comprising a alkoxylated quaternary ammonium salt of the present disclosure through the injectors of the diesel engine into the combustion chamber, and igniting the compression ignition fuel. In some aspects, the method may also comprise mixing into the diesel fuel at least one of the optional additional ingredients described above.

[0039] In one embodiment, the fuels of the present disclosure may be essentially free, such as devoid, of polyhydrocarbyl-succinimides, -Mannich compounds, -acids, - amides, -esters, -amide/acids and -acid/esters. In another embodiment, the fuel is essentially free of a quaternary ammonium salt of a hydrocarbyl succinimide. The term "essentially free" is defined for purposes of this application to be concentrations having substantially no measurable effect on injector cleanliness or deposit formation.

EXAMPLES

[0040] The following examples are illustrative of exemplary embodiments of the disclosure. In these examples as well as elsewhere in this application, all parts and percentages are by weight unless otherwise indicated. It is intended that these examples are being presented for the purpose of illustration only and are not intended to limit the scope of the invention disclosed herein.

Comparative Example 1 - Propoxylated Coco-diethanolamide. A mixture of coconut fatty acid (251 grams) and diethanolamine (128 grams) were heated in 150°C for 8 hours under nitrogen atmosphere to give the fatty amide/ester mixture as a viscous brown oil (294 grams). The resulting reaction mixture (275.5 grams) and dimethyl ethanolamine (1.4 grams) were charged into a stainless steel pressure reactor. The reactor was heated to 115° C and propylene oxide (54.5 grams) was charged to the reactor. The resulting mixture was heated an additional 12 hours and then cooled to room temperature to give the final product as a brown oil.

Comparative Example 2 - Amide of isostearic acid and diethanolamine.

Comparative Example 3 - Oleylamidopropyldimethylbetaine Oleylamido propyl dimethylamine (about 366 g, 78 wt.% in an aromatic solvent) was combined with 113 grams of sodium chloroacetate and was heated in a mixture of 125 mL isopropanol and 51 grams of water at 80°C for 5.5 hours. Isopropanol (600 mL) and 2-ethylhexanol (125 grams) were added to the reaction product and the mixture was concentrated by heating to remove water. The resultant mixture was filtered through a filter medium to give product as a yellow oil.

Comparative Example 4 - Dimethyloleylamine oxide.

Comparative Example 5 - bis-hydroxylethyl cocoamine.

Comparative Example 6 - tallow alkylamidopropyl-dimethylamine oxide.

Comparative Example 7 - 1-hydroxyethyl, 2-heptadecenyl imidazoline.

Inventive Example 1

[0041] A mixture of oleylamido propyl dimethylamine, propylene oxide and oleic acid was used in a molar ratio of 1 to 1 to 1 and the mixture was heated 50° C. in a reaction vessel until essentially all propylene oxide was consumed. Volatiles were removed under reduced pressure to give the desired product as a brownish oil.

Inventive Example 2

[0042] An alkoxylated quaternary ammonium salt was made according to the same procedures set forth in Inventive Example 1 with the exception that ethylene oxide was used in place of propylene oxide.

Inventive Example 3

[0043] An alkoxylated quaternary ammonium salt was made according to the same procedures set forth in Inventive Example 1 with the exception that dimethyl tridecyloxy-propoxylated amine was used in place of oleylamido propyl dimethylamine.

Inventive Example 4

[0044] An alkoxylated quaternary ammonium salt was made according to the same procedures set forth in Inventive Example 2 with the exception that di-cocomethyl amine was used in place of oleylamido propyl dimethylamine.

Inventive Example 5

[0045] An alkoxylated quaternary ammonium salt was made according to the same procedures set forth in Inventive Example 2 with the exception that 30 mole % excess ethylene oxide was used.

Inventive Example 6

[0046] C_{20}-$_{24}$ alkenyl succinic anhydride (181 grams) was mixed glycidol (33.7 grams) at room temperature. The mixture was warmed to 41° C for 15 minutes. Oleylamidopropyl dimethylamine (166 grams) was then added to the mixture followed by aromatic solvent (57 grams) and 2-ethylhexanol (87 grams). The mixture was heated at 55° C for 1 hour, then 60° C for 3 hours, then 65° C for 1 hour to give product as a yellowish oil.

[0047] In the following example, a friction test was conducted using a high frequency reciprocating rig (HFRR) under a 200 gram load with a stroke distance of 1 millimeter at 50 Hz according to diesel fuel test ASTM D6079 except that the test was conducted in gasoline fuel at 25°C. The base fuel contained no additives. Each of the other fuel compositions contained a typical commercial Mannich base detergent package at 280ppm. The treat rate of the additive and the results are given in the following table.

Table 1 - Fuel HFRR data

No.		Additive Treat rate (ppmw)	HFRR Wear (micrometer)
1	Base fuel (no additives)	0	750
2	Base fuel plus Mannich base detergent package at 280 ppm	0	755
3	No. 2 plus additive of Comparative Ex. 1	152	685
4	No. 2 plus additive of Comparative Ex. 2	152	740
5	No. 2 plus additive of Comparative Ex. 4	152	775
6	No. 2 plus additive of Comparatives Ex. 5	152	695
7	No. 2 plus additive of Inventive Ex 1	152	520
8	No. 2 plus additive of Inventive Ex 2	152	480
9	No. 2 plus additive of Inventive Ex 3	152	595
10	No. 2 plus additive of Inventive Ex 6	152	425

[0048] As shown by the foregoing results in Table 1, the additive of the inventive examples (nos. 7-10) provided significant and unexpected wear reduction compared to the additives of comparative example nos. 3-6. The greatest wear reduction in gasoline fuel was obtained by the alkoxylated quaternary ammonium salt (no. 10). The comparative examples provided only slight or no reduction in wear compared to the inventive examples.

[0049] In the following example, a friction test was conducted on a GF-5 lubricating oil that was devoid of friction modifiers using a high frequency reciprocating rig (HFRR) under a 4N load with a stroke distance of 1 millimeter at 20 Hz at 70° C, 100° C and 130° C according to ASTM D6079. The base lubricating oil contained a GF-5 dispersant/inhibitor (DI) package that contained no friction modifiers. The treat rate of the additive and the results are given in the following table.

Table 2 - Oil HFRR data

No.		Additve Treat rate (wt.%)	Coefficients of friction		
			70° C	100° C	130° C
1	Base lubricant plus DI package	0	0.149	0.156	0.159

(continued)

No.		Additve Treat rate (wt.%)	Coefficients of friction		
2	No. 1 plus additive of Comparative Ex. 2	1	0.148	0.142	0.129
3	No. 1 plus additive of Comparative Ex. 4	1	0.149	0.147	0.132
4	No. 1 plus additive of Inventive Ex. 1	1	0.129	0.130	0.121
5	No. 1 plus additive of Inventive Ex. 5	1	0.131	0.124	0.112
6	No. 1 plus additive of Inventive Ex. 6	1	0.133	0.124	0.106

[0050] As shown by the foregoing examples, the inventive examples (Runs 4-6) exhibited significantly reduced friction in a lubricant composition compared to the comparative examples (Runs 2 and 3) and the base lubricant devoid of friction modifiers (Run 1).

[0051] In the following examples, the corrosion potential of various fuel compositions containing conventional additives and the inventive additives were determined using a NACE corrosion test: NACE TM0172-2001. In all of the examples, the additive treat rate was 100 ppm. The NACE standard provides a procedure for conducting a test to determine the corrosive properties of gasoline and distillate fuels in preparation for transport through a pipeline. According to the test method, the surface of a cylindrical steel test specimen was prepared by polishing with 100 grit paper and then immersed in a mixture of the test fuel and distilled water at 38°C. The mixture was stirred and was maintained at 38°C for 4 hours. The test specimen was then rated by percent of the test surface corroded according to the following rating scale:

A 0% on cylinder

B++ less than 0.1% (or 2 or 3 spots of no more than 1-mm diameter)

B+ Less than 5%

B 5 to 25%

C 25 to 50%

D 50 to 75%

E 75 to 100%

[0052] Experience has shown that if enough inhibitor is present to produce a rating of B+ or better as defined in the standard, general corrosion in flowing pipelines may be controlled. The results of the corrosion test are given in the following table.

Table 3 - NACE Corrosion Test results

No.		Additve Treat rate (ppmw)	NACE Rating
1	Base fuel (no additives)	0	E
2	additive of Comparative Ex 2	100	E
3	Commercial friction modifier	100	E
4	additive of Comparative Ex 3	100	E
5	additive of Comparative Ex 6	100	C
6	additive of Comparative Ex 7	100	C
7	additive of Inventive Ex 1	100	B
8	additive of Inventive Ex 3	100	B+
9	additive of Inventive Ex 4	100	B+
10	additive of Inventive Ex 5	100	A

[0053] As shown by the foregoing examples, the inventive examples Nos. 7-10 provided unexpectedly better corrosion protection potential than the commercial friction modifier additive (No. 3) or the additives of comparative examples 2, 3, 6 and 7 (Nos. 2 and 4-6).

[0054] In order to determine the effect that the additives made according to the disclosure have on friction in an engine, the additives were tested in an electrically motored research engine. Using a non-fired (electrically motored) engine to measure parasitic friction as a function of lubricant properties eliminates all other sources of signal, such as effects on combustion efficiency or engine cleanliness. Additives of Comparative Example 2 (Curve A) and Inventive Example 2 (Curve B) were added at 1 wt.% in the GF-5 lubricant used in the engine test above. A modern V6, 4-cycle engine was used as the test engine. The engine was turned by a variable-speed electric motor. Because this was a non-fired engine, this test stand was equipped with external oil and coolant temperature control. The oil temperature during each run was maintained at 115°C with GF-5 PCMO quality engine oil that contained no friction modifying agent. The percent of efficiency improvement relative to the lubricant without additives was calculated by the following equation:

$$[\text{Torque(engine oil without FM)-torque(additized oil with FM)}]/\text{torque(engine oil without FM)} *100$$

The results are shown in FIG. 1. As shown by FIG. 1, the inventive additive (Curve B) provided a significant and unexpected benefit in friction improvement in the test compared to the friction improvement provided by Comparative Example 2.

[0055] It is noted that, as used in this description the singular forms "a," "an," and "the," include plural referents unless expressly and unequivocally limited to one referent. Thus, for example, reference to "an antioxidant" includes two or more different antioxidants. As used herein, the term "include" and its grammatical variants are intended to be non-limiting, such that recitation of items in a list is not to the exclusion of other like items that can be substituted or added to the listed items

[0056] Unless indicated to the contrary, the numerical parameters set forth in the following description are approximations that can vary depending upon the desired properties sought to be obtained by the present disclosure. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

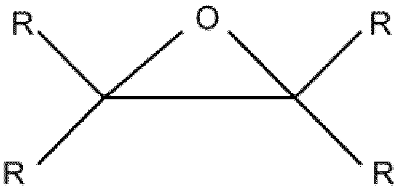
Claims

1. Use of a fuel composition to reduce wear in a fuel delivery system of an engine, wherein the fuel composition comprises gasoline and from 10 to 500 ppm by weight based on a total weight of the fuel composition of an alkoxylated quaternary ammonium salt derived from an epoxide, a tertiary amine, and an optional protonating agent,

2. The use of claim 1, wherein the engine comprises a fuel injected gasoline engine.

3. The use of claim 1 or 2, wherein the tertiary amine comprises an amido amine derived from an acid or an etheramine having from 1 to 54 carbon atoms.

4. The use of any one of claims 1-3, wherein the epoxide is selected from compounds of the formula:



wherein each R is independently selected from H and a C_1 to C_{50} hydrocarbyl group.

5. The use of any one of claims 1-3, wherein the epoxide is selected from ethylene oxide, propylene oxide, and glycidol.

6. The use of any one of claims 1-5, including the protonating agent and wherein the protonating agent is a carboxylic acid selected from fatty acids; formic acid; acetic acid; propionic acid; butyric acid; an alkenyl or polyalkenyl succinic

acid, acid/amide, or acid/ester; polymeric acids; and mixtures thereof.

7. The use of any one of claims 1-6, wherein the fuel composition contains from 80 to 120 ppm by weight of the alkoxylated quaternary ammonium salt based on a total weight of the fuel composition.

8. The use of any one of claims 1-7, wherein the use reduces friction and increases torque in the engine.

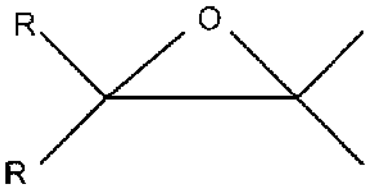
Patentansprüche

1. Verwendung einer Kraftstoffzusammensetzung zur Verringerung des Verschleißes in einem Kraftstoffzufuhrsystem eines Motors, wobei die Kraftstoffzusammensetzung Benzin und 10 bis 500 ppm nach Gewicht, bezogen auf das Gesamtgewicht der Kraftstoffzusammensetzung, eines alkoxylierten quaternären Ammoniumsalzes umfasst, das von einem Epoxid, einem tertiären Amin und einem optionalen Protonierungsmittel abgeleitet ist.

2. Verwendung nach Anspruch 1, wobei der Motor einen Benzinmotor mit Kraftstoffeinspritzung umfasst.

3. Verwendung nach Anspruch 1 oder 2, wobei das tertiäre Amin ein Amidoamin umfasst, das von einer Säure oder einem Etheramin mit 1 bis 54 Kohlenstoffatomen abgeleitet ist.

4. Verwendung nach einem der Ansprüche 1 bis 3, wobei das Epoxid ausgewählt ist aus Verbindungen der Formel:



wobei jedes R unabhängig ausgewählt ist aus H und einer C_1-C_{50}-Hydrocarbylgruppe.

5. Verwendung nach einem der Ansprüche 1 bis 3, wobei das Epoxid ausgewählt ist aus Ethylenoxid, Propylenoxid und Glycidol.

6. Verwendung nach einem der Ansprüche 1 bis 5, einschließlich des Protonierungsmittels, und wobei das Protonierungsmittel eine Carbonsäure ist, die aus Fettsäuren, Ameisensäure, Essigsäure, Propionsäure, Buttersäure, einer Alkenyl- oder Polyalkenylbernsteinsäure, Säure/Amid oder Säure/Ester, Polymersäuren und Gemischen davon ausgewählt ist.

7. Verwendung nach einem der Ansprüche 1 bis 6, wobei die Kraftstoffzusammensetzung 80 bis 120 ppm nach Gewicht des alkoxylierten quaternären Ammoniumsalzes, bezogen auf das Gesamtgewicht der Kraftstoffzusammensetzung, enthält.

8. Verwendung nach einem der Ansprüche 1 bis 7, wobei die Verwendung die Reibung verringert und das Drehmoment im Motor erhöht.

Revendications

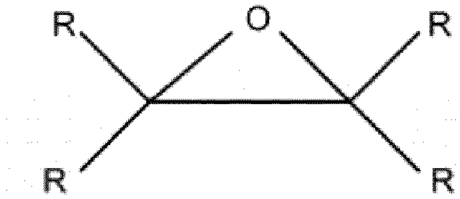
1. Utilisation d'une composition de carburant pour réduire l'usure dans un système de distribution de carburant d'un moteur, où la composition de carburant comprend de l'essence et de 10 à 500 ppm en poids sur la base d'un poids total de la composition de carburant d'un sel d'ammonium quaternaire alcoxylé dérivé d'un époxyde, une amine tertiaire et un agent de protonation facultatif,

2. Utilisation selon la revendication 1, où le moteur comprend un moteur à essence à injection de carburant.

3. Utilisation selon la revendication 1 ou 2, où l'amine tertiaire comprend une amidoamine dérivée d'un acide ou un

éther d'amine ayant de 1 à 54 atomes de carbone.

4. Utilisation selon l'une quelconque des revendications 1 à 3, où l'époxyde est choisi parmi des composés de formule :



dans laquelle chaque R est choisi indépendamment parmi H et un groupe hydrocarbyle en C_1 à C_{50}.

5. Utilisation selon l'une quelconque des revendications 1 à 3, où l'époxyde est choisi parmi l'oxyde d'éthylène, l'oxyde de propylène et le glycidol.

6. Utilisation selon l'une quelconque des revendications 1 à 5, comprenant l'agent de protonation et où l'agent de protonation est un acide carboxylique choisi parmi des acides gras ; l'acide formique ; l'acide acétique ; l'acide proprionique ; l'acide butyrique ; un acide, acide/amide ou acide/ester alcényl- ou polyalcénylsuccinique ; des acides polymères ; et des mélanges de ceux-ci.

7. Utilisation selon l'une quelconque des revendications 1 à 6, où la composition de carburant contient de 80 à 120 ppm en poids du sel d'ammonium quaternaire alcoxylé sur la base d'un poids total de la composition de carburant.

8. Utilisation selon l'une quelconque des revendications 1 à 7, où l'utilisation réduit le frottement et augmente le couple dans le moteur.

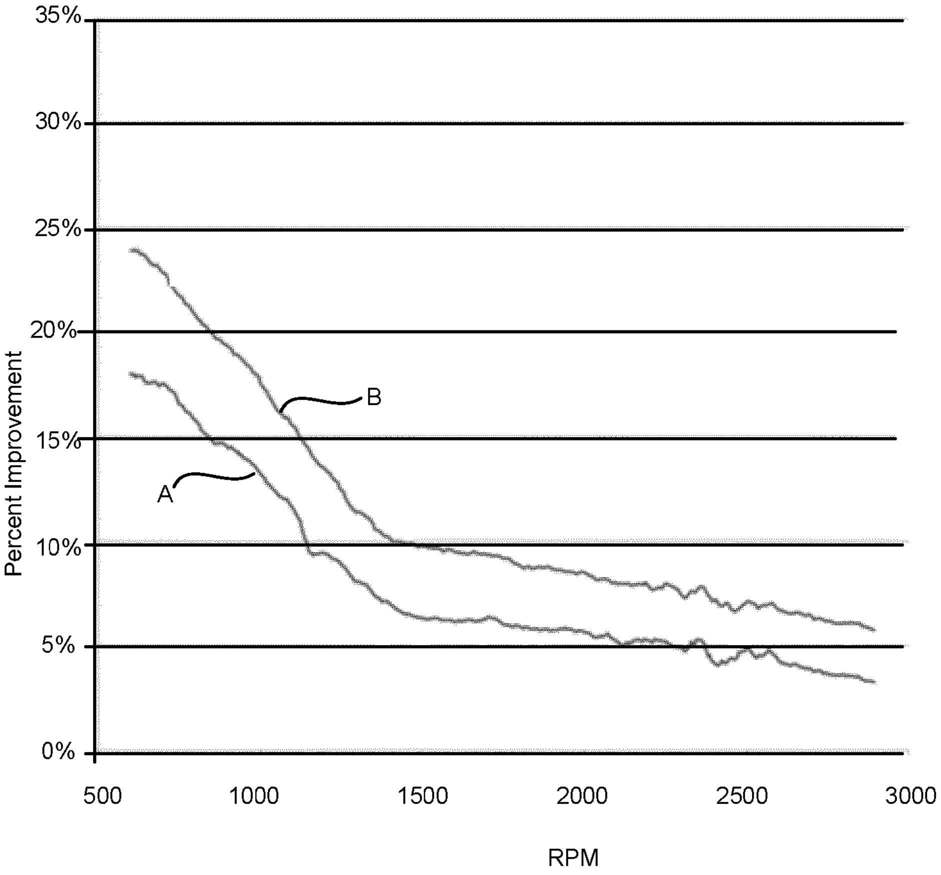

35%
30%
25%
20%
15%
10%
5%
0%
Percent Improvement
500
1000
1500
2000
2500
3000
RPM
A
B

FIG. 1

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