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

(57) Use of a fuel composition for reducing friction or wear in a fuel delivery system of an engine or corrosion in fuel delivery system of an engine or fuel storage terminal. The fuel composition includes gasoline and from

about 10 to about 500 ppm by weight based on a total weight of the fuel composition of an alkoxyated quaternary ammonium salt derived from an epoxide, a tertiary amine, and optional protonating agent.

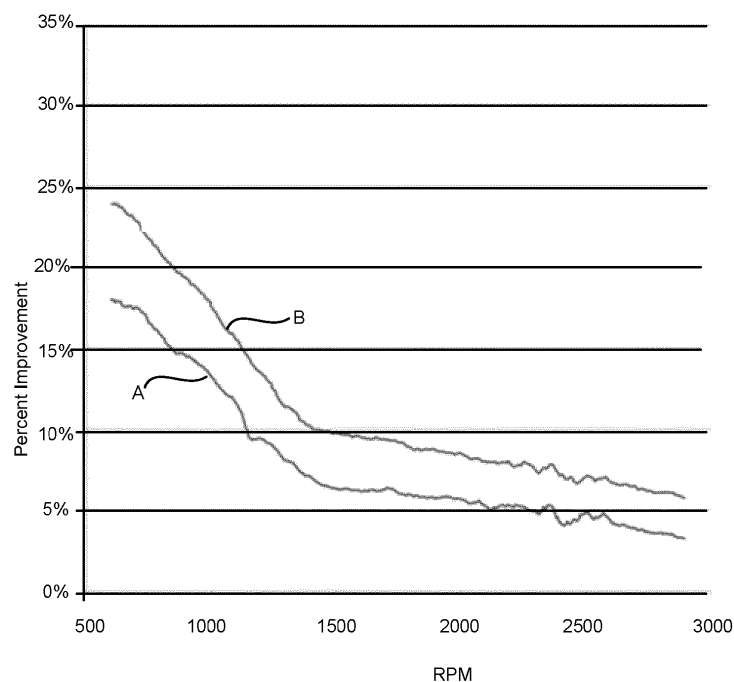


FIG. 1

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] 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.

[0004] In accordance with the disclosure, exemplary embodiments provide uses of a fuel composition for reducing friction or wear in an engine including a fuel delivery system or for reducing corrosion in an engine including a fuel delivery system or in a fuel storage terminal. The fuel composition includes gasoline and from about 10 to about 500 ppm by weight based on a total weight of the fuel composition, of an alkoxyated quaternary ammonium salt derived from an epoxide, a tertiary amine, and an optional protonating agent.

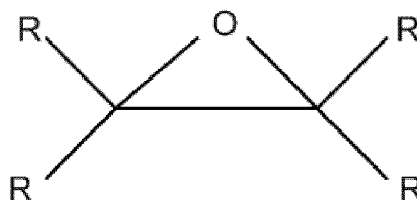
[0005] In one embodiment of the disclosure, there is provided the use of a fuel composition to reduce corrosion in a fuel delivery system of an engine or in a fuel storage terminal. The fuel composition includes gasoline and from about 10 to about 500 ppm by weight based on a total weight of the fuel composition of an alkoxyated quaternary ammonium salt derived from an epoxide, a tertiary amine, and an optional protonating agent.

[0006] An advantage of the methods described herein is that the additive for the fuel composition may not only improve the friction and wear properties of the fuel, but the additive may also be effective to improve fuel economy and/or reduce the corrosion potential of the fuel.

[0007] 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, wear, and corrosion performance than conventional quaternary ammonium salts made from amines derived from acylating agents.

[0008] 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 about 1 to about 54 carbon atoms. In another embodiment, the additive may be derived from an ether amine such as an alkylether amine.

[0009] In one embodiment, the epoxide is selected from compounds of the formula:



wherein each R is independently selected from H and a C₁ to C₅₀ hydrocarbyl group.

[0010] In a further embodiment, the fuel composition contains from about 60 to about 180 ppm by weight, such as from 70 to about 170 ppm by weight, or from about 80 to about 150 ppm by weight of the alkoxyated 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.

[0011] 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 alkoxyated quaternary ammonium salt based on the total weight of the oil composition.

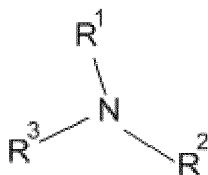
[0012] Additional embodiments and advantages of the disclosure will be set forth in part in the detailed description which follows, and/or can be learned by practice of the disclosure. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the disclosure, as claimed.

BRIEF DESCRIPTION OF THE DRAWING

[0013] 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

[0014] The fuel additive component of the present application may be used in a minor amount (less than 50 wt.%) 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:



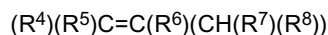
wherein each of R^1 , R^2 , and R^3 is selected from hydrocarbyl groups containing from 1 to 200 carbon atoms, 1 to 100 carbon atoms, or 1 to 50 carbon atoms, optionally, a carboxylic acid or a phenol, and a quaternizing agent to provide an alkoxyated quaternary ammonium salt. In one embodiment at least 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 dissociation constant (pK_a) of less than about 13, such as a carboxylic acid or an alkyl phenol. The alkoxyated 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 about 1 to about 200 mg KOH/g. Regardless of how the alkoxyated 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.

[0015] 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. Hetero-atoms 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.

[0016] As used herein, the term "major amount" is understood to mean an amount greater than or equal to 50 wt. %, for example from about 80 to about 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.

[0017] 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:

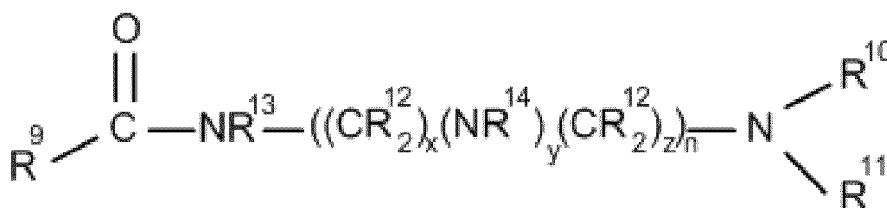


wherein each of R^4 and R^5 is, independently, hydrogen or a hydrocarbon based group. Each of R^6 , R^7 and R^8 is, independently, hydrogen or a hydrocarbon based group; preferably at least one is a hydrocarbon based group containing at least 20 carbon atoms.

[0018] As used herein, the term, "substantial absence" only allows the presence of a small amount of a component as an impurity.

Amine Compound

[0019] 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 hydrocarbonyl 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:



wherein each of R^{10} , and R^{11} is selected from hydrocarbonyl 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 hydrocarbonyl 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 hydrocarbonyl group R^9 to R^{14} may be independently selected from linear, branched, substituted, cyclic, saturated, unsaturated hydrocarbonyl groups, and may contain one or more hetero atoms. Suitable hydrocarbonyl 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 hydrocarbonyl 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.

[0020] 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 thereof with tertiary amines may be exhaustively or partially alkylated to a tertiary amine and further alkoxyated to a quaternary salt.

[0021] 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.

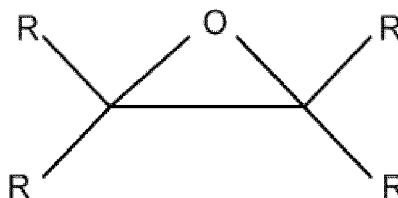
[0022] When the amine is an ether amine, it may be a hydrocarbonyl ether amine or a polyamine. For example, the amine may have the formula $R^{15}-[O-CH_2-CH(CH_3)]_y-NR^{16}R^{17}$, wherein R^{15} is a hydrocarbonyl radical having from 8 to 18 carbon atoms and y is an integer ranging from 1 to 6, and 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

[0023] 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 about 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, pentadecanic acid, palmitic acid, heptadecanic acid, stearic acid, nonadecanic acid, arachidic acid, isobutyric acid, isovaleric acid, isocaproic acid, ethylbutyric acid, methyl-valeric acid, isocaproic acid, propylvaleric acid, ethyl-caproic acid, isocaproic 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-methyl-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, dodecenic 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, mono methyl maleate, 1,5-octanedicarboxylic acid, 5,6-decane-dicarboxylic acid, 1,7-decanedicarboxylic acid, 4,6-dimethyl-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-dimethyl-7,1-octadecanediene-1,18-dicarboxylic acid, 7,12-dimethyl-1,18-octadecanedicarboxylic acid, 6,8-diphenyl-1,14-tetradecanedicarboxylic acid, 1,1-cyclopentanedicarboxylic acid, 1,1-cyclopentanedicarboxylic acid, 1,2-cyclopentanedicarboxylic 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, C₁-C₂₀-alkyl phenols, and polyalkyl phenols or substituted Mannich bases.

Quaternizing Agent

[0024] 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 C₁ to C₅₀ 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-Diepoxyoctane

1,2,7,8-Diepoxyoctane
 1,2-Epoxybutane
 cis-2,3-Epoxybutane
 3,4-Epoxy-1-butene
 5 3,4-Epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate
 1,2-Epoxydodecane
 1,2-Epoxyhexadecane
 1,2-Epoxyhexane
 1,2-Epoxy-5-hexene
 10 1,2-Epoxy-2-methylpropane
 exo-2,3-Epoxybornane
 1,2-Epoxyoctane
 1,2-Epoxy-pentane
 1,2-Epoxy-3-phenoxypropane
 15 (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
 20 Isophorone oxide
 Methyl-1,2-cyclopentene oxide
 2-Methyl-2-vinylloxirane
 α -Pinene oxide
 Ethylene oxide
 25 ($\pm$)-propylene oxide
 Polyisobutene oxide
 cis-Stilbene oxide
 Styrene oxide
 Glycidol
 30 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.

35 **[0025]** The alkoxyated 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
 40 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 about 1:1 to 10:1, for example from about 1:1 to 5:1, or from about 1:1 to about 2:1 moles of acid per mole of epoxy equivalents. In one embodiment, the anion of the quaternary ammonium salt is a carboxylate anion.

45 **[0026]** The reaction may be carried out at temperature ranging from about 30° to about 90°C, for example from about 45° to about 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 about 2:1 to about 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
 50 with mineral oil, diesel fuel, kerosene, alcohol, or an inert hydrocarbon solvent to prevent the product from being too viscous, if necessary.

55 **[0027]** 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 de-activators, carrier fluid, marker dyes, organic nitrate ignition accelerators, cyclomatic manganese tricarbonyl compounds, and the like. In some aspects, the compositions described herein may contain about 10 weight percent or less, or in other aspects, about 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.

[0028] 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 about 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.

[0029] 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, the disclosure of which is herein incorporated by reference in its entirety. Such metal deactivators include, for example, salicylidene-o-aminophenol, disalicylidene ethylenediamine, disalicylidene propylenediamine, N,N'-disalicylidene-1,2-diaminopropane, triazole, toluetriazole, and other substituted triazoles.

[0030] In some embodiments of this application, 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. For example, the gasoline or diesel fuels of this disclosure may contain, on an active ingredient basis, an amount of the quaternary ammonium salt in the range of about 1 mg to about 100 mg of quaternary ammonium salt per Kg of fuel, such as in the range of about 5 mg to about 50 mg of per Kg of fuel or in the range of from about 5 mg to about 25 mg of the quaternary ammonium salt per Kg of fuel. The active ingredient basis excludes the weight of (i) unreacted components associated with and remaining in the product as produced and used, and (ii) solvent(s), if any, used in the manufacture of the product either during or after its formation.

[0031] The additives of the present application, including the alkoxyated quaternary ammonium salt described above, and optional additives used in formulating the fuels of 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.

[0032] The fuels of the present application 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 about 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.

[0033] Accordingly, aspects of the present application are directed to methods for reducing friction or wear in a gasoline engine or fuel system for a gasoline engine as well as for reducing a corrosion potential for the fuel in the engine, fuel system or fuel terminal. 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.

[0034] In some aspects, the methods comprise injecting a hydrocarbon-based compression ignition fuel comprising an alkoxyated 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.

[0035] In one embodiment, the fuels of the present application 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 or quaternary ammonium salt of a hydrocarbyl Mannich compound. 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

[0036] 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-hydroxyethyl cocoamine.

Comparative Example 6 - tallow alkylamidopropyl-dimethylamine oxide.

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

Inventive Example 1

[0037] 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

[0038] An alkoxyated 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

[0039] An alkoxyated 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

[0040] An alkoxyated 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

[0041] An alkoxyated 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

[0042] C₂₀₋₂₄ 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.

[0043] 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

[0044] 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.

[0045] 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.		Additive 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
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

[0046] 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).

[0047] 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%

[0048] 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.		Additive 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

[0049] 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).

[0050] 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:

[Torque(engine oil without FM)-torque(additized oil with FM)]/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.

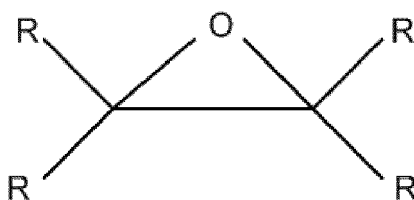
[0051] It is noted that, as used in this specification and the appended claims, the singular forms "a," "an," and "the," include plural referents unless expressly and unequivocally limited to one referent. Thus, for example, reference to "an antioxidant" includes two or more different antioxidants. As 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

[0052] For the purposes of this specification and appended claims, unless otherwise indicated, all numbers expressing quantities, percentages or proportions, and other numerical values used in the specification and claims, are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims 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.

[0053] While particular embodiments have been described, alternatives, modifications, variations, improvements, and substantial equivalents that are or can be presently unforeseen can arise to applicants or others skilled in the art. Accordingly, the appended claims as filed and as they can be amended are intended to embrace all such alternatives, modifications variations, improvements, and substantial equivalents.

Claims

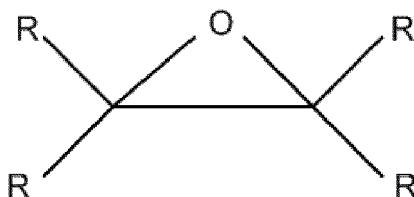
1. Use of a fuel composition to reduce wear in a fuel delivery system of an engine, wherein the fuel composition comprises gasoline and from about 10 to about 500 ppm by weight based on a total weight of the fuel composition of an alkoxyated quaternary ammonium salt derived from an epoxide, a tertiary 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 C₁ to C₅₀ 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 alkoxyated 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.
9. Use of a fuel composition to reduce corrosion in a fuel delivery system of an engine or in a fuel storage terminal, 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 alkoxyated quaternary ammonium salt derived from an epoxide and a tertiary amine reacted in the presence of an optional protonating agent.
10. The use of claim 9, wherein the tertiary amine comprises an amido amine derived from acid having from 1 to 54 carbon atoms.
11. The use of any one of claims 9-10, wherein the epoxide is selected from compounds of the formula:



wherein each R is independently selected from H and a C₁ to C₅₀ hydrocarbyl group.

12. The use of any one of claims 9-10, wherein the epoxide is selected from ethylene oxide, propylene oxide, and glycidol.
13. The use of any one of claims 9-12, 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, polyisobutenyl succinic acid, acid/amide, or acid/ester, and polymeric acids, and mixtures thereof.
14. The use of any one of claims 9-13, wherein the fuel composition contains from 80 to 120 ppm by weight of the alkoxyated quaternary ammonium salt based on a total weight of the fuel composition.
15. The use of an oil of lubricating viscosity comprising an alkoxyated quaternary ammonium salt derived from an epoxide and a tertiary amine in an amount of 0.1 to 1.0 wt.% to reduce engine friction.
16. The use of any one of claims 9-15, wherein the alkoxyated quaternary ammonium salt is derived from alkenyl or polyalkenyl succinic anhydride, a hydroxyl-containing epoxide and a tertiary amidopropyldimethylamine

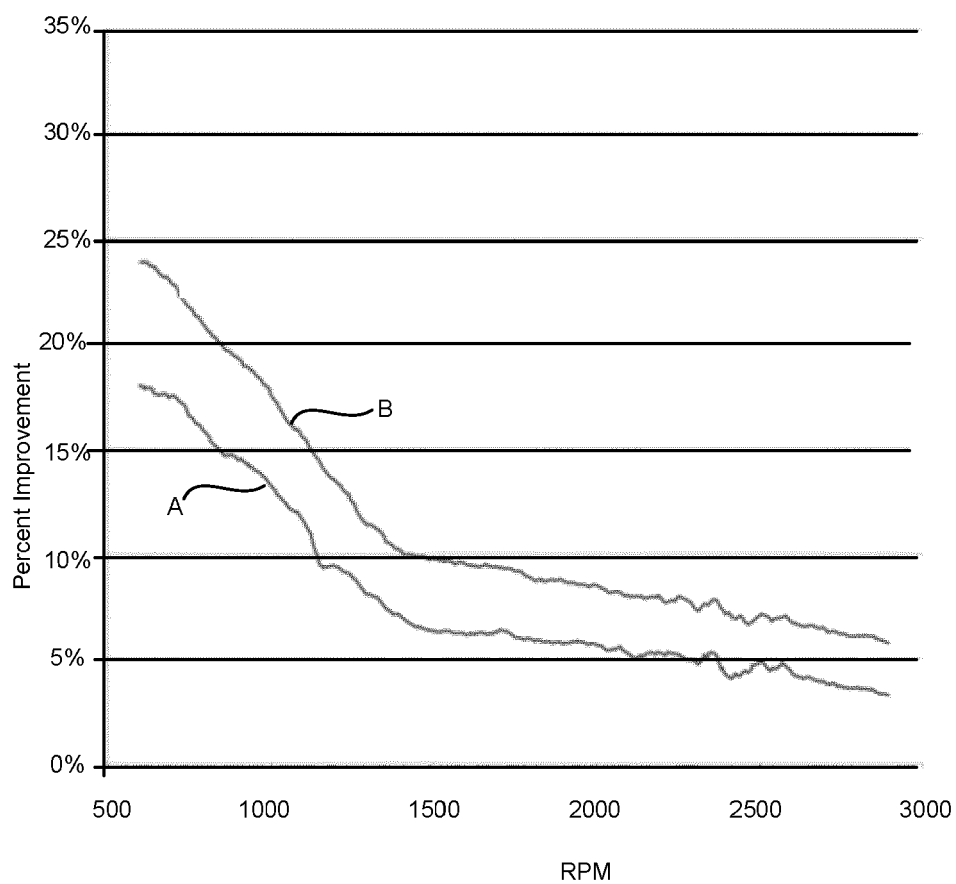


FIG. 1



EUROPEAN SEARCH REPORT

Application Number
EP 14 18 1490

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			TECHNICAL FIELDS SEARCHED (IPC)
			C10L C10M C10N
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 4 February 2015	Examiner Greß, Tobias
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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EPO FORM 1503 03.82 (P04C01)



Application Number

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CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing claims for which payment was due.

☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

☐ The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).



LACK OF UNITY OF INVENTION
SHEET B

Application Number

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The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 1-8

Use of a fuel composition to reduce wear in a fuel delivery system of an engine, wherein the fuel composition comprises gasoline and from about 10 to about 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. claims: 9-14(completely); 16(partially)

Use of a fuel composition to reduce corrosion in a fuel delivery system of an engine or in a fuel storage terminal, 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 and a tertiary amine reacted in the presence of an optional protonating agent.

3. claims: 15(completely); 16(partially)

The use of an oil of lubricating viscosity comprising an alkoxylated quaternary ammonium salt derived from an epoxide and a tertiary amine in an amount of 0.1 to 1.0 wt.% to reduce engine friction.

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 14 18 1490

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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