

FUEL ADDITIVES FOR LOWERING DEPOSIT AND PARTICULATE EMISSION

TECHNICAL FIELD

[001] This disclosure relates to fuel additives. More specifically, this disclosure describes compositions and methods that promote deposit cleaning performance and lower particulate emissions.

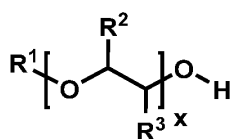
BACKGROUND

[002] Traditional fuel additives developed for port fuel injection (PFI) gasoline engines are generally not optimized for controlling formation of deposits in direct injection spark ignition (DISI) engines, sometimes referred to as direct injection gasoline (DIG) or gasoline injection (GDI) engines. Unlike PFI engines, DISI engines deliver fuel directly into the combustion chamber. When fuel is directly injected, it is immediately exposed to high temperatures and pressures. In this environment, combustion products can accumulate on the external and/or internal surfaces of the injector and nozzle (known as injector fouling).

[003] The formation of deposits, both around the injector nozzle and inside the combustion chamber, can have significant negative impact on one or more of fuel flow rate, injection duration, and spray pattern. This, in turn, can lead to increased emission, increased particulate matter (PM) formation, reduced fuel economy, loss of power/performance, increased wear, and/or reduced equipment life.

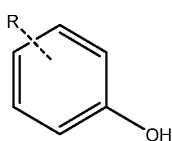
SUMMARY

[004] In one aspect, there is provided a fuel composition comprising: i) a hydrocarbon-based fuel boiling in the gasoline or diesel range; ii) a carrier fluid comprising an alkyl polyethoxylate having the following structure:



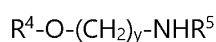
wherein each R^2 and R^3 is independently hydrogen, $\text{C}_1\text{--C}_4$ hydrocarbyl group, or $\text{C}_1\text{--C}_3$ alcohol, wherein R^1 is $\text{C}_4\text{--C}_{100}$ hydrocarbyl group, carboxyl group, ether group, thioether group, or aromatic group, wherein x is from 1 to 20,

or a hydrocarbyl phenol having the following structure:



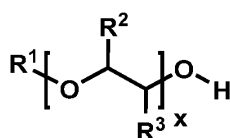
wherein R is a hydrocarbyl group from $\text{C}_4\text{--C}_{100}$;

iii) an amine-based detergent given by the following formula:



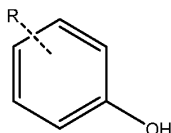
wherein the amine-based detergent is present in about 10 ppm to about 750 ppm by weight based on total weight of the fuel composition, wherein R^4 is a hydrocarbyl group having 8 to 20 carbons, R^5 is hydrogen or $(\text{CH}_2)_z\text{NH}_2$ moiety, and wherein y , z are independently integers having a value of 2 or greater; and iv) one or more nitrogen-containing detergent.

[005] In another aspect, there is provided a method for controlling carbon deposits in an internal combustion engine comprising: providing a fuel in the internal combustion engine, wherein the fuel comprises: i) a hydrocarbon-based fuel boiling in the gasoline or diesel range; ii) a carrier fluid comprising an alkyl polyethoxylated having the following structure:

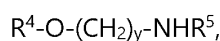


wherein each R^2 and R^3 is independently hydrogen, C_1 - C_4 hydrocarbyl group, or C_1 - C_3 alcohol, wherein R^1 is C_4 - C_{100} hydrocarbyl group, carboxyl group, ether group, thioether group, or aromatic group, wherein x is from 1 to 20,

or a hydrocarbyl phenol having the following structure:



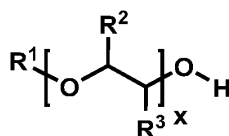
wherein R is a hydrocarbyl group from C_4 - C_{100} ; iii) an amine-based detergent having the following formula:



wherein the amine-based detergent is present in about 10 ppm to about 750 ppm by weight based on total weight of the fuel composition, wherein R^4 is a hydrocarbyl group having 8 to 20 carbons, R^5 is hydrogen or $(CH_2)_zNH_2$ moiety, and wherein y , z are independently integers having a value of 2 or greater; and iv) one or more nitrogen-containing detergent.

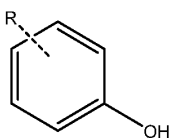
[006] In another aspect, there is provided a concentrate composition comprising: about 30 to 90 wt % of an organic solvent boiling in a range of from 65°C to 205°C ; and about 10 to 70 wt % of a detergent mixture comprising:

- i) a carrier fluid comprising an alkyl polyethoxylated having the following structure:

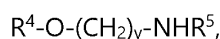


wherein each R^2 and R^3 is independently hydrogen, C_1 - C_4 hydrocarbyl group, or C_1 - C_3 alcohol, wherein R^1 is C_4 - C_{100} hydrocarbyl group, carboxyl group, ether group, thioether group, or aromatic group, wherein x is from 1 to 20,

or a hydrocarbyl phenol having the following structure:



wherein R is a hydrocarbyl group from C₄-C₁₀₀; ii) an amine-based detergent given by the following formula:



wherein the amine-based detergent is present in about 10 ppm to about 750 ppm by weight based on total weight of the fuel composition, wherein R⁴ is a hydrocarbyl group having 8 to 20 carbons, R⁵ is hydrogen or (CH₂)_zNH₂ moiety, and wherein y, z are independently integers having a value of 2 or greater; and iii) one or more nitrogen-containing detergent.

BRIEF DESCRIPTION OF DRAWINGS

[007] FIGS. 1A-1I are described in the Example section.

DETAILED DESCRIPTION

[008] This disclosure provides compositions and methods for improving engine performance, specifically improving deposit cleaning performance and/or lowering particulate emissions. The present invention may be effective at controlling carbon deposits in an internal combustion engine.

[009] In general, the fuel composition of the present invention comprises (i) a hydrocarbon-based fuel, (ii) carrier fluid, (iii) an amine-based detergent, and (iv) one or more nitrogen-containing detergent.

Hydrocarbon-based Fuel

[010] The hydrocarbon-based fuel includes gasoline and diesel.

[011] Gasoline fuel refers to a composition containing at least predominantly C₄-C₁₂ hydrocarbons. In one embodiment, gasoline or gasoline boiling range

components is further defined to refer to a composition containing at least predominantly C₄-C₁₂ hydrocarbons and further having a boiling range of from about 37.8°C (100°F) to about 204°C (400°F). In an alternative embodiment, gasoline is defined to refer to a composition containing at least predominantly C₄-C₁₂ hydrocarbons, having a boiling range of from about 37.8°C (100°F) to about 204°C (400°F), and further defined to meet ASTM D4814.

[012] Diesel fuel refers to middle distillate fuels containing at least predominantly C₁₀-C₂₅ hydrocarbons. In one embodiment, diesel is further defined to refer to a composition containing at least predominantly C₁₀-C₂₅ hydrocarbons, and further having a boiling range of from about 165.6°C (330°F) to about 371.1°C (700°F). In an alternative embodiment, diesel is as defined above to refer to a composition containing at least predominantly C₁₀-C₂₅ hydrocarbons, having a boiling range of from about 165.6°C (330°F) to about 371.1°C (700°F), and further defined to meet ASTM D975.

[013] The hydrocarbon-based fuel is present in a major amount by weight % of the total fuel composition. In some embodiments, the hydrocarbon-based fuel is present in about 50 wt% or greater, 55 wt% or greater, 60 wt% or greater, 65 wt% or greater, 70 wt% or greater, 75 wt% or greater, 80 wt% or greater, 85 wt% or greater, 90 wt% or greater, 95 wt% or greater or between any range from about 50 wt% to up to below 100 wt%.

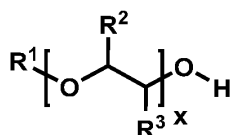
[014] According to some embodiments, the gasoline employed in the present invention may be clean burning gasoline (CBG). CBG refers to gasoline formulations that contain reduced levels of sulfur, aromatics and olefins. The exact formulation may vary depending on local regulatory definitions.

Carrier Fluid

[015] A fuel-soluble, non-volatile carrier fluid or oil may also be used with compounds of this disclosure. The carrier fluid is a chemically inert hydrocarbon-soluble liquid vehicle which substantially increases the non-volatile residue (NVR), or solvent-free liquid fraction of the fuel additive composition while not overwhelmingly

contributing to octane requirement increase. In some embodiments, the carrier fluid is a surfactant.

[016] The carrier fluid of the present invention may be an alkyl polyethoxylate given by the following Formula 1:

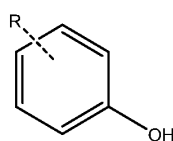


Formula 1A

wherein each R^2 and R^3 is independently hydrogen, C_1 - C_4 hydrocarbyl group, or C_1 - C_3 alcohol, wherein R^1 is C_4 - C_{100} hydrocarbyl group, carboxyl group, ether group, thioether group, or aromatic group, wherein x is from 1 to 20.

[017] The term “hydrocarbyl” refers to a chemical group or moiety derived from hydrocarbons including saturated and unsaturated hydrocarbons. Examples of hydrocarbyl groups include alkenyl, alkyl, polyalkenyl, polyalkyl, phenyl, and the like. Specific examples of hydrocarbyl groups include butyl, isopropyl, and polyisobutenyl groups.

[018] In some embodiments, the carrier fluid of the present invention may be a hydrocarbyl phenol having the following structure:



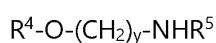
Formula 1B

wherein R is a hydrocarbyl group from C_4 - C_{100} . Specific examples of hydrocarbyl phenols include tetrapropenyl phenol, PIB phenol, butyl phenol, octylphenol, and the like.

[019] The carrier fluid may be employed in an amount ranging from 35 to 5000 ppm by weight of the hydrocarbon fuel (e.g., 50 to 3000 ppm of the fuel). When employed in a fuel concentrate, carrier fluids may be present in amounts ranging from 20 to 60 wt % (e.g., 30 to 50 wt %).

Amine-based Detergent

[020] The amine-based detergent (more specifically, a linear/branched aliphatic ether amine) of the present invention is represented by the following formula:



Formula 2

where R^4 is a hydrocarbyl group having 8 to 20 carbons, R^5 is hydrogen or $(CH_2)_zNH_2$ moiety, and y, z are independently integers having a value of 2 or greater. The hydrocarbyl group may be saturated or unsaturated. In some embodiments, the hydrocarbyl group may contain more than one unsaturated bond.

[021] As an advantage, the fuel additives of the present invention can deliver more basic nitrogen at the same treat rate compared to conventional amine-based fuel detergents (such as polyisobutylamine, polyether amine, etc.). This feature is important in determining detergency. As another advantage, the low molecular weight of the additives of the present invention along with their low decomposition temperature and high volatility prevents the additives from generating harmful deposits.

[022] Particularly illustrative aliphatic ether amines compatible with the present invention include isotridecyloxypropylamine and 2-ethylhexyloxypropyl amine. These are illustrative examples that are not intended to be limiting.

[023] In some embodiments, the primary fuel additive can be present in about 10 ppm to about 750 ppm (such as 20 to 700, 30 to 650, 50 to 600, 100 to 500, 200 to 400, 250 to 350, and so forth) based on the total fuel composition.

Nitrogen-containing Detergent

[024] The fuel composition of the present invention includes one or more nitrogen-containing detergent. Suitable secondary fuel additives may be classified as aliphatic hydrocarbyl-substituted amines, hydrocarbyl-substituted poly(oxyalkylene)amines, hydrocarbyl-substituted succinimides, Mannich reaction products, polyalkylphenoxyaminoalkanes, nitro and amino aromatic esters of polyalkylphenoxyalkanols, and nitrogen-containing carburetor/injector detergents. Each class of secondary fuel additive will be described in more detail herein.

[025] In particular, the aliphatic hydrocarbyl-substituted amines employed in the present invention may be straight or branched chain hydrocarbyl-substituted amines having at least one basic nitrogen and wherein the hydrocarbyl group has a number average molecular weight of about 700 to 3,000. Specific examples of aliphatic hydrocarbyl-substituted amines include polyisobutenyl amines and polyisobutyl amines. These amines can be derived as monoamines or polyamines. Preparation of aliphatic amines are generally known and described in detail in U.S. Pat. Nos. 3,438,757; 3,565,804; 3,574,576; 3,848,056; 3,960,515; 4,832,702; and 6,203,584, all of which are hereby incorporated by reference.

[026] In particular, the hydrocarbyl-substituted poly(oxyalkylene)amines employed in the present invention (also referred to as "polyether amines") may include hydrocarbyl poly(oxyalkylene)amines (monoamines or polyamines) wherein the hydrocarbyl group contains from about 1 to about 30 carbon atoms. The number of oxyalkylene units can range from about 5 to about 100. The amine moiety is derived from ammonia, primary alkyl or secondary dialkyl monoamine, or polyamine having a terminal amino nitrogen atom. The oxyalkylene moiety may be oxypropylene or oxybutylene or a mixture thereof. Hydrocarbyl-substituted poly(oxyalkylene)amines are described in U.S. Pat. No. 6,217,624, and U.S. Pat. No. 5,112,364, which are hereby incorporated herein by reference. Specific examples of hydrocarbyl-substituted poly(oxyalkylene)monoamine include alkylphenyl poly(oxyalkylene)monoamine wherein the poly(oxyalkylene) moiety contains oxypropylene units or oxybutylene units or mixtures of oxypropylene and oxybutylene units. The alkyl group on the

alkylphenyl moiety is a straight or branched-chain alkyl of about 1 to about 24 carbon atoms. A preferred alkylphenyl moiety is tetrapropenylphenyl where the alkyl group is a branched-chain alkyl of 12 carbon atoms derived from a propylene tetramer.

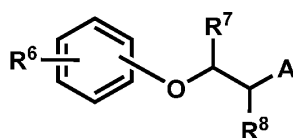
[027] More particularly, additional hydrocarbyl-substituted poly(oxyalkylene)amines include hydrocarbyl-substituted poly(oxyalkylene)aminocarbamates disclosed in U.S. Pat. Nos. 4,288,612; 4,236,020; 4,160,648; 4,191,537; 4,270,930; 4,233,168; 4,197,409; 4,243,798 and 4,881,945, which are hereby incorporated by reference. These hydrocarbyl poly(oxyalkylene)aminocarbamates contain at least one basic nitrogen atom and have an average molecular weight of about 500 to 10,000, preferably about 500 to 5,000, and more preferably about 1,000 to 3,000. A preferred aminocarbamate is alkylphenyl poly(oxybutylene)aminocarbamate wherein the amine moiety is derived from ethylene diamine or diethylene triamine.

[028] In particular, the hydrocarbyl-substituted succinimides employed in the present invention include polyalkyl and polyalkenyl succinimides wherein the polyalkyl or polyalkenyl group has an average molecular weight of about 500 to 5,000, and preferably about 700 to 3,000. The hydrocarbyl-substituted succinimides are typically prepared by reacting a hydrocarbyl-substituted succinic anhydride with an amine or polyamine having at least one reactive hydrogen bonded to an amine nitrogen atom. Preferred hydrocarbyl-substituted succinimides include polyisobutenyl and polyisobutanyl succinimides, and derivatives thereof. Hydrocarbyl-substituted succinimides are described in U.S. Pat. Nos. 5,393,309; 5,588,973; 5,620,486; 5,916,825; 5,954,843; 5,993,497; and 6,114,542, and British Patent No. 1,486,144, all of which are hereby incorporated herein by reference.

[029] In particular, the Mannich reaction products employed in the present invention include products typically obtained from Mannich condensation of a high molecular weight alkyl-substituted hydroxyaromatic compound, an amine containing at least one reactive hydrogen, and an aldehyde. The high molecular weight alkyl-substituted hydroxyaromatic compounds are preferably polyalkylphenols, such as

polypropylphenol and polybutylphenol, especially polyisobutylphenol, wherein the polyakyl group has an average molecular weight of about 600 to 3,000. The amine reactant is typically a polyamine, such as alkylene polyamines, especially ethylene or polyethylene polyamines, for example, ethylene diamine, diethylene triamine, triethylene tetramine, and the like, for example, 1-(2-aminoethyl)piperazine. The aldehyde reactant is generally an aliphatic aldehyde, such as formaldehyde, including paraformaldehyde and formalin, and acetaldehyde. A preferred Mannich reaction product is obtained by condensing a polyisobutylphenol with formaldehyde and diethylene triamine, wherein the polyisobutyl group has an average molecular weight of about 1,000. The Mannich reaction products suitable for use in the present invention are described, for example, in U.S. Pat. Nos. 4,231,759, U.S. Pat. Nos 5,697,988, and U.S. Pat. Nos 6,749,651 the disclosures of each of which are incorporated herein by reference.

[030] A still further class of detergent additive suitable for use in the present invention are polyalkylphenoxyaminoalkanes. Preferred polyalkylphenoxyaminoalkanes include those having the following formula:



Formula 3

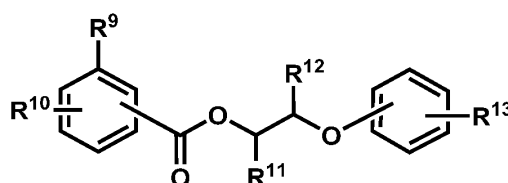
wherein R^6 is a polyalkyl group having an average molecular weight in the range of about 600 to 5,000; R^7 and R^8 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and A is amino, N-alkyl amino having about 1 to about 20 carbon atoms in the alkyl group, N,N-dialkyl amino having about 1 to about 20 carbon atoms in each alkyl group, or a polyamine moiety having about 2 to about 12 amine nitrogen atoms and about 2 to about 40 carbon atoms. The polyalkylphenoxyaminoalkanes of

Formula 3 above and their preparations are described in detail in U.S. Pat. No. 5,669,939, which is hereby incorporated herein by reference.

[031] Certain detergent mixtures may be particularly useful as secondary additives in accordance with the present invention.

[032] In some embodiments, mixtures of polyalkylphenoxyaminoalkanes and poly(oxyalkylene)amines may be employed. These mixtures are described in detail in U.S. Pat. No. 5,851,242, which is hereby incorporated by reference.

[033] In some embodiments, mixtures of nitro and amino aromatic esters of polyalkylphenoxyalkanols may be employed. Preferred nitro and amino aromatic esters of polyalkylphenoxyalkanols include those having the formula:

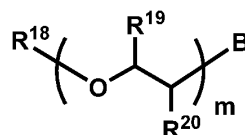


Formula 4

wherein: R^9 is nitro or $-(CH_2)-NR^{14}R^{15}$, wherein R^{14} and R^{15} are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; R^{10} is hydrogen, hydroxy, nitro or $-NR^{16}R^{17}$, wherein R^{16} and R^{17} are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; R^{11} and R^{12} are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and R^{13} is a polyalkyl group having an average molecular weight in the range of about 450 to 5,000. The aromatic esters of polyalkylphenoxyalkanols shown in Formula 4 above and their preparations are described in detail in U.S. Pat. No. 5,618,320, which is hereby incorporated herein by reference.

[034] Mixtures of nitro and amino aromatic esters of polyalkylphenoxyalkanols and hydrocarbyl-substituted poly(oxyalkylene)amines may also be employed in the present invention. These mixtures are described in detail in U.S. Pat. No. 5,749,929, which is hereby incorporated by reference. Preferred hydrocarbyl-substituted

poly(oxyalkylene)amines which may be employed as detergent additives in the present invention include those having the following formula:



Formula 5

wherein: R^{18} is a hydrocarbyl group having from about 1 to about 30 carbon atoms; R^{19} and R^{20} are independently hydrogen or lower alkyl having about 1 to about 6 carbon atoms and each $\text{—O—CHR}^{19}\text{—CHR}^{20}\text{—}$ unit is independent of other $\text{—O—CHR}^{19}\text{—CHR}^{20}\text{—}$ units; m is from about 5 to about 100; B is amino, N-alkyl amino having about 1 to about 20 carbon atoms in the alkyl group, N,N-dialkyl amino having about 1 to about 20 carbon atoms in each alkyl group, or a polyamine moiety having about 2 to about 12 amine nitrogen atoms and about 2 to about 40 carbon atoms; and m is an integer from about 5 to about 100. The hydrocarbyl-substituted poly(oxyalkylene)amines of Formula 5 above and their preparations are described in detail in U.S. Pat. No. 6,217,624, which is hereby incorporated by reference. The hydrocarbyl-substituted poly(oxyalkylene)amines of Formula 5 are preferably utilized either by themselves or in combination with other detergent additives, particularly with the polyalkylphenoxyaminoalkanes or the nitro and amino aromatic esters of polyalkylphenoxyalkanols. More preferably, the detergent additives employed in the present invention will be combinations of the hydrocarbyl-substituted poly(oxyalkylene)amines with the nitro and amino aromatic esters of polyalkylphenoxyalkanols. A particularly preferred hydrocarbyl-substituted poly(oxyalkylene)amine detergent additive is dodecylphenoxy poly(oxybutylene)amine and a particularly preferred combination of detergent additives is the combination of dodecylphenoxy poly(oxybutylene)amine and 4-polyisobutylphenoxyethyl para-aminobenzoate.

[035] Another class of detergent additive suitable for use in the present invention include nitrogen-containing carburetor/injector detergents. The carburetor/injector detergent additives are typically low molecular weight compounds having a number average molecular weight of about 100 to about 600 and possessing at least one polar moiety and at least one non-polar moiety. The non-polar moiety is typically a linear or branched-chain alkyl or alkenyl group having about 6 to about 40 carbon atoms. The polar moiety is typically nitrogen-containing. Typical nitrogen-containing polar moieties include amines (for example, as described in U.S. Pat. No. 5,139,534 and PCT International Publication No. WO 90/10051), ether amines (for example, as described in U.S. Pat. No. 3,849,083 and PCT International Publication No. WO 90/10051), amides, polyamides and amide-esters (for example, as described in U.S. Pat. Nos. 2,622,018; 4,729,769; and 5,139,534; and European Patent Publication No. 149,486), imidazolines (for example, as described in U.S. Pat. No. 4,518,782), amine oxides (for example, as described in U.S. Pat. Nos. 4,810,263 and 4,836,829), hydroxyamines (for example, as described in U.S. Pat. No. 4,409,000), and succinimides (for example, as described in U.S. Pat. No. 4,292,046). Each of these references are hereby incorporated by reference.

[036] Each secondary fuel additive can be present in about 50 ppm to about 2500 ppm (such as 100 to 2000, 200 to 1500, 300 to 1000 and the like) by weight of the fuel composition. More preferably, the secondary fuel additive is present in about 50 ppm to about 1000 ppm by weight of the fuel composition.

Other Additives

[037] The fuel composition may comprise other generally known fuel additives. Suitable examples include, but are not limited to, antioxidants, metal deactivators, demulsifiers, oxygenates, antiknock agents, dispersants and other detergents. In diesel fuel, other well-known additives can be employed such as pour point depressants, flow improvers, and the like.

[038] Each of the foregoing additives, when used, is used at a functionally effective amount to impart the desired properties to the fuel composition. Generally,

the concentration of each of these additives, when used, may range, unless otherwise specified, from about 0.001 to about 20 wt. %, such as about 0.01 to about 10 wt. %.

Concentrate

[039] The compounds of the present disclosure may be formulated as a concentrate using an inert stable oleophilic (i.e., soluble in hydrocarbon fuel) organic solvent boiling in a range of 65°C to 205°C. An aliphatic or an aromatic hydrocarbon solvent may be used, such as benzene, toluene, xylene, or higher-boiling aromatics or aromatic thinners. Aliphatic alcohols containing 2 to 8 carbon atoms, such as ethanol, isopropanol, methyl isobutyl carbinol, *n*-butanol and the like, in combination with the hydrocarbon solvents are also suitable for use with the present additives. In the concentrate, the amount of the additive may range from 10 to 70 wt % (e.g., 20 to 40 wt %).

[040] The following examples are intended to be non-limiting.

EXAMPLES

[041] Table 1 below summarizes the additives used to test injector fouling and/or deposit control performance. Base Fuel is unadditized gasoline composition.

Table 1

Figure	Formulation	Fuel Injector flow restoration (DU/CU)
1A	Base fuel without detergent	-3%
1B	3191 ppmw of PEA	62%
1C	2127 ppmw of PEA + 1000 ppmw of Surfactant A	41%
1D	2127 ppmw of PEA + 1000 ppmw of Surfactant B	28%
1E	2127 ppmw of PEA + 1000 ppmw of Surfactant A +150 ppmw of isotridecyloxypropyl amine	79%
1F	2127 ppmw of PEA + 1000 ppmw of Surfactant B +150 ppmw of isotridecyloxypropyl amine (Run 1)	100%

1G	2127 ppmw of PEA +1000 ppmw of Surfactant B +150 ppmw of isotridecyloxypropyl amine (Run 2)	96%
1H	2127 ppmw of PEA +1000 ppmw of C ₂₀ ~C ₂₄ hydrocarbyl phenol +150 ppmw of isotridecyloxypropyl amine	48%
1I	2127 ppmw of PEA +1000 ppmw of C ₆₅ ~C ₇₅ of hydrocarbyl phenol +150 ppmw of isotridecyloxypropyl amine	75%

[042] Testing was done on a 2012 2.0L GM LHU which contains an inline, 4 cylinder, turbocharged engine. The test was a Dirty-Up/Clean-Up (DU/CU) test where the engine first completed a 100-hour DU segment, to create deposits and foul the injectors, and that is followed by a 1-Tank CU segment.

[043] Formulation Tests: The formulation contained polyetheramine (PEA), 1000 ppmw of a non-ionic surfactant (Surfactant A and Surfactant B) and 150 ppmw of isotridecyloxypropyl amine. Surfactant A is ethoxylated (C₁₂-C₁₄) secondary alcohol. Surfactant B is nonylphenol ethoxylate.

[044] DU Fuel: Specialty, high sulfur, E0 fuel

[045] DU Cycle: Steady-state 2000rpm/100Nm

[046] 1-Tank CU Fuel: This testing was completed using a PUL E0 49-state non-additized base fuel.

[047] 1-Tank CU Cycle: 5-stage cycle with idle, low speed and load segments and moderate speed and load segments. Because of the change in both fuel and cycle conditions between the DU and the CU phases of testing, we ran a base fuel run, to validate that there is no CU of injectors without additive. The formulation is shown in Table 1 and the images are shown in Figures 1A-1I.

[048] All documents described herein are incorporated by reference herein, including any priority documents and/or testing procedures to the extent they are not inconsistent with this text. As is apparent from the foregoing general description and the specific embodiments, while forms of the present disclosure have been illustrated and described, various modifications can be made without departing from the spirit

and scope of the present disclosure. Accordingly, it is not intended that the present disclosure be limited thereby.

[049] For the sake of brevity, only certain ranges are explicitly disclosed herein. However, ranges from any lower limit may be combined with any upper limit to recite a range not explicitly recited, as well as, ranges from any lower limit may be combined with any other lower limit to recite a range not explicitly recited, in the same way, ranges from any upper limit may be combined with any other upper limit to recite a range not explicitly recited. Additionally, within a range includes every point or individual value between its end points even though not explicitly recited. Thus, every point or individual value may serve as its own lower or upper limit combined with any other point or individual value or any other lower or upper limit, to recite a range not explicitly recited.

[050] Likewise, the term "comprising" is considered synonymous with the term "including." Likewise whenever a composition, an element or a group of elements is preceded with the transitional phrase "comprising," it is understood that we also contemplate the same composition or group of elements with transitional phrases "consisting essentially of," "consisting of," "selected from the group of consisting of," or "is" preceding the recitation of the composition, element, or elements and vice versa.

[051] The terms "a" and "the" as used herein are understood to encompass the plural as well as the singular.

[052] Various terms have been defined above. To the extent a term used in a claim is not defined above, it should be given the broadest definition persons in the pertinent art have given that term as reflected in at least one printed publication or issued patent. Furthermore, all patents, test procedures, and other documents cited in this application are fully incorporated by reference to the extent such disclosure is not inconsistent with this application and for all jurisdictions in which such incorporation is permitted.

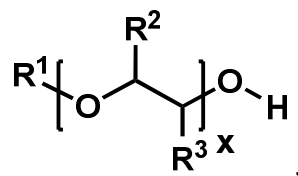
[053] The foregoing description of the disclosure illustrates and describes the present disclosure. Additionally, the disclosure shows and describes only the preferred embodiments but, as mentioned above, it is to be understood that the disclosure is capable of use in various other combinations, modifications, and environments and is capable of changes or modifications within the scope of the concept as expressed herein, commensurate with the above teachings and/or the skill or knowledge of the relevant art. While the foregoing is directed to embodiments of the present disclosure, other and further embodiments of the disclosure may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

[054] It is understood that when combinations, subsets, groups, etc. of elements are disclosed (e.g., combinations of components in a composition, or combinations of steps in a method), that while specific reference of each of the various individual and collective combinations and permutations of these elements may not be explicitly disclosed, each is specifically contemplated and described herein.

[055] The embodiments described hereinabove are further intended to explain best modes known of practicing it and to enable others skilled in the art to utilize the disclosure in such, or other, embodiments and with the various modifications required by the particular applications or uses. Accordingly, the description is not intended to limit it to the form disclosed herein. Also, it is intended that the appended claims be construed to include alternative embodiments.

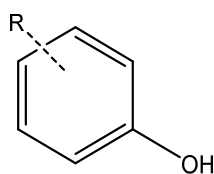
CLAIMS

1. A fuel composition comprising:
 - i) a hydrocarbon-based fuel boiling in the gasoline or diesel range;
 - ii) a carrier fluid comprising a compound having the following structure:



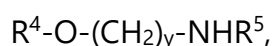
wherein each R^2 and R^3 is independently hydrogen, C_1 - C_4 hydrocarbyl group, or C_1 - C_3 alcohol, wherein R^1 is C_4 - C_{100} hydrocarbyl group, carboxyl group, ether group, thioether group, or aromatic group, wherein x is from 1 to 20;

or a hydrocarbyl phenol having the following structure:



wherein R is a hydrocarbyl group from C_4 - C_{100} ;

- iii) an amine-based detergent having the following formula,

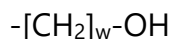


wherein the amine-based detergent is present in 10 ppm to 750 ppm by weight based on total weight of the fuel composition; wherein R^4 is a hydrocarbyl group having 8 to 20 carbons, R^5 is hydrogen or $(CH_2)_zNH_2$ moiety, and wherein y , z are independently integers having a value of 2 or greater; and

- iv) one or more nitrogen-containing detergent.

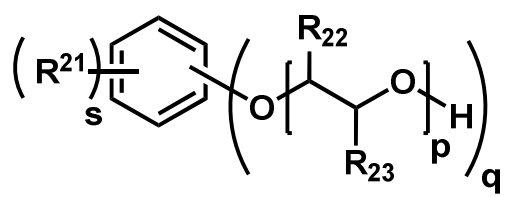
2. The fuel composition of claim 1, wherein the carboxyl group is a carboxylic acid, ester, amide, or ketone.

3. The fuel composition of claim 1, wherein the C₁ – C₃ alcohol has a structure represented by



wherein w is 1 to 3.

4. The fuel composition of claim 1, wherein the compound is represented by the following structure:



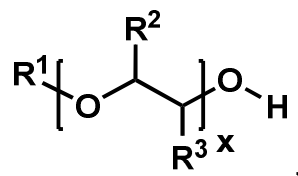
wherein each R²² and R²³ is independently hydrogen, C₁-C₄ hydrocarbyl group, or C₁-C₃ alcohol; wherein p is from 1 to 20, q is from 1 to 3, s is from 1 to 3, wherein q + s < 6; and R²¹ is C₁-C₁₀₀ hydrocarbyl group, carboxyl group, ether group, thioether group, amino alkyl group, or hydroxyl group.

5. The fuel composition of claim 1, wherein the fuel composition comprises 50 ppmw to 2000 ppmw of the carrier fluid or 100 ppmw to 750 ppmw of the amine-based detergent.

6. A method for controlling carbon deposits in an internal combustion engine comprising:

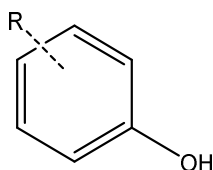
providing a fuel in the internal combustion engine, wherein the fuel comprises:

- i) a hydrocarbon-based fuel boiling in the gasoline or diesel range;
- ii) a carrier fluid comprising an alkyl polyethoxylated having the following structure:



wherein each R^2 and R^3 is independently hydrogen, C_1 - C_4 hydrocarbyl group, or C_1 - C_3 alcohol, wherein R^1 is C_4 - C_{100} hydrocarbyl group, carboxyl group, ether group, thioether group, or aromatic group, wherein x is from 1 to 20,

or a hydrocarbyl phenol having the following structure:



wherein R is a hydrocarbyl group from C_4 - C_{100} ;

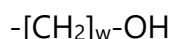
- iii) an amine-based detergent having the following formula, $\text{R}^4\text{-O}-(\text{CH}_2)_y\text{-NHR}^5$,

wherein the amine-based detergent is present in 10 ppm to 750 ppm by weight based on total weight of the fuel composition; wherein R^4 is a hydrocarbyl group having 8 to 20 carbons, R^5 is hydrogen or $(\text{CH}_2)_z\text{NH}_2$ moiety, and wherein y , z are independently integers having a value of 2 or greater; and

- iv) one or more nitrogen-containing detergent.

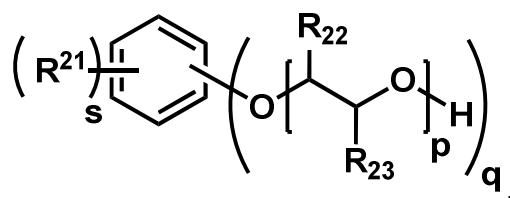
7. The method of claim 6, wherein the carboxyl group is a carboxylic acid, ester, amide, or ketone.

8. The method of claim 6, wherein the $\text{C}_1 - \text{C}_3$ alcohol has a structure represented by



wherein w is 1 to 3.

9. The method of claim 6, wherein the compound is represented by the following structure:



wherein each R^{22} and R^{23} is independently hydrogen, C_1 - C_4 hydrocarbyl group, or C_1 - C_3 alcohol; wherein p is from 1 to 20, q is from 1 to 3, s is from 1 to 3, wherein $q + s < 6$; and R^{21} is C_1 - C_{100} hydrocarbyl group, carboxyl group, ether group, thioether group, amino alkyl group, or hydroxyl group.

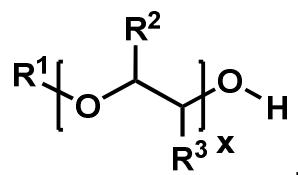
10. The method of claim 6, wherein the fuel composition comprises 50 ppmw to 2000 ppmw of the carrier fluid.

11. A concentrate composition comprising:

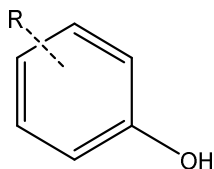
30 to 90 wt % of an organic solvent boiling in a range of from 65°C to 205°C and;

10 to 70 wt % of a detergent mixture comprising:

i) a carrier fluid comprising an alkyl polyethoxylated having the following structure:

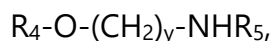


wherein each R^2 and R^3 is independently hydrogen, C_1 - C_4 hydrocarbyl group, or C_1 - C_3 alcohol, wherein R^1 is C_4 - C_{100} hydrocarbyl group, carboxyl group, ether group, thioether group, or aromatic group, wherein x is from 1 to 20,
or a hydrocarbyl phenol having the following structure



wherein R is a hydrocarbyl group from C₄-C₁₀₀;

ii) an amine-based detergent having the following formula,

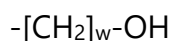


wherein R₄ is a hydrocarbyl group having 8 to 20 carbons, R₅ is hydrogen or (CH₂)_zNH₂ moiety, and wherein y, z are independently integers having a value of 2 or greater; and

iii) one or more nitrogen-containing detergent.

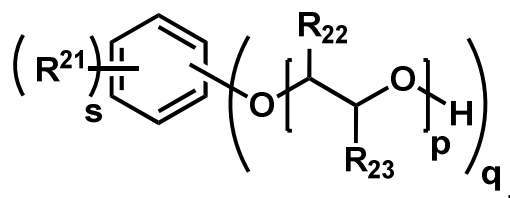
12. The concentrate of claim 11, wherein the carboxyl group is a carboxylic acid, ester, amide, or ketone.

13. The concentrate of claim 11, wherein the C₁ – C₃ alcohol has a structure represented by



wherein w is 1 to 3.

14. The concentrate of claim 11, wherein the compound is represented by formula 6,



wherein each R²² and R²³ is independently hydrogen, C₁-C₄ hydrocarbyl group, or C₁-C₃ alcohol; wherein p is from 1 to 20, q is from 1 to 3, s is from 1 to 3, wherein q + s < 6; and R²¹ is C₁-C₁₀₀ hydrocarbyl group, carboxyl group, ether group, thioether group, amino alkyl group, or hydroxyl group.

15. Use of a fuel composition according to any one of claims 1-5 in an internal combustion engine to reduce injector fouling, as determined by assessing fuel injector flow restoration in accordance with the test method described in the description.