

FUEL ADDITIVES FOR MITIGATING INJECTOR NOZZLE FOULING AND REDUCING PARTICULATE EMISSIONS

TECHNICAL FIELD

[001] This disclosure relates to fuel components that can improve engine performance. More specifically, this disclosure describes compositions and methods for mitigating injector nozzle fouling and reducing particulate emissions in direct injection spark ignition engines.

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. This is largely due to the fact that 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/or 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: a hydrocarbon-based fuel boiling in the gasoline or diesel range; an amine-based detergent given by formula $R_1-O-(CH_2)_m-NHR_2$, wherein the detergent is present in about 10 ppm to about 750 ppm by weight based on total weight of the fuel

composition; wherein R_1 is a hydrocarbyl group having 8 to 20 carbons, R_2 is hydrogen or $(CH_2)_nNH_2$ moiety, and wherein m , n are independently integers having a value of 3 or greater; and one or more nitrogen-containing detergent.

[005] 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: (1) an amine-based detergent given by formula $R_1-O-(CH_2)_m-NHR_2$, wherein R_1 is a hydrocarbyl group having 8 to 20 carbons, R_2 is hydrogen or $(CH_2)_nNH_2$ moiety, and wherein m , n are independently integers having a value of 3 or greater; and (2) one or more nitrogen-containing detergent.

[006] In yet another aspect, there is provided a method of controlling injector fouling, the method comprising: supplying to a direct injection engine a fuel composition comprising: a hydrocarbon-based fuel boiling in the gasoline or diesel range; an amine-based detergent given by formula $R_1-O-(CH_2)_m-NHR_2$, 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_1 is a hydrocarbyl group having 8 to 20 carbons, R_2 is hydrogen or $(CH_2)_nNH_2$ moiety, and wherein m , n are independently integers having a value of 3 or greater; and one or more nitrogen-containing detergent.

BRIEF DESCRIPTION OF DRAWINGS

[007] FIG. 1 is an illustration described in the Example section.

[008] FIG. 2 is an illustration described in the Example section.

[009] FIG. 3 is an illustration described in the Example section.

[010] FIG. 4 is an illustration described in the Example section.

[011] FIGS. 5A-5C are illustrations described in the Example section.

[012] FIGS. 6A-6C are illustrations described in the Example section.

[013] FIGS. 7A-7C are illustrations described in the Example section.

[014] FIGS. 8A-8C are illustrations described in the Example section.

[015] FIGS. 9A-9C are illustrations described in the Example section.

[016] FIGS. 10A-10C are illustrations described in the Example section.

[017] FIGS. 11A-11B are illustrations described in the Example section.

[018] FIG. 12 is an illustration described in the Example section.

DETAILED DESCRIPTION

[019] The present invention describes compositions and methods for deposit control in direct injection engines. More specifically, the present invention provides detergent additive compositions that can be utilized as components of fuel compositions and methods of using the compositions thereof.

[020] The fuel composition of the present invention comprises (i) a hydrocarbon-based fuel, (ii) a primary fuel additive and (iii) one or more secondary fuel additives.

Hydrocarbon-based Fuel

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

[022] 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.

[023] 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.

[024] 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%.

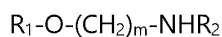
[025] According to some embodiments, the gasoline employed in the present invention may be clean burning gasoline (CBG). CBG refers to gasoline formulations that contain reduced levels of sulfur, aromatics and olefins. The exact formulation may vary depending on local regulatory definitions.

[026] 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. The carrier fluid may be a natural or synthetic oil, such as mineral oil, refined petroleum oils, synthetic polyalkanes and alkenes, including hydrogenated and unhydrogenated polyalphaolefins, synthetic polyoxyalkylene-derived oils, such as those described in U.S. Patent Nos. 3,756,793; 4,191,537; and 5,004,478; and in European Patent Appl. Pub. Nos. 356,726 and 382,159.

[027] The carrier fluids may be employed in amounts 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 %).

Primary Fuel Additive

[028] The primary fuel additive of the present invention is an amine-based detergent (more specifically, a linear/branched aliphatic ether amine) having the following formula:



Formula I

where R_1 is a hydrocarbyl group having 8 to 20 carbons, R_2 is hydrogen or $(CH_2)_nNH_2$ moiety, and m , n are independently integers having a value of 3 or greater. The hydrocarbyl group may be saturated or unsaturated. In some embodiments, the hydrocarbyl group may contain more than one unsaturated bond.

[029] 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.

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

[031] 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.

Secondary Fuel Additive

[032] The fuel composition of the present invention includes one or more secondary fuel additives. The secondary fuel additive is a nitrogen-containing detergent that provides enhanced detergency when paired with the primary fuel additive of the present invention.

[033] 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.

[034] 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.

[035] 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.

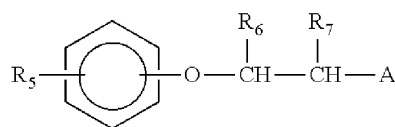
[036] More particularly, additional hydrocarbyl-substituted poly(oxyalkylene)amines include hydrocarbyl-substituted poly(oxyalkylene)aminocarbamates disclosed in U.S. Pat. Nos. 4,288,612; 4,236,020; 4,160,648; 4,191,537; 4,270,930; 4,233,168; 4,197,409; 4,243,798 and 4,881,945, which are hereby incorporated 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.

[037] 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.

[038] 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. 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 and 5,697,988, the disclosures of each of which are incorporated herein by reference.

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



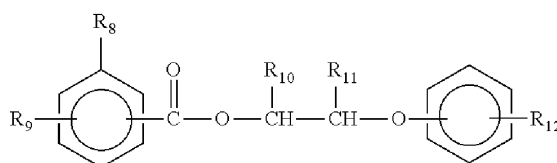
Formula II

wherein R₅ is a polyalkyl group having an average molecular weight in the range of about 600 to 5,000; R₆ and R₇ 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 II above and their preparations are described in detail in U.S. Pat. No. 5,669,939, which is hereby incorporated herein by reference.

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

[041] 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.

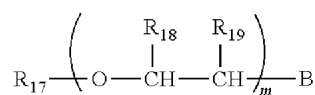
[042] In some embodiments, mixtures of nitro and amino aromatic esters of polyalkylphenoxyalkanols may be employed. Preferred nitro and amino aromatic esters of polyalkylphenoxyalkanols include those having the formula:



Formula III

wherein: R_8 is nitro or $-(CH_2)-NR_{13}R_{14}$, wherein R_{13} and R_{14} are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; R_9 is hydrogen, hydroxy, nitro or $-NR_{15}R_{16}$, wherein R_{15} and R_{16} are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; R_{10} and R_{11} are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and R_{12} 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 III above and their preparations are described in detail in U.S. Pat. No. 5,618,320, which is hereby incorporated herein by reference.

[043] 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 IV

wherein: R_{17} is a hydrocarbyl group having from about 1 to about 30 carbon atoms; R_{18} and R_{19} are each independently hydrogen or lower alkyl having about 1 to about 6 carbon atoms and each R_{18} and R_{19} is independently selected in each $\text{—O—CHR}_{18}\text{—CHR}_{19}\text{—}$ unit; 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 IV 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 IV 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.

[044] 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.

[045] 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

[046] 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.

[047] 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

[048] 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 %).

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

EXAMPLES

[050] Table 1 below summarizes the additives used to test injector fouling and/or deposit control performance. Additives used in the following tests include isotridecyloxypropylamine (Example 1), and polyoxybutylene amine (Example 2). Base Fuel is unadditized gasoline composition.

Table 1

	Name
Ex. 1	isotridecyloxypropylamine
Ex. 2	Polyoxybutylene amine

[051] Example 1 was blended in gasoline and tested for their ability to mitigate DISI injector fouling in a test vehicle using the test method described herein. A 2017 VW Jetta SE equipped with 1.4L turbocharged DISI 4-cylinder gasoline was the test vehicle used in this Example.

[052] FIG. 1 illustrates engine speed and load test conditions observed during a vehicle drive cycle. The vehicle drive cycle is based on 10 hills extracted from the transient phase of the Environmental Protection Agency (EPA) Urban Dynamometer

Drive Schedule (UDDS) with additional idle periods added. Total drive cycle is 20 minutes in duration and the overall test duration is 2,000-miles.

[053] Additive testing is conducted in a “keep clean” configuration which starts with a clean injector and combustion chamber. This test configuration evaluates the ability of a given deposit control additive to keep the injector and combustion chamber clean over the duration of the test.

[054] The test fuel samples were formulated with the target deposit control additive. Three injector “keep clean” tests were performed: (i) two tests using the unadditized base fuel and (ii) one test using the same base fuel as in (i) blended with 200 ppmw of Example 1. Injector fuel restriction (average) after the designated drive cycles are summarized in Table 2 below.

[055] As shown, the injector fuel restriction substantially decreased during additized fuel use as compared to during nonadditized fuel use. Injector fuel restriction measures the decrease in fuel flow from the injector, representing the presence of deposits in the injector orifices. Injector restriction can force the engine controller to make additional control adjustments to maintain proper engine fuel delivery, and the presence of deposits in the injector orifices can impact fuel mixing, leading to decreased engine performance and increased particulate emissions. Injector face images of each formulation after completion of test are shown in FIG. 2 and correspond to Table 2.

Table 2

Fuel Sample	Average			
Tested injector Pulse Width	1.5 ms	2.5 ms	3.5 ms	4.5 ms
Base fuel	1.79	1.53	1.39	1.61
Base fuel	2.18	1.98	1.67	1.54
Base fuel + 200 ppmw Ex 1	0.34	0.44	0.56	0.71

[056] A test engine was also used to evaluate PM emissions of Example 1. A 2016 BMW B48O DISI 2.0L 16-valve turbocharged engine was used in this test.

[057] The engine drive cycle is 360s in duration with engine speeds ranging from idle to 3000-RPM, and load varying up to 100-Nm. The overall test duration is 96 hours. FIG. 3 illustrates engine speed and load test conditions.

[058] PM measurements were made in the engine test stand using an AVL Micro Soot Sensor (MSS). The MSS provides a continuous, fast-response measurement of solid particulate mass and correlates well with the traditional, gravimetric method of PM measurement.

[059] In the PM emissions trace shown in FIG. 4 (a small 2000 second segment of the larger test), one can observe how quickly PM emissions rise and fall as engine conditions change. In order to provide a useful metric for these data, one can look toward official measurement methodologies used in regulatory vehicle emissions certification (e.g. U.S. Federal Test Procedure, or FTP). In these cases, regulatory agencies will simply report the sum total quantity of emissions from the vehicle tailpipe over an entire drive cycle. Applying a similar strategy to the PM dataset, we integrate PM emissions over the course of one test drive cycle. This integration is then repeated for each drive cycle and results in a PM emissions trendline over the entirety of the test duration.

[060] FIGS. 5A-5C illustrate the results of PM emissions trendlines (96 hour test) for fuel compositions with 150 ppmw of Example 2 (FIG. 5A), with 150 ppmw of Example 2 and 150 ppmw of Example 1 (FIG. 5B), and with 150 ppmw of Example 2 and 750 ppmw of Example 1 (FIG. 5C).

[061] FIGS. 6A-6C illustrate the results of the PM emissions trendlines (96 hour test) for fuel compositions with 2000 ppmw of Example 3 (FIG. 6A), with 2000 ppmw of Example 2 and 150 ppmw of Example 1 (FIG. 6B), and with 2000 ppmw of Example 2 and 750 ppmw of Example 1 (FIG. 6C).

[062] FIGS. 7A-7C and FIGS. 8A-8C illustrate results of direct injection spark-ignition (DISI) rig injector flow tests. These graphs show percent restriction relative to clean injector flow for various pulse widths (1.5 ms, 2.5 ms, 3.5 ms, and 4.5 ms) at 100 bar injection pressure. The samples tested include fuel compositions with 150 ppmw

of Example 2 (FIG. 7A), with 150 ppmw of Example 2 and 150 ppmw of Example 1 (FIG. 7B), and with 150 ppmw of Example 2 and 750 ppmw of Example 1 (FIG. 7C). The samples also include fuel compositions with 2000 ppmw of Example 2 (FIG. 8A), with 2000 ppmw of Example 2 and 150 ppmw of Example 1 (FIG. 8B), and with 2000 ppmw of Example 2 and 750 ppmw of Example 1 (FIG. 8C).

[063] FIGS. 9A-9C show injector face images that were taken after end of vehicle or engine test (prior to flow tests) corresponding to samples containing fuel compositions with 150 ppmw of Example 2 (FIG. 9A), with 150 ppmw of Example 2 and 150 ppmw of Example 1 (FIG. 9B), and with 150 ppmw of Example 2 and 750 ppmw of Example 1 (FIG. 9C).

[064] FIGS. 10A-10C show injector face images that were taken after end of vehicle or engine test (prior to flow tests) corresponding to samples containing fuel compositions with 2000 ppmw of Example 2 (FIG. 10A), with 2000 ppmw of Example 2 and 150 ppmw of Example 1 (FIG. 10B), and with 2000 ppmw of Example 2 and 750 ppmw of Example 1 (FIG. 10C).

[065] FIG. 11A shows average injector tip deposit volume (mm^3) for fuel compositions with 150 ppmw of Example 2 (left bar), with 150 ppmw of Example 2 and 150 ppmw of Example 1 (middle bar), and with 150 ppmw of Example 2 and 750 ppmw of Example 1 (right bar). FIG. 11B shows average injector tip deposit volume (mm^3) for fuel compositions with 2000 ppmw of Example 2 (left bar), with 2000 ppmw of Example 2 and 150 ppmw of Example 1 (middle bar), and 2000 ppmw of Example 2 and 750 ppmw of Example 1 (right bar). These measurements were taken end of vehicle or engine test (prior to flow tests).

[066] Table 3 below summarizes samples that were tested and rated for anti-corrosion property using NACE TM0172 standard test method. Base fuel is unadditized fuel. FIG. 12 provides visual confirmation of the anti-corrosion test.

Table 3

Samples	NACE Corrosion in ASTM Type II Water	
	% corrosion	Rating

Base fuel (trial 1)	70.68	D
Base fuel (trial 2)	74.03	D
Base fuel + 400 ppmw of Example 1 + 350 ppmw of Example 2 (trial 1)	15.69	B
Base fuel + 400 ppmw of Example 1 + 350 ppmw of Example 2 (trial 2)	3.97	B+

[067] 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.

[068] 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.

[069] 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.

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

[071] 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.

[072] 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.

[073] 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.

[074] 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.

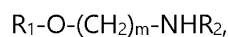
CLAIMS

1. A fuel composition comprising:
a hydrocarbon-based fuel boiling in the gasoline or diesel range;
an amine-based detergent given by formula
$$R_1-O-(CH_2)_m-NHR_2,$$
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_1 is a hydrocarbyl group having 8 to 20 carbons, R_2 is hydrogen or $(CH_2)_nNH_2$ moiety, and wherein m, n are independently integers having a value of 3 or greater; and
one or more nitrogen-containing detergent.
2. The fuel composition of claim 1, wherein R_1 is linear or branched.
3. The fuel composition of claim 1, wherein the one or more nitrogen-containing detergent is an aliphatic hydrocarbyl amine, hydrocarbyl-substituted poly(oxyalkylene)amine, hydrocarbyl-substituted succinimide, Mannich reaction product, nitro and amino aromatic ester of polyalkylphenoxyalkanol, or polyalkylphenoxyaminoalkane.
3. The fuel composition of claim 1, wherein the amine-based detergent or the one or more nitrogen-containing detergent is a monoamine or a polyamine.
4. The fuel composition of claim 1, wherein the amine-based detergent is present in about 10 ppm to 750 ppm of the fuel composition.
5. The fuel composition of claim 1, wherein the one or more nitrogen-containing detergent is present in about 50 ppm to about 2500 ppm of the fuel composition.

6. The fuel composition of claim 1, further comprising antioxidants, metal deactivators, demulsifiers, oxygenates, antiknock agents, dispersants, pour point depressants, or flow improvers.
7. 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:
(1) an amine-based detergent given by formula
$$R_1-O-(CH_2)_m-NHR_2,$$

wherein R_1 is a hydrocarbyl group having 8 to 20 carbons, R_2 is hydrogen or $(CH_2)_nNH_2$ moiety, and wherein m , n are independently integers having a value of 3 or greater; and
(2) one or more nitrogen-containing detergent.
8. The concentrate composition of claim 7, wherein R_1 is linear or branched.
9. The concentrate composition of claim 7, wherein the one or more nitrogen-containing detergent is an aliphatic hydrocarbyl amine, hydrocarbyl-substituted poly(oxyalkylene)amine, hydrocarbyl-substituted succinimide, Mannich reaction product, nitro and amino aromatic ester of polyalkylphenoxyalkanol, or polyalkylphenoxyaminoalkane.
10. The concentrate composition of claim 7, wherein the amine-based detergent or the one or more nitrogen-containing detergent is a monoamine or a polyamine.
11. A method of controlling injector fouling, the method comprising:
supplying to a direct injection engine a fuel composition comprising:
a hydrocarbon-based fuel boiling in the gasoline or diesel range;

an amine-based detergent given by 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_1 is a hydrocarbyl group having 8 to 20 carbons, R_2 is hydrogen or $(CH_2)_nNH_2$ moiety, and wherein m , n are independently integers having a value of 3 or greater; and
one or more nitrogen-containing detergent.

12. The method of claim 11, wherein R_1 is linear or branched.
13. The method of claim 11, wherein the one or more nitrogen-containing detergent is an aliphatic hydrocarbyl amine, hydrocarbyl-substituted poly(oxyalkylene)amine, hydrocarbyl-substituted succinimide, Mannich reaction product, nitro and amino aromatic ester of polyalkylphenoxyalkanol, or polyalkylphenoxyaminoalkane.
13. The method of claim 11, wherein the amine-based detergent or the one or more nitrogen-containing detergent is a monoamine or a polyamine.
14. The method of claim 11, wherein the amine-based detergent is present in about 10 ppm to 750 ppm of the fuel composition.
15. The method of claim 11, wherein the one or more nitrogen-containing detergent is present in about 50 ppm to about 2500 ppm of the fuel composition.
16. The method of claim 11, wherein the fuel composition further comprises antioxidants, metal deactivators, demulsifiers, oxygenates, antiknock agents, dispersants, pour point depressants, or flow improvers.