

## **ARYLOXY ALKYLAMINES AS FUEL ADDITIVES FOR REDUCING INJECTOR FOULING IN DIRECT INJECTION SPARK IGNITION GASOLINE ENGINES**

### **TECHNICAL FIELD**

[001] This disclosure relates to fuel additives and fuel compositions containing the same. More specifically, this disclosure describes compositions and methods for controlling deposit formation in direct injection spark ignition gasoline engines.

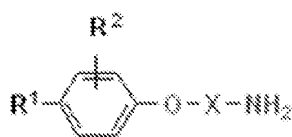
### **BACKGROUND**

[002] Traditional fuel additives developed for port fuel injection (PFI) gasoline engines are generally not optimized for controlling the formation of deposits in injectors of direct injection spark ignition (DISI) engines, sometimes referred to as direct injection gasoline (DIG) or gasoline direct injection (GDI) engines. This is largely since 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 injectors 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.

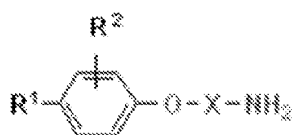
### **SUMMARY**

[004] In one aspect, there is provided a fuel composition comprising gasoline; and aryloxy alkylamine additive having the following structure:



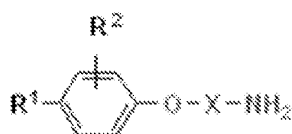
wherein the aryloxy alkylamine additive is present in about 10 to about 750 ppm by weight based on total weight of the fuel composition; wherein X is a hydrocarbyl group having 1 or 2 carbon atoms; and wherein R<sup>1</sup> and R<sup>2</sup> are independently hydrogen or hydrocarbyl group having up to 36 carbon atoms.

[005] In another aspect, there is provided a concentrate composition comprising about 0 to 90 wt % of an organic solvent boiling in a range of from 65°C to 205°C and about 10 to 100 wt % of a fuel additive comprising: an aryloxy alkylamine given by formula



wherein X is a hydrocarbyl group having 1 or 2 carbon atoms; and wherein R<sup>1</sup> and R<sup>2</sup> are independently hydrogen or substituted hydrocarbyl group having up to 36 carbon atoms.

[006] In yet another aspect, there is provided a method of reducing injector fouling in a direct injection spark ignition gasoline engine comprising providing a gasoline composition comprising: aryloxy alkylamine additive having the following structure



wherein the aryloxy alkylamine additive is present in about 10 to about 750 ppm by weight based on total weight of the fuel composition; wherein X is a hydrocarbyl group having 1 or 2 carbon atoms; and wherein R<sup>1</sup> and R<sup>2</sup> are independently hydrogen, substituted alkyl or alkenyl group having up to 36 carbon atoms.

### BRIEF DESCRIPTION OF DRAWINGS

[007] FIG. 1 shows a graph described in the Examples.

[008] FIGS. 2A-2C show photographs described in the Examples.

### DETAILED DESCRIPTION

[009] 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.

[010] The fuel composition of the present invention comprises (i) a hydrocarbon-based fuel; and (ii) an aryloxy alkylamine fuel additive. In some embodiments, the fuel composition may comprise a secondary fuel additive.

#### Hydrocarbon-based Fuel

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

[012] Gasoline fuel refers to a composition containing at least predominantly C<sub>4</sub>-C<sub>12</sub> hydrocarbons. In one embodiment, gasoline or gasoline boiling range components is further defined to refer to a composition containing at least predominantly C<sub>4</sub>-C<sub>12</sub> 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 C<sub>4</sub>-C<sub>12</sub> 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.

[013] Diesel fuel refers to middle distillate fuels containing at least predominantly C<sub>10</sub>-C<sub>25</sub> hydrocarbons. In one embodiment, diesel is further defined to refer to a composition containing at least predominantly C<sub>10</sub>-C<sub>25</sub> 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 C<sub>10</sub>-C<sub>25</sub> 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.

[014] 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%.

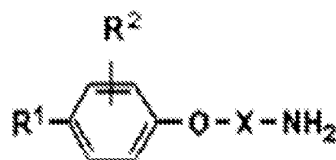
[015] According to some embodiments, the gasoline employed in the present invention may be clean burning gasoline (CBG). CBG refers to gasoline formulations that contain reduced levels of sulfur, aromatics and olefins. The exact formulation may vary depending on local regulatory definitions.

[016] 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.

[017] 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 %).

#### Aryloxy alkylamine Fuel Additive

[018] The aryloxy alkylamine fuel additive of the present invention reduces injector fouling in a direct injection spark ignition gasoline engine. The additive is a nitrogen-containing detergent having the following formula:



Formula I

wherein  $R^1$  and  $R^2$  are independently hydrogen, or a hydrocarbyl group having up to 36 carbon atoms.  $R^2$  can be positioned at the ortho- or meta- position with respect to the oxygen atom. X is a hydrocarbyl group having 1 or 2 carbon atoms. X may be saturated or unsaturated. In some embodiments, it may be preferable for one of  $R^1$  or  $R^2$  to be a hydrocarbyl group and the other to be a hydrogen.

[019] In some embodiments, the hydrocarbyl group is an alkyl group or an alkenyl group. Alkyl groups refer to saturated hydrocarbyl groups, which can be linear, branched, cyclic, or a combination of cyclic, linear and/or branched. Alkenyl groups refer to unsaturated hydrocarbyl groups, which can be linear, branched, cyclic, or a combination of cyclic, linear and/or branched.

[020] Suitable examples of aryloxy alkylamines include, but are not limited to, 2-(phenoxy)ethyl-1-amine, 2-(4-butylphenoxy)ethyl-1-amine, 2-(4-octylphenoxy)ethyl-1-amine, 2-(4-nonylphenoxy)ethyl-1-amine, 2-(4-dodecylphenoxy)ethyl-1-amine, 2-(4-octadecylphenoxy)ethyl-1-amine, 2-(4-eicosanylphenoxy)ethyl-1-amine, 2-(4-docosanylphenoxy)ethyl-1-amine, 2-(4-tetracosanylphenoxy)ethyl-1-amine.

[021] The aryloxy alkylamines may be obtained commercially or by any known compatible synthesis method with. For example, aryloxy alkylamines may be obtained by reacting salt of alkylphenol with a chloroacetaldehyde. The resulting product is then reacted with an amino alcohol and then hydrogenated in the presence of a nickel catalyst to generate the aryloxy alkylamine. A more detailed description of aryloxy

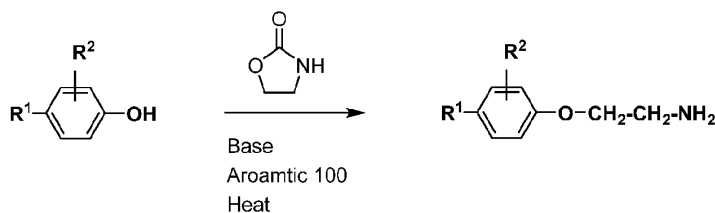
alkylamine synthesis can be found in U.S. Patent No. 3,954,872, which is hereby incorporated by reference.

### Synthesis

[022] In general, the fuel additives of the present invention may be synthesized by any known compatible method. Description of two known synthesis methods are described herein.

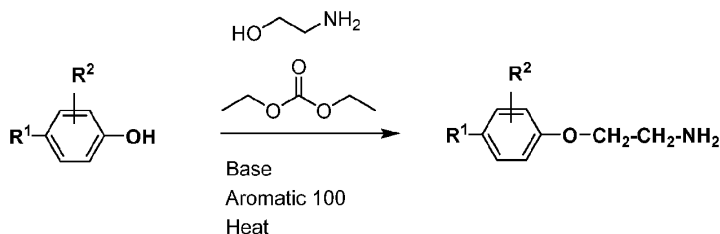
[023] In the first method (Method A), an alkylphenol is initially reacted with a base (e.g., potassium hydroxide) to form an alkylphenoxide said, which will further react with 2-oxazolidinone in an aromatic solvent under reflux conditions to provide the corresponding aminoethylated product.

#### Method A



[024] In the second method (Method B), an alkylphenol is also initially reacted with a base (e.g., potassium hydroxide) to form an alkylphenoxide, which will further react with 2-oxazolidinone generated in situ from the reaction between ethanolamine and diethyl carbonate in an aromatic solvent under reflux conditions to provide the corresponding aminoethylated product.

#### Method B



[025] For illustrative purposes, the following example of Method B is provided.

[026] A 1000 mL two-neck round bottom flask was charged with a mixture of 4-eicosanylphenol, 4-docosanylphenol, 4-tetracosanylphenol, 2-eicosanylphenol, 2-docosanylphenol, and 2-tetracosanylphenol with an averaged molecular weight of 402.71 g/mol (120 g, 0.298 mol, 1.00 equiv), KOH (2.96 g, 0.0447 mol, 0.150 equiv, 85% active), 150 mL of Aromatic 100 solvent equipped with mechanical stirrer, a Dean-Stark trap and a reflux condenser, and the reaction mixture was refluxed under vigorous stirring and a purging nitrogen atmosphere for 1 hour to remove water. The reaction mixture was cooled to about 120 °C, and ethanolamine (21.87 g, 0.358 mol, 1.20 equiv) and diethyl carbonate (42.3 g, 0.358 mol, 1.20 equiv) were added in that order. The reaction mixture was then warmed to 120 °C under gentle N<sub>2</sub> flow until the theoretical amount of ethanol was evolved from the reaction, which was then warmed to 175 °C with vigorous stirring under a gentle flow of nitrogen for 19 hours. The crude reaction mixture was diluted with 250 mL of ethyl acetate and was washed with 3 x 200 mL of water and 200 mL of brine. The organic layer was dried with MgSO<sub>4</sub>, filtered, and concentrated to give crude product as an amber color oil (128.0 g). It was analyzed by NMR spectroscopy and HPLC.

#### Secondary Fuel Additives

[027] 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.

[028] 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.

[029] 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.

[030] 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.

[031] 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

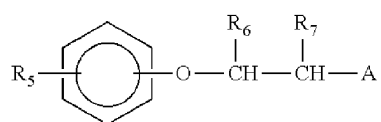
are hereby incorporated by reference. These hydrocarbyl poly(oxyalkylene)aminocarbamates contain at least one basic nitrogen atom and have an average molecular weight of about 500 to 10,000, preferably about 500 to 5,000, and more preferably about 1,000 to 3,000. A preferred aminocarbamate is alkylphenyl poly(oxybutylene)aminocarbamate wherein the amine moiety is derived from ethylene diamine or diethylene triamine.

[032] 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.

[033] 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 polyalkyl 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.

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



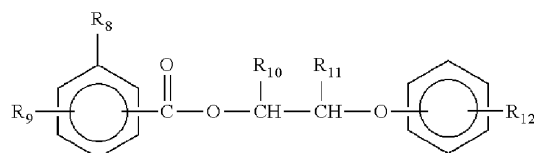
Formula II

wherein R<sub>5</sub> is a polyalkyl group having an average molecular weight in the range of about 600 to 5,000; R<sub>6</sub> and R<sub>7</sub> 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.

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

[036] 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.

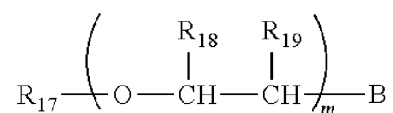
[037] In some embodiments, mixtures of nitro and amino aromatic esters of polyalkylphenoxyalkanols may be employed. Preferred nitro and amino aromatic esters of polyalkylphenoxyalkanols include those having the formula:



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.

[038] 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  $—O—CHR_{18}—CHR_{19}—$  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.

[039] 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.

[040] 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

[041] 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.

[042] 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

[043] 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 %).

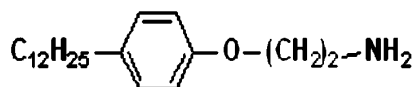
[044] The following examples are intended to be non-limiting.

## EXAMPLES

### Inventive Example 1

[045] Inventive Example 1 is 2-(4-dodecylphenoxy)ethyl-1-amine shown below (Formula V).

[046] 4-Dodecylphenol (200.0 g, 0.76 mol) was dissolved in 1000 mL of naphtha (Aromatic 100) solvent in a 2L 3-neck round bottom flask. To this mixture was added potassium hydroxide (4.3 g) followed by hexanol (78 g, 0.76 mol) and the resulting mixture was stirred at room temperature under a nitrogen atmosphere for 30 minutes by using a mechanical stirrer. After that the mixture was heated to reflux (about 165-170 °C) and stirred under nitrogen for an additional 2 hours. During this time period, distillate liquid (e.g., water/hexanol and aromatic solvent) was collected in a Dean-Stark trap apparatus. After stirring for 2 hours, the mixture was cooled to 120 °C and 2-oxazolidinone (66.0 g, 0.76 mol) was added. The mixture was heated at reflux and stirred under nitrogen for 18 hours (overnight). The mixture was allowed to cool to room temperature, diluted with hexanes (100 mL) and the organic phase was washed with water (200 mL), brine (4 x 100 mL), dried over anhydrous MgSO<sub>4</sub>, and filtered through a pad of Celite filter aid. The filtrate was concentrated under reduced pressure and then under high vacuum to give an amber colored oil as crude product (240 g).

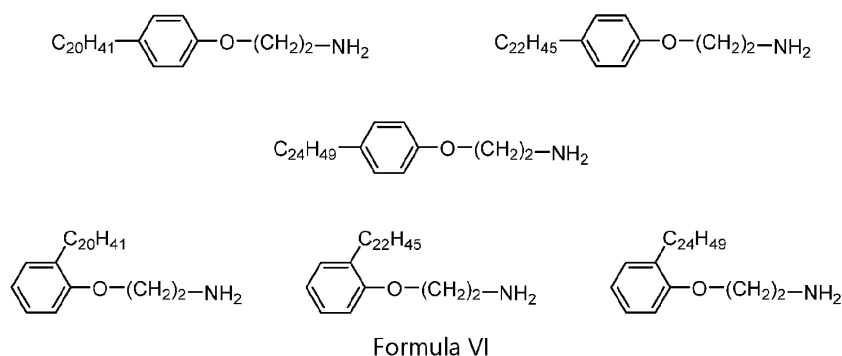


Formula V

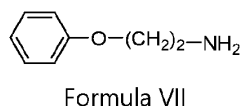
### Inventive Example 2

[047] Inventive Example 2 is a mixture of 2-(4-eicosanylphenoxy)ethyl-1-amine, 2-(4-docosanylphenoxy)ethyl-1-amine, and 2-(4-tetracosanylphenoxy)ethyl-1-amine shown below (Formula VI). It was obtained by Method A as described below.

[048] A mixture of 4-eicosanylphenol, 4-docosanylphenol, 4-tetracosanylphenol, 2-eicosanylphenol, 2-docosanylphenol, and 2-tetracosanylphenol with an averaged molecular weight of 402.71 g/mol (151.71 g, 0.377 mol) was dissolved in Aromatic 100 solvent (700 mL) in a 2L 3-neck round bottom flask. To this mixture was added potassium hydroxide (2.1 g) followed by hexanol (38.5 g, 0.377 mol) and the resulting mixture was stirred at room temperature under a nitrogen atmosphere for 30 minutes by using a mechanical stirrer. After that the mixture was heated to reflux (about 165-170 °C) and stirred under nitrogen for an additional 2 hours. During this time period, distillate liquid (e.g., water/hexanol and aromatic solvent) was collected in a Dean-Stark trap apparatus. After stirring for 2 hours, the mixture was cooled to 120 °C and 2-oxazolidinone (32.77 g, 0.377 mol) was added. The mixture was heated at reflux and stirred under nitrogen for 18 hours (overnight). The mixture was allowed to cool to room temperature, diluted with hexanes (200 mL) and the organic phase was washed with water (200 mL), brine (4 x 100 mL), dried over anhydrous MgSO<sub>4</sub>, and filtered through a pad of Celite filter aid. The filtrate was concentrated under reduced pressure and then under high vacuum to give a dark colored oil as crude product (150.2 g). The crude product was purified by column chromatography using a mixture of ethyl acetate/methanol gradient to give a pale yellow oil (105.8 g).

Inventive Example 3

[049] Inventive Example 3 is a commercially available 2-(phenoxy)ethyl-1-amine shown below (Formula VII).

Inventive Example 4

[050] 4-Nonylphenol (200.0 g, 0.908 mol) was dissolved in Aromatic 100 solvent (500 mL) in a 2L 3-neck round bottom flask. To this mixture was added potassium hydroxide (2.1 g) followed by hexanol (92.74 g, 0.908 mol) and the resulting mixture was stirred at room temperature under a nitrogen atmosphere for 30 minutes by using a mechanical stirrer. After that the mixture was heated to reflux (about 165-170 °C) and stirred under nitrogen for an additional 2 hours. During this time period, distillate liquid (e.g., water/hexanol and aromatic solvent) was collected in a Dean-Stark trap apparatus. After stirring for 2 hours, the mixture was cooled to 120 °C and 2-oxazolidinone (102.75 g, 1.180 mol) was added. The mixture was heated at reflux and stirred under nitrogen for 18 hours (overnight). The mixture was allowed to cool to 70 °C and ethylenediamine (10.91 g, 0.182 mol) was added and the mixture was heated at reflux for 4 hours. The mixture was cooled to room temperature and

Magnesol® (100 g) was added and stirred for 30 minutes. The mixture was filtered and concentrated under high vacuum to yield a light yellow oil as crude product (243.67 g). This crude product was further washed with water (3 x 500 mL), brine (500 mL), dried over anhydrous  $\text{MgSO}_4$ , and filtered through a pad of Celite filter aid. The filtrate was concentrated under reduced pressure and then under high vacuum. The crude product was purified by column chromatography using a mixture of ethyl acetate/methanol gradient to give a pale yellow oil.

[051] The Inventive Examples were blended in gasoline and tested for its ability to mitigate DISI direct injector fouling in a test vehicle. A 2017 VW Jetta SE vehicle equipped with a 1.4L 16-valve turbocharged DISI engine was used as the test vehicle.

[052] FIG. 1 shows vehicle speed conditions observed during the specified 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] Injector “keep clean” tests were performed on four fuel samples: (i) unadditized base fuel, (ii) 200 ppmw of inventive example 1 added to sample (i), (iii) 200 ppmw of inventive example 2 added to sample (i), and (iv) 200 ppmw of inventive example 3 added to sample (i).

[055] A set of four clean injectors were used at the start of each vehicle test. At the end of test, photographs of the four injectors were taken of the deposits formed. FIG. 2 show photographs of injectors before and after the engine test.

[056] Flow restriction of the injectors were also measured. Table 1 shows average injector flow restriction (%) measured at end of engine test compared to the base fuel reference (i.e., unadditized gasoline).

[057] As shown, Inventive Example 1 provided much lower flow restriction (0.39% on average) when compared to the base fuel reference (2.81% on average). Inventive Examples 2 and 3 also provided lower flow restriction (1.47% and 2.15% on average, respectively)

[058] 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.

Table 1

|                                          | Base Fuel Reference | Base Fuel + Inventive Example 1 (200 ppmw) | Base Fuel + Inventive Example 2 (200 ppmw) | Base Fuel + Inventive Example 3 (200 ppmw) |
|------------------------------------------|---------------------|--------------------------------------------|--------------------------------------------|--------------------------------------------|
| Average Restriction [%]                  | 2.81                | 0.39                                       | 1.47                                       | 2.15                                       |
| Decrease in % restriction from base fuel | -                   | -2.42                                      | -1.34                                      | -0.66                                      |

[059] A second test was also conducted using an engine on a dynamometer stand. A 2017 Honda DISI 1.5L 16-valve turbocharged engine was the test vehicle engine used. The engine drive cycle is 720 s in duration with engine speeds ranging from idle to 4000 RPM, and load varying up to 160 Nm. The overall test duration is 50 hours (test duration for baseline fuel with 200 ppmw of Example 2 was 25 hours). FIG. 3 illustrates engine speed and load test conditions.

[060] A set of four clean injectors were used at the start of each engine test. At the end of test, photographs (FIG. 4) of the four injectors were taken of the deposits formed.

[061] 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.

[062] In the PM emissions trace shown in FIG. 5 (a 3600 second segment of the larger 50 hr. 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.

[063] FIGS. 6A-6C illustrate the PM emissions traces from a baseline fuel (FIG. 6A), the baseline fuel with 200ppmw of Inventive Example 1 (FIG. 6B), and the baseline fuel with 200ppmw of Inventive Example 2 (FIG. 6C). The addition of Inventive Example 1 or Inventive Example 2 at 200 ppmw maintains PM emissions at the same level as at start of test with a clean injector across the full duration of the test.

[064] 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.

[065] 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.

[066] 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.

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

[068] 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.

[069] 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

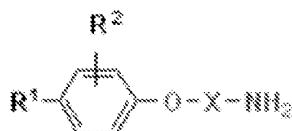
relevant art. While the foregoing is directed to embodiments of the present disclosure, other and further embodiments of the disclosure may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

[070] 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.

[071] 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**

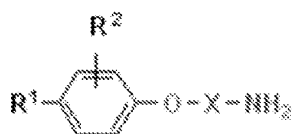
1. A fuel composition comprising:  
gasoline; and  
aryloxy alkylamine additive having the following structure:



- wherein the aryloxy alkylamine additive is present in about 10 to about 750 ppm by weight based on total weight of the fuel composition;
- wherein X is a hydrocarbyl group having 1 or 2 carbon atoms; and
- wherein R<sup>1</sup> and R<sup>2</sup> are independently hydrogen or substituted hydrocarbyl group having up to 36 carbon atoms.
2. The fuel composition of claim 1, wherein X is ethylene group.
  3. The fuel composition of claim 1, further comprising:  
a nitrogen-containing detergent.
  4. The fuel composition of claim 3, wherein the 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.
  5. The fuel composition of claim 1, further comprising antioxidants, metal deactivators, demulsifiers, oxygenates, antiknock agents, dispersants, pour point depressants, or flow improvers.
  6. The fuel composition of claim 1, wherein the aryloxy alkylamine is 2-(4-dodecylphenoxy)ethyl-1-amine, 2-(phenoxy)ethyl-1-amine, 2-(4-butylphenoxy)ethyl-

1-amine, 2-(4-octylphenoxy)ethyl-1-amine, 2-(4-nonylphenoxy)ethyl-1-amine, 2-(4-octadecylphenoxy)ethyl-1-amine, 2-(4-eicosanylphenoxy)ethyl-1-amine, 2-(4-docosanylphenoxy)ethyl-1-amine, or 2-(4-tetracosanylphenoxy)ethyl-1-amine.

7. A concentrate composition comprising:  
about 10 to 90 wt % of an organic solvent boiling in a range of from 65°C to 205°C and;  
about 10 to 100 wt % of a fuel additive comprising:  
an aryloxy alkylamine given by formula



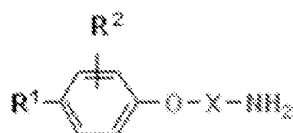
- wherein X is a hydrocarbyl group having 1 or 2 carbon atoms; and  
wherein R<sup>1</sup> and R<sup>2</sup> are independently hydrogen or substituted hydrocarbyl group having up to 36 carbon atoms.
8. The concentrate composition of claim 7, wherein X is ethylene group.
9. The concentrate composition of claim 7, further comprising:  
a nitrogen-containing detergent.
10. The concentrate composition of claim 9, wherein the 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.
11. The concentrate composition of claim 7, wherein at least one of R<sup>1</sup> and R<sup>2</sup> is hydrogen.

12. The concentrate composition of claim 7, wherein the aryloxy alkylamine is 2-(4-dodecylphenoxy)ethyl-1-amine, 2-(phenoxy)ethyl-1-amine, 2-(4-butylphenoxy)ethyl-1-amine, 2-(4-octylphenoxy)ethyl-1-amine, 2-(4-nonylphenoxy)ethyl-1-amine, 2-(4-octadecylphenoxy)ethyl-1-amine, 2-(4-eicosanylphenoxy)ethyl-1-amine, 2-(4-docosanylphenoxy)ethyl-1-amine, or 2-(4-tetracosanylphenoxy)ethyl-1-amine.

13. A method of reducing injector fouling in a direct injection spark ignition gasoline engine comprising:

providing a gasoline composition comprising:

aryloxy alkylamine additive having the following structure



wherein the aryloxy alkylamine additive is present in about 10 to about 750 ppm by weight based on total weight of the fuel composition;

wherein X is a hydrocarbyl group having 1 or 2 carbon atoms; and

wherein R¹ and R² are independently hydrogen, substituted alkyl or alkenyl group having up to 36 carbon atoms.

14. The method of claim 13, wherein X is ethylene group.

15. The method of claim 13, further comprising:

a nitrogen-containing detergent.

16. The method of claim 13, wherein the 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.

17. The method of claim 16, further comprising antioxidants, metal deactivators, demulsifiers, oxygenates, antiknock agents, dispersants, pour point depressants, or flow improvers.

18. The method of claim 13, wherein the aryloxy alkylamine is 2-(4-dodecylphenoxy)ethyl-1-amine, 2-(phenoxy)ethyl-1-amine, 2-(4-butylphenoxy)ethyl-1-amine, 2-(4-octylphenoxy)ethyl-1-amine, 2-(4-nonylphenoxy)ethyl-1-amine, 2-(4-octadecylphenoxy)ethyl-1-amine, 2-(4-eicosanylphenoxy)ethyl-1-amine, 2-(4-docosanylphenoxy)ethyl-1-amine, or 2-(4-tetracosanylphenoxy)ethyl-1-amine.