

FUEL ADDITIVE COMPOSITIONS AND METHODS FOR CONTROLLING CARBON DEPOSITS IN AN INTERNAL COMBUSTION ENGINES

CROSS REFERENCE TO RELATED APPLICATIONS

[001] This application claims the priority benefit of U.S. Provisional Application No. 63/455,285, filed March 29, 2023, the disclosure of which is incorporated herein by reference.

TECHNICAL FIELD

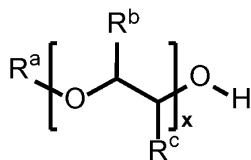
[002] This disclosure relates to fuel additives. More specifically, this disclosure describes compositions and methods that promote deposit cleaning performance.

BACKGROUND

[003] Modern engines can be susceptible to various types of deposit build-up. For example, carbon build-up occurring in intake valves can lead to reduced airflow to the cylinders. This can lead to reduction in performance such as decreased power and torque, lower fuel economy, higher emissions, and the like. Thus, there is a need to effectively clean intake valve surfaces in a way that is cost and time effective.

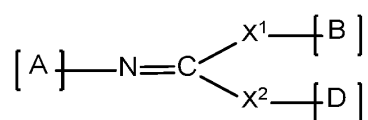
SUMMARY

[004] In one aspect, there is provided a fuel composition comprising:
i) a hydrocarbon-based fuel comprising gasoline, diesel; ii) one or more carrier fluids comprising an alkyl polyethoxylate of Formula 1:



Formula 1

wherein each R^b and R^c is independently hydrogen, C_1 - C_4 hydrocarbyl group, or C_1 - C_3 alcohol, wherein R^a is C_4 - C_{100} hydrocarbyl group, carboxyl group, ether group, thioether group, or aromatic group, wherein x is from 1 to 20; and iii) one or more nitrogen-containing detergent of Formula 2:

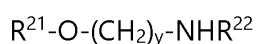


Formula 2

or an acceptable salt thereof; wherein X^1 and X^2 are independently H, C, N, O, or S and wherein X^1 or X^2 independently includes one or more C_2 - C_{20} alkyl group or one or more aromatic ring; wherein each A, B and D is independently hydrogen, monovalent organic groups, and monovalent heterorganic groups in the form of groups or moieties that are bonded through a carbon atom; wherein any two or more of A, B and D optionally can be bonded together to form a cyclic structure; and wherein X^1 and X^2 optionally can be bonded together to form a cyclic structure; .

[005] In another aspect, the fuel composition further comprises an aliphatic hydrocarbyl-substituted amine or a hydrocarbyl-substituted poly(oxyalkylene)amine.

[006] In another aspect, the fuel composition further comprises: iv) one or more amine-based detergents of Formula 8:

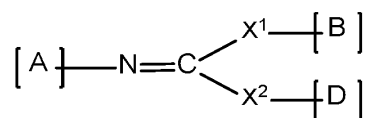


Formula 8

wherein R^{21} is a hydrocarbyl group having 8 to 20 carbons, R^{22} is hydrogen or $(CH_2)_zNH_2$ moiety, and y, z are independently integers having a value of 2 or greater.

[007] 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

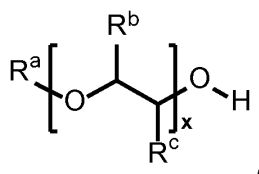
comprising gasoline or diesel; and iii) one or more nitrogen-containing detergent of Formula 2:



Formula 2

or an acceptable salt thereof; wherein X^1 and X^2 are independently H, C, N, O, or S or wherein X^1 or X^2 independently includes one or more $C_2 - C_{20}$ alkyl group or one or more aromatic ring; wherein each A, B and D is hydrogen, monovalent organic group, or monovalent heterorganic group in the form of groups or moieties that are bonded through a carbon atom and wherein any two or more of A, B and D optionally can be bonded together to form a cyclic structure; and wherein X^1 and X^2 optionally can be bonded together to form a cyclic structure.

[008] In another aspect, the fuel used in the method further comprises: ii) one or more carrier fluids comprising an alkyl polyethoxylate of Formula 1:

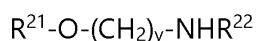


Formula 1

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

[009] In another aspect, a fuel used in the method further comprises: an aliphatic hydrocarbyl-substituted amine or a hydrocarbyl-substituted poly(oxyalkylene)amine.

[010] In another aspect, a fuel used in the method further comprises: iv) one or more amine-based detergents of Formula 8:



Formula 8

wherein R^{21} is a hydrocarbyl group having 8 to 20 carbons, R^{22} is hydrogen or $(CH_2)_zNH_2$ moiety, and y, z are independently integers having a value of 2 or greater.

[011] 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: ii) one or more carrier fluids as described herein, iii) one or more nitrogen-containing detergents as described herein.

[012] In another aspect, the concentrate compositions may further comprise iv) one or more amine-based detergents, as described herein.

DETAILED DESCRIPTION

[013] 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. In particular, the significant improvements in deposit control may be achieved through the use of compositions comprising at least the (iii) one or more nitrogen-containing detergents disclosed herein.

Fuel Compositions

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

Hydrocarbon-based Fuel

[015] The hydrocarbon-based fuel includes gasoline, or diesel. The hydrocarbon-based fuel may include ethanol. In some embodiments, the ethanol is present in about 50% by volume (vol %) or less, such as 45% or less, 40% or less, 35% or less, 30% or less, 25% or less, 20% or less, 15% or less, 10% or less, 5% or less.

[016] In certain embodiments, the hydrocarbon-based fuel comprises gasoline and ethanol. Blends of gasoline and ethanol suitable for use in the compositions and methods comprise between about 5 and about 35 vol% ethanol such as about 10 to 20 vol% ethanol, or about 15 to about 25 vol% ethanol. In certain embodiments, the hydrocarbon-based fuel is an E20 base fuel or a gasoline fuel comprising 20 vol% ethanol. In certain embodiments, the hydrocarbon-based fuel is an E10 base fuel or a gasoline fuel comprising 10 vol% ethanol.

[017] 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.

[018] 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.

[019] 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%.

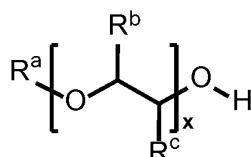
[020] According to some embodiments, the gasoline employed in the present invention may be clean burning gasoline (CBG). CBG refers to gasoline formulations that contain reduced levels of sulfur, aromatics and olefins. The exact formulation may vary depending on local regulatory definitions.

Carrier Fluid

[021] The composition of the present invention comprises one or more carrier fluids. Without being limited by theory, it is believed that the carrier fluid can enhance the compatibility of the nitrogen-containing detergent in the hydrocarbon-based fuel.

[022] 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. A fuel-soluble, non-volatile carrier fluid or oil may also be used with compounds of this disclosure. In some embodiments, the carrier fluid is a surfactant.

[023] The carrier fluid of the present invention comprises, or consists essentially, of an alkyl polyethoxylate compound given by the following Formula 1:



Formula 1

wherein each R^b and R^c is independently hydrogen, C₁-C₄ hydrocarbyl group, or C₁-C₃ alcohol, wherein R^a is C₄-C₁₀₀ hydrocarbyl group, carboxyl group, ether group, thioether group, or aromatic group, wherein x is from 1 to 20.

[024] 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.

[025] In certain embodiments, the alkyl polyethoxylated compound is nonylphenol ethoxylate. In certain embodiments, the alkyl polyethoxylated compound is ethoxylated (C₁₂-C₁₄) secondary alcohol.

[026] In certain embodiments, x is in the range of 1 to 15, such as 2 to 11, 1 to 6, or 7 to 12.

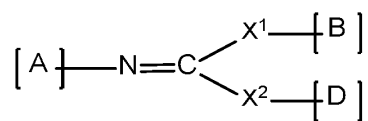
[027] In certain embodiments, R^a is a C₄-C₁₀₀ aromatic group, such as an alkyl-substituted phenyl group. In certain embodiments, R^a is a C₄-C₁₄ hydrocarbyl group, such as C₅-C₁₃, C₆-C₁₂, or C₇-C₁₁ hydrocarbyl group.

[028] The carrier fluid may be employed in an amount ranging from about 35 to about 5000 ppm by weight (i.e., ppmw) of the hydrocarbon fuel (e.g., about 50 ppmw to about 4000 ppmw, about 100 ppmw to about 3000 ppmw, or about 1000 ppmw to about 3000 ppmw). 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 %). In one embodiment, the fuel composition comprises about 35 ppmw to about 5000 ppmw of the carrier fluid.

Nitrogen-containing Detergent

[029] The composition of the present invention comprises one or more nitrogen-containing detergents.

[030] In one embodiment, the nitrogen-containing detergent is a compound given by the following Formula 2:



Formula 2

or an acceptable salt thereof; wherein X^1 and X^2 are independently H, C, N, O, or S and wherein X^1 or X^2 independently includes one or more C_2 - C_{20} alkyl group (e. g., C_1 - C_6 alkyl) or one or more aromatic ring; wherein each A, B and D is selected from hydrogen, monovalent organic groups (e.g., aromatic or aliphatic groups), and monovalent heterorganic groups ((e.g., aromatic or aliphatic groups which comprise one or more N, O, S or P) in the form of groups or moieties that are bonded through a carbon atom; and wherein any two or more of A, B and D optionally can be bonded together to form a cyclic structure (e.g., a five-, six-, or seven-membered ring); and wherein X^1 and X^2 optionally can be bonded together to form a cyclic structure (e.g., a five-, six-, or seven-membered ring). In some embodiments, A, B, and D do not contain acid functionality such as carboxylic or sulfonic moiety.

[031] Cyclic structures may be aromatic or non-aromatic, as well as vary from being fully saturated to fully unsaturated, including partially saturated or partially unsaturated.

[032] In certain embodiments, the cyclic structure formed from the bonding of two or more of A, B and D is aromatic. In certain embodiments, the cyclic structure formed from the bonding of two or more of A, B and D is non-aromatic.

[033] The cyclic structure formed from the bonding of two or more of A, B and D may vary from being fully saturated to fully unsaturated. In certain embodiments, the cyclic structure formed from the bonding of two or more of A, B and D is fully saturated. In certain embodiments, the cyclic structure formed from the bonding of two or more of A, B and D is partially unsaturated. In certain embodiments, the cyclic structure formed from the bonding of two or more of A, B and D is fully saturated.

[034] In certain embodiments, the cyclic structure formed from the bonding of X^1 and X^2 is aromatic. In certain embodiments, the cyclic structure formed from the bonding of X^1 and X^2 is non-aromatic.

[035] In certain embodiments, [A] is H. In certain embodiments, [B] is H. In certain embodiments, [D] is H.

[036] In certain embodiments, one of X^1 and X^2 is not H. In certain embodiments, both of X^1 and X^2 are not H.

[037] In certain embodiments, one of X^1 and X^2 is N. In certain embodiments, both of X^1 and X^2 are N. In certain embodiments, X^1 is N bonded to one C₂ - C₂₀ alkyl group (e. g., C₁- C₆ alkyl) and bonded to [B]. In certain embodiments, X^1 is N bonded to one aromatic ring and bonded to [B]. In certain embodiments, X^1 is N bonded to H and bonded to [B]. In certain embodiments, X^2 is N bonded to one C₂-C₂₀ alkyl group (e. g., C₁- C₆ alkyl) and bonded to [D]. In certain embodiments, X^2 is N bonded to one aromatic ring and bonded to [D]. In certain embodiments, X^2 is N bonded to H and bonded to [D].

[038] In certain embodiments, X^1 is N bonded to one aromatic ring and bonded to [B] and X^2 is N bonded to one aromatic ring and bonded to [D].

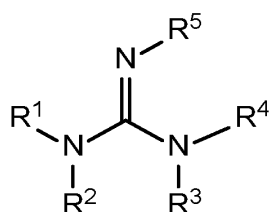
[039] In certain embodiments, one of X^1 and X^2 is C. In certain embodiments, both of X^1 and X^2 are C. In certain embodiments, X^1 is C bonded to one C₂-C₂₀ alkyl group (e. g., C₁- C₆ alkyl), bonded to H, and bonded to [B]. In certain embodiments, X^1 is C bonded to one aromatic ring, bonded to H, and bonded to [B]. In certain embodiments, X^1 is CH₂ and bonded to [B]. In certain embodiments, X^2 is C bonded to one C₂-C₂₀alkyl group (e. g., C₁- C₆ alkyl), bonded to H, and bonded to [D]. In certain embodiments, X^2 is C bonded to one aromatic ring, bonded to H, and bonded to [D]. In certain embodiments, X^2 is CH₂ and bonded to [D].

[040] In certain embodiments, X^1 is O bonded to [B]. In certain embodiments, X^2 is O bonded to [D]. In certain embodiments, X^1 is S bonded to [B]. In certain embodiments, X^2 is S bonded to [D].

[041] In certain embodiments, the organic and heterorganic groups of A, C, and D may have from 1 to 10 carbon atoms (e.g., 1 to 6 carbon atoms).

[042] Suitable examples of compounds of Formula 2 include, but are not limited to: guanidines, aminoguanidines, amidines, benzamidines, imidazoles, benzimidazoles, aminobenzimidazoles, and triazoles.

[043] In certain embodiments, the nitrogen-containing detergent is a guanidine, a substituted guanidine, a derivative thereof, or an acceptable salt thereof. Useful guanidine compounds include those that can be represented by the following Formula 3,



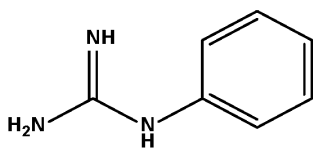
Formula 3

wherein R^1 , R^2 , R^3 , R^4 and R^5 are each independently hydrogen, monovalent organic groups (e.g., aromatic or aliphatic groups), or monovalent heterorganic groups (e.g., aromatic or aliphatic groups which comprise one or more N, O, S or P) in the form of groups or moieties that are bonded through a carbon atom; and wherein any two or more of R^1 , R^2 , R^3 , R^4 and R^5 optionally can be bonded together to form a cyclic structure (e.g., a five-, six, or seven-membered ring). The cyclic structures may be aromatic or non-aromatic, as well as vary from being fully saturated to fully unsaturated. The organic and heterorganic groups may have from 1 to 10 carbon atoms (e.g., 1 to 6 carbon atoms). In some embodiments, A, B, and D do not contain acid functionality such as carboxylic or sulfonic moiety.

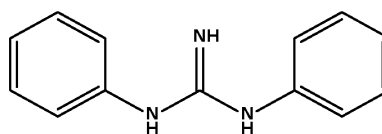
[044] In certain embodiments, one or more of R^1 , R^2 , R^3 , R^4 and R^5 is an aromatic group, for example phenyl or substituted phenyl. In certain embodiments, two or more of R^1 , R^2 , R^3 , R^4 and R^5 is an aromatic group. In certain embodiments, three

or more of R^1 , R^2 , R^3 , R^4 and R^5 is an aromatic group. In certain embodiments, the compound is a diphenyl guanidine.

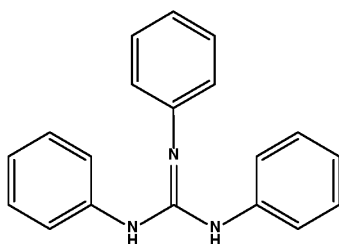
[045] Representative examples of compounds of Formula 3 include 1-phenylguanidine (Formula 3A), 1,3-diphenylguanidine (Formula 3B), 1,2,3-triphenylguanidine (Formula 3C), N-phenyl-1H-benzo[d]imidazol-2-amine (Formula 3D), N-phenyl-1H-imidazol-2-amine (Formula 3E), 2-aminoimidazole (Formula 3F), 2-aminobenzimidazole (Formula 3G), 1-phenylbiguanide (Formula 3H), 2-guanidinobenzimidazole (Formula 3I), 2-phenyl-2-imidazoline (Formula 3J), 1,1,3,3-tetramethylguanidine (TMG; Formula 3K), 2-tert-butyl-1,1,3,3-tetramethylguanidine (BTMG; Formula 3L), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD; Formula 3M), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD; Formula 3N) and (Z)-N,N'-dicyclohexylmorpholine-4-carboximidamide (Formula 3O). Representative structures shown below.



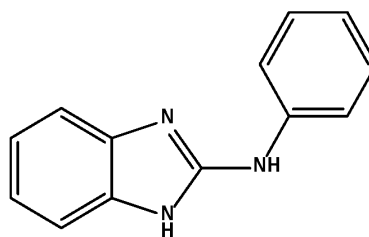
Formula 3A



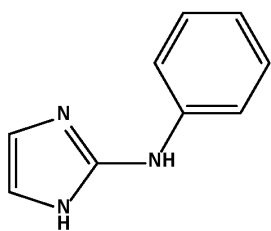
Formula 3B



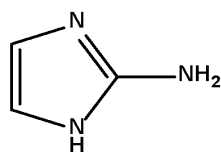
Formula 3C



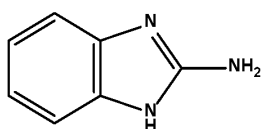
Formula 3D



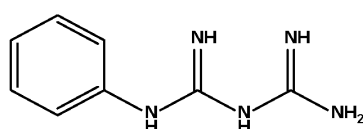
Formula 3E



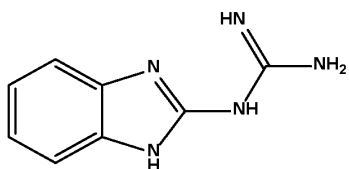
Formula 3F



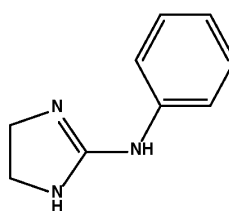
Formula 3G



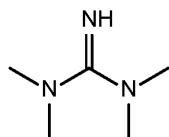
Formula 3H



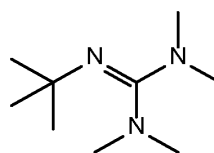
Formula 3I



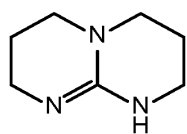
Formula 3J



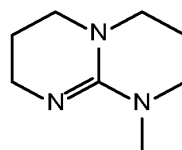
Formula 3K



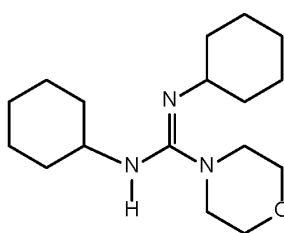
Formula 3L



Formula 3M

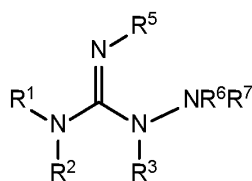


Formula 3N



Formula 3O

[046] In certain embodiments, the nitrogen-containing detergent is an aminoguanidine, a substituted aminoguanidine, a derivative thereof, or an acceptable salt thereof. Useful aminoguanidine compounds include those that can be represented by the following Formula 4,



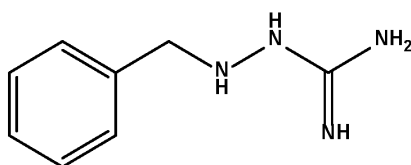
Formula 4

wherein R^1 , R^2 , R^3 , R^5 , R^6 and R^7 are each independently selected from hydrogen, monovalent organic groups (e.g., aromatic or aliphatic groups), and monovalent heterorganic groups ((e.g., aromatic or aliphatic groups which comprise one or more N, O, S or P) in the form of groups or moieties that are bonded through a carbon atom;

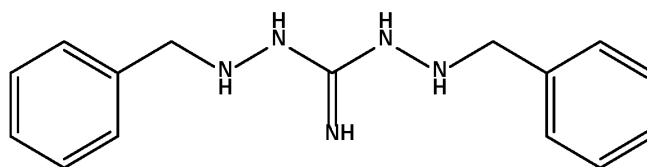
and wherein any two or more of R^1 , R^2 , R^3 , R^5 , R^6 and R^7 optionally can be bonded together to form a cyclic structure (e.g., a five-, six, or seven-membered ring). The cyclic structures may be aromatic or non-aromatic, as well as vary from being fully saturated to fully unsaturated. The organic and heterorganic groups may have from 1 to 10 carbon atoms (e.g., 1 to 6 carbon atoms). In some embodiments, A, B, and D do not contain acid functionality such as carboxylic or sulfonic moiety.

[047] In certain embodiments, one or more of R^1 , R^2 , R^3 , R^5 , R^6 and R^7 is an aromatic group, for example phenyl or substituted phenyl. In certain embodiments, two or more of R^1 , R^2 , R^3 , R^5 , R^6 and R^7 is an aromatic group. In certain embodiments, three or more of R^1 , R^2 , R^3 , R^5 , R^6 and R^7 is an aromatic group.

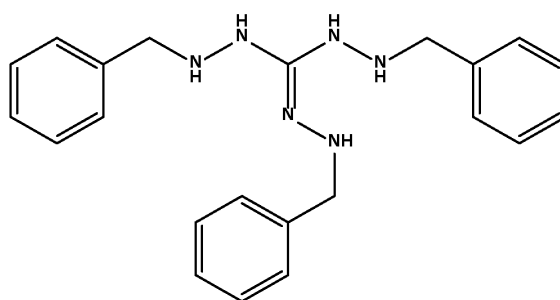
[048] Representative examples of compounds of Formula 4 include 2-benzylhydrazine-1-carboximidamide (Formula 4A), N',2-dibenzylhydrazine-1-carboximidhydrazide (Formula 4B), and N',N'',2-tribenzylhydrazine-1-carbohydrazonhydrazide (Formula 4C). Representative structures shown below.



Formula 4A

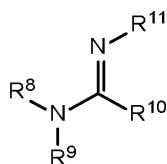


Formula 4B



Formula 4C

[049] In certain embodiments, the nitrogen-containing detergent is an amidine, a substituted amidine, a benzamidine, a substituted benzamidine, or an acceptable salt thereof. Useful amidines include those that can be represented by the following Formula 5:



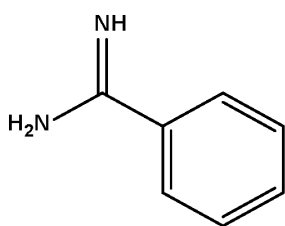
Formula 5

wherein R^8 , R^9 , R^{10} and R^{11} are each independently selected from hydrogen, monovalent organic groups, monovalent heterorganic groups (e.g., comprising nitrogen, oxygen, sulfur or phosphorus, in the form of groups or moieties that are bonded through a carbon atom, and combinations thereof; and wherein any two or more of R^8 , R^9 , R^{10} and R^{11} optionally can be bonded together to form a cyclic structure (e.g., a five-, six, or seven-membered ring). The cyclic structures may be aromatic or non-aromatic, as well as vary from being fully saturated to fully unsaturated. The organic and heterorganic groups may have from 1 to 10 carbon atoms (e.g., 1 to 6 carbon atoms). In some embodiments, R^8 , R^9 , R^{10} , and R^{11} do not contain acid functionality such as carboxylic or sulfonic moiety.

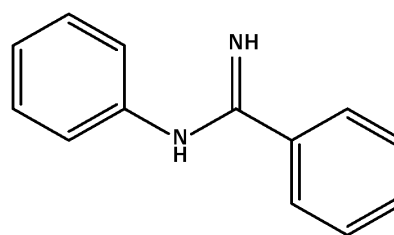
[050] In certain embodiments, one or more of wherein R^8 , R^9 , R^{10} and R^{11} is an aromatic group, for example phenyl or substituted phenyl. In certain embodiments,

two or more of wherein R^8 , R^9 , R^{10} and R^{11} is an aromatic group. In certain embodiments, three or more of wherein R^8 , R^9 , R^{10} and R^{11} is an aromatic group.

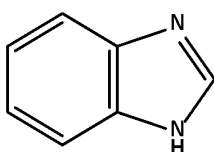
[051] Representative examples of compounds of Formula 5 include benzimidamide (or benzamidine; Formula 5A), *N*-phenylbenzimidamide (Formula 5B), benzimidazole (Formula 5C), 2-phenyl-1*H*-benzo[d]imidazole (Formula 5D), 2-phenylimidazole (Formula 5E), and *N*-phenylpyridin-2-amine (Formula 5F), 1,4,5,6-tetrahydropyrimidine (Formula 5G), 1,2-dimethyl-1,4,5,6-tetrahydropyrimidine (Formula 5H), 1,2-diethyl-1,4,5,6-tetrahydropyrimidine (Formula 5I), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN; Formula 5J), 1,8-diazabicyclo[5.4.0]-undeca-7-ene (DBU; Formula 5K), benzimidazole (Formula 5L), oxazol-2-amine (Formula 5M), 4,5-dihydrooxazol-2-amine (Formula 5N), thiazol-2-amine (Formula 5O), 4,5-dihydrothiazol-2-amine (Formula 5P), benzo[d]thiazol-2-amine (Formula 5Q), and 2-phenyl-1*H*-benzo[d]imidazole (Formula 5R). Representative structures are shown below.



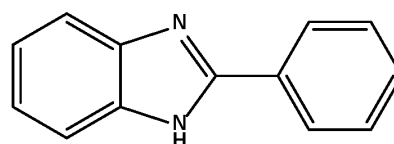
Formula 5A



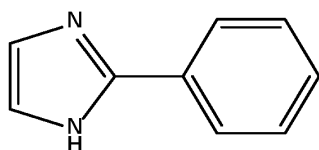
Formula 5B



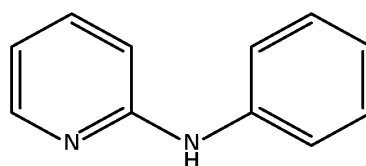
Formula 5C



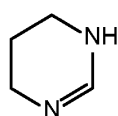
Formula 5D



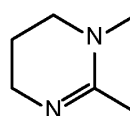
Formula 5E



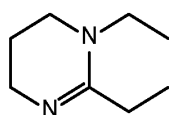
Formula 5F



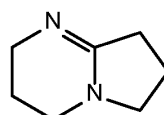
Formula 5G



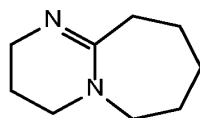
Formula 5H



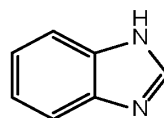
Formula 5I



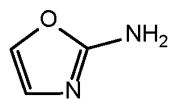
Formula 5J



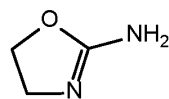
Formula 5K



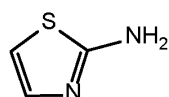
Formula 5L



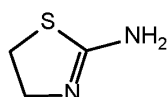
Formula 5M



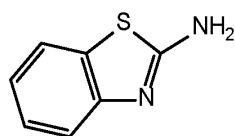
Formula 5N



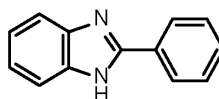
Formula 5O



Formula 5P

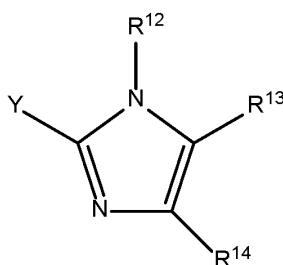


Formula 5Q



Formula 5R

[052] In certain embodiments, the nitrogen-containing detergent is an imidazole, a substituted imidazole, a benzimidazole, a substituted benzimidazole, an aminobenzimidazole, a substituted aminobenzimidazole, or an acceptable salt thereof. Useful imidazoles, substituted imidazoles, benzimidazoles, substituted benzimidazoles, aminobenzimidazoles, and substituted aminobenzimidazoles include those that can be represented by the following Formula 6:



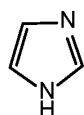
Formula 6

wherein Y is R¹⁵ or NR¹⁶R¹⁷; wherein R¹², R¹³, R¹⁴, R¹⁵, R¹⁶ and R¹⁷ are each independently selected from hydrogen, monovalent organic groups, monovalent heterorganic groups (e.g., comprising nitrogen, oxygen, sulfur or phosphorus, in the form of groups or moieties that are bonded through a carbon atom, and combinations thereof; and wherein any two or more of R¹², R¹³, R¹⁴, R¹⁵, R¹⁶ and R¹⁷ optionally can be bonded together to form a cyclic structure (e.g., a five-, six, or seven-membered ring). The

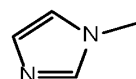
cyclic structures may be aromatic or non-aromatic, as well as vary from being fully saturated to fully unsaturated. The organic and heterorganic groups may have from 1 to 10 carbon atoms (e.g., 1 to 6 carbon atoms). In some embodiments, A, B, and D do not contain acid functionality such as carboxylic or sulfonic moiety.

[053] In certain embodiments, one or more of wherein R^{12} , R^{13} , R^{14} , R^{15} , R^{16} and R^{17} is an aromatic group, for example phenyl or substituted phenyl. In certain embodiments, two or more of wherein R^{12} , R^{13} , R^{14} , R^{15} , R^{16} and R^{17} is an aromatic group. In certain embodiments, three or more of wherein R^{12} , R^{13} , R^{14} , R^{15} , R^{16} and R^{17} is an aromatic group.

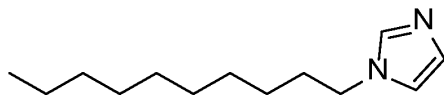
[054] Representative examples of compounds of Formula 6 include imidazole (Formula 6A), 1-methylimidazole (Formula 6B), 1-decylimidazole (Formula 6C), 1-ethylimidazole (Formula 6D), 1-propylimidazole (Formula 6E), 1-n-butylimidazole (Formula 6F), 2-methylimidazole (Formula 6G), 2-isopropylimidazole (Formula 6H), 4-methylimidazole (Formula 6I), 1,2-dimethylimidazole (Formula 6J), 2-ethyl-4(5)-methylimidazole (Formula 6K), 1-vinylimidazole (Formula 6L), 2-ethylimidazole (Formula 6M), and 1-dodecylimidazole (Formula 6N). Representative structures are shown below.



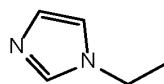
Formula 6A



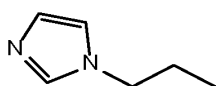
Formula 6B



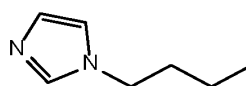
Formula 6C



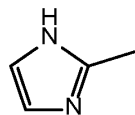
Formula 6D



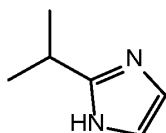
Formula 6E



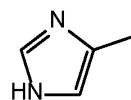
Formula 6F



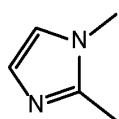
Formula 6G



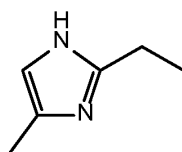
Formula 6H



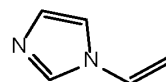
Formula 6I



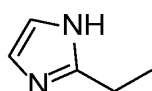
Formula 6J



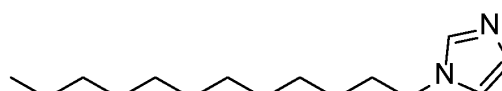
Formula 6K



Formula 6L

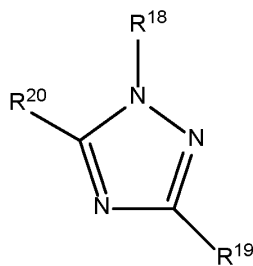


Formula 6M



Formula 6N

[055] In certain embodiments, the nitrogen-containing detergent is a triazole, a substituted triazole, or an acceptable salt thereof. Useful triazoles and substituted triazoles include those that can be represented by the following Formula 7:

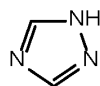


Formula 7

wherein R¹⁸, R¹⁹ and R²⁰ are each independently selected from hydrogen, monovalent organic groups, monovalent heterorganic groups (e.g., comprising nitrogen, oxygen, sulfur or phosphorus, in the form of groups or moieties that are bonded through a carbon atom, and combinations thereof; and wherein any two or more of R¹⁸, R¹⁹ and R²⁰ optionally can be bonded together to form a cyclic structure (e.g., a five-, six, or seven-membered ring). The cyclic structures may be aromatic or non-aromatic, as well as vary from being fully saturated to fully unsaturated. The organic and heterorganic groups may have from 1 to 10 carbon atoms (e.g., 1 to 6 carbon atoms). In some embodiments, R¹⁸, R¹⁹ and R²⁰ do not contain acid functionality such as carboxylic or sulfonic moiety.

[056] In certain embodiments, one or more of wherein R¹⁸, R¹⁹ and R²⁰ is an aromatic group, for example phenyl or substituted phenyl. In certain embodiments, two or more of wherein R¹⁸, R¹⁹ and R²⁰ is an aromatic group.

[057] A representative example of a compound of Formula 7 is 1, 2, 4-triazole (Formula 7A), shown below.



Formula 7A

Amine-based Detergent

[058] The composition of the present invention may comprise one or more amine-based detergents.

[059] Each amine-based detergent can be present in the exemplary compositions in an amount of about 10 ppm to about 3000 ppm, such as about 1000 to about 2500, about 1250 to about 2250, 1500 to about 2000, 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.

[060] In certain embodiments, the amine-based detergent is an aliphatic hydrocarbyl-substituted amine compound or a hydrocarbyl-substituted poly(oxyalkylene)amine.

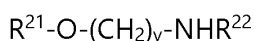
[061] In particular, the aliphatic hydrocarbyl-substituted amines employed in the present invention may be straight or branched chain hydrocarbyl-substituted amines having at least one basic nitrogen and wherein the hydrocarbyl group has a number average molecular weight of about 700 to 3,000. Specific 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.,

[062] In certain embodiments, the amine-based detergent is a hydrocarbyl-substituted poly(oxyalkylene)amine compound (also referred to as a "polyether amine"). In particular, the hydrocarbyl-substituted poly(oxyalkylene)amines employed in the present invention 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.

[063] 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.

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



Formula 8

where R^{21} is a hydrocarbyl group having 8 to 20 carbons, R^{22} 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.

[065] As an advantage, the amine-based detergents 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 amine-based detergents of the present invention along with their low decomposition temperature and high volatility prevents the amine-based detergents from generating harmful deposits.

[066] Particularly illustrative aliphatic ether amines compatible with the present invention include isotridecyloxypropylamine and 2-ethylhexyloxypropyl

amine. In certain embodiments, the amine-based detergent comprises or consists essentially of isotridecyloxypropylamine. These are illustrative examples that are not intended to be limiting.

Other Additives

[067] 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.

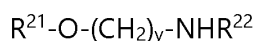
[068] Each of the foregoing additives, when used, is used at a functionally effective amount to impart the desired properties to the fuel composition. Generally, the concentration of each of these additives, when used, may range, unless otherwise specified, from about 0.001 to about 20 wt. %, such as about 0.01 to about 10 wt. %.

Concentrate

[069] 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 %).

[070] In one embodiment, a concentrate composition comprises: 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: one or more carrier fluids as disclosed herein, one or more nitrogen-containing compounds as disclosed herein.

[071] In certain embodiments, the concentrate composition further comprises:
iv) one or more amine-based detergents selected from compounds of Formula 8:



Formula 8

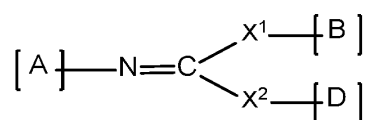
wherein R^{21} is a hydrocarbyl group having 8 to 20 carbons, R^{22} is hydrogen or $(CH_2)_zNH_2$ moiety, and y, z are independently integers having a value of 2 or greater.

Methods of Use

[072] The nitrogen-containing detergents can be used advantageously in compositions and methods for improving engine performance, specifically improving deposit cleaning performance and/or lowering particulate emissions. In certain embodiments, the exemplary nitrogen-containing detergents, alone or in the form of fuel compositions or concentrate compositions, can be applied by any suitable means to an internal combustion engine for the purpose of controlling, preventing or reducing carbon deposits. In particular, the significant improvements in deposit control (e.g., intake valve deposit control) may be achieved through the use of compositions comprising at least the (iii) one or more nitrogen-containing detergents disclosed herein.

[073] In one embodiment, the method is for controlling carbon deposits in an internal combustion engine.

[074] In one embodiment, the method comprises: providing a fuel in the internal combustion engine, wherein the fuel comprises: i) a hydrocarbon-based fuel comprising gasoline, diesel or a blend of gasoline and ethanol; and ii) one or more nitrogen-containing detergents as disclosed herein, for example nitrogen-containing compounds selected from compounds of Formula 2:

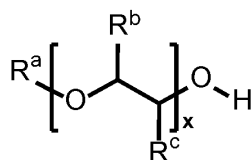


Formula 2

or an acceptable salt thereof; wherein X^1 and X^2 are independently H, C, N, O, or S and wherein X^1 or X^2 independently includes one or more $C_2 - C_{20}$ alkyl group or one or more aromatic ring; wherein each A, B and D is selected from hydrogen, monovalent

organic groups, and monovalent heterorganic groups in the form of groups or moieties that are bonded through a carbon atom; and wherein any two or more of A, B and D optionally can be bonded together to form a cyclic structure; and wherein X¹ and X² optionally can be bonded together to form a cyclic structure; or one or more nitrogen-containing detergents selected from an aliphatic hydrocarbyl-substituted amine or a hydrocarbyl-substituted poly(oxyalkylene)amine. In some embodiments, A, B, and D do not contain acid functionality such as carboxylic or sulfonic moiety.

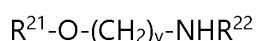
[075] In certain embodiments, the fuel used in the method further comprises:
ii) one or more carrier fluids comprising an alkyl polyethoxylate selected from compounds of Formula 1:



Formula 1

wherein each R^b and R^c is independently hydrogen, C₁-C₄ hydrocarbyl group, or C₁-C₃ alcohol, wherein R^a is C₄-C₁₀₀ hydrocarbyl group, carboxyl group, ether group, thioether group, or aromatic group, wherein x is from 1 to 20.

[076] In certain embodiments, a fuel used in the method further comprises:
iv) one or more amine-based detergents selected from compounds of Formula 8:



Formula 8

wherein R²¹ is a hydrocarbyl group having 8 to 20 carbons, R²² is hydrogen or (CH₂)_zNH₂ moiety, and y, z are independently integers having a value of 2 or greater.

[077] In certain embodiments, the nitrogen-containing detergents and carrier fluids, optionally in combination with amine-containing detergents, can be applied to

an internal combustion engine in the form of a concentrate composition as described herein.

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

EXAMPLES

Examples 1-4. Deposit Control Performance of Exemplary and Comparative Compositions

[079] Testing was done on a 2006 3.5L Chevy Impala Flex Fuel engine which contains a V6-cylinder, naturally aspirated engine. The test was a Dirty-Up/Clean-Up (DU/CU) test where the engine first completed a 100-hour DU segment, to create intake valve deposits, followed by a 1-Tank (20 gal.) CU segment. The 100-hr DU segment is run with an E20 base fuel (base fuel containing 20 vol% ethanol), which was prepared by diluting a 49-state PUL E10 unadditized fuel down to an E20 with additional ethanol. The 1-Tank CU segment is run with that same E20 base fuel as well as the test additive compositions or exemplary compositions. At the completion of the DU and CU segments, the intake valves were removed and weighed and a % IVD CU value was calculated.

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

[081] 1-Tank CU Cycle: 5-stage cycle with idle, low speed and load segments and moderate speed and load segments.

[082] The tested compositions contained the E20 base fuel and one or more of the following additives: 1,3-diphenylguanidine (DPG, an exemplary nitrogen-containing detergent), nonylphenol ethoxylate (Carrier Fluid A), an ethoxylated (C₁₂-C₁₄) secondary alcohol (Carrier Fluid B), and isotridecyloxypropyl amine (an exemplary amine-based detergent).

[083] Table 1 shows the intake valve deposit (IVD) removal resulting from CU treatment with each test composition.

Table 1

Example	Composition	IVD removal
1	2000 ppmw DPG	18.7%
2	2000 ppmw DPG + 2000 ppmw Carrier Fluid A	58.6%
3	2000 ppmw DPG + 2000 ppmw Carrier Fluid B	76.5%
4	2000 ppmw DPG + 2000 ppmw Carrier Fluid A + 150 ppmw isotridecyloxypropyl amine	80%
Comparative	2000 ppmw Carrier Fluid B + 150 ppmw isotridecyloxypropyl amine	-39.8%

[084] 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.

[085] 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.

[086] 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.

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

[088] 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.

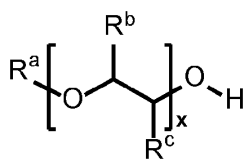
[089] The foregoing description of the disclosure illustrates and describes the present disclosure. Additionally, the disclosure shows and describes only the preferred embodiments but, as mentioned above, it is to be understood that the disclosure is capable of use in various other combinations, modifications, 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.

[090] 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.

[091] 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.

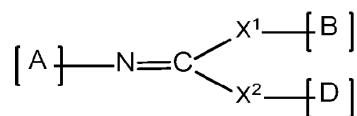
CLAIMS

1. A fuel composition comprising:
- i) a hydrocarbon-based fuel comprising gasoline, diesel or a blend of gasoline and ethanol;
 - ii) one or more carrier fluids comprising an alkyl polyethoxylate defined as follows:



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

- iii) one or more nitrogen-containing detergents defined as follows:



or an acceptable salt thereof;

wherein X^1 and X^2 are independently H, C, N, O, or S and wherein X^1 or X^2 independently includes one or more C_2 - C_{20} alkyl group or one or more aromatic ring;

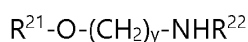
wherein each A, B and D is independently selected from hydrogen, monovalent organic groups, and monovalent heterorganic groups in the form of groups or moieties that are bonded through a carbon atom;

wherein any two or more of A, B and D optionally can be bonded together to form a cyclic structure; and

wherein X^1 and X^2 optionally can be bonded together to form a cyclic structure; or

one or more nitrogen-containing detergents selected from an aliphatic hydrocarbyl-substituted amine or a hydrocarbyl-substituted poly(oxyalkylene)amine.

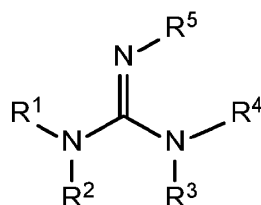
2. The fuel composition of claim 1, wherein the composition further comprises:
iv) one or more amine-based detergents defined as follows:



wherein R^{21} is a hydrocarbyl group having 8 to 20 carbons, R^{22} is hydrogen or $(CH_2)_zNH_2$ moiety, and y, z are independently integers having a value of 2 or greater.

3. The fuel composition of claim 1, wherein the one or more nitrogen containing detergents are guanidine, a substituted guanidine, a derivative thereof, or an acceptable salt thereof.

4. The fuel composition of claim 3, wherein the guanidine, a substituted guanidine, a derivative thereof, or an acceptable salt thereof, is based on the following structure:

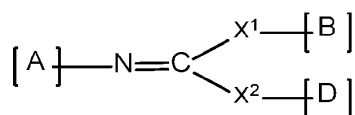


Formula 3

wherein R^1, R^2, R^3, R^4 and R^5 are each independently selected from hydrogen, monovalent organic groups and monovalent heterorganic groups in the form of groups or moieties that are bonded through a carbon; and

wherein any two or more of R^1, R^2, R^3, R^4 and R^5 optionally can be bonded together to form a cyclic structure.

5. The fuel composition of claim 1, wherein the one or more nitrogen-containing detergents comprises diphenyl guanidine.
6. The fuel composition of claim 1, wherein the one or more carrier fluids comprise nonylphenol ethoxylate.
7. The fuel composition of claim 1, wherein the one or more carrier fluids comprise an ethoxylated (C₁₂-C₁₄) secondary alcohol.
8. The fuel composition of claim 1, wherein the fuel composition comprises about 35 ppmw to about 5000 ppmw of the carrier fluids and about 500 ppmw to about 3000 ppmw of the one or more nitrogen-containing detergents.
9. The fuel composition of claim 2, wherein the fuel composition comprises about 35 ppmw to about 5000 ppmw of the carrier fluids, about 500 ppmw to about 3000 ppmw of the one or more nitrogen-containing detergents, and about 100 ppmw to 750 ppmw of the one or more amine-based detergents.
10. 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 comprising gasoline, diesel or a blend of gasoline and ethanol;
 - and
 - ii) one or more nitrogen-containing detergents defined as follows:



Formula 2

or an acceptable salt thereof;

wherein X^1 and X^2 are independently H, C, N, O, or S and wherein X^1 or X^2 independently includes one or more $C_2 - C_{20}$ alkyl group or one or more aromatic ring;

wherein each A, B and D is selected from hydrogen, monovalent organic groups, and monovalent heterorganic groups in the form of groups or moieties that are bonded through a carbon atom; and

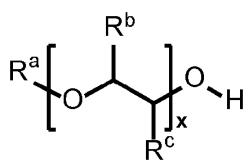
wherein any two or more of A, B and D optionally can be bonded together to form a cyclic structure; and

wherein X^1 and X^2 optionally can be bonded together to form a cyclic structure; or

one or more nitrogen-containing detergents selected from an aliphatic hydrocarbyl-substituted amine or a hydrocarbyl-substituted poly(oxyalkylene)amine.

11. The method of claim 10, wherein the fuel further comprises:

iii) one or more carrier fluids comprising an alkyl polyethoxylate defined as follows:

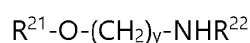


Formula 1

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

12. The method of claim 10, wherein the fuel further comprises:

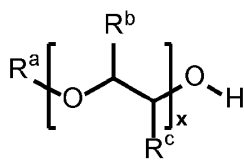
one or more amine-based detergents defined as follows:



wherein R^{21} is a hydrocarbyl group having 8 to 20 carbons, R^{22} is hydrogen or $(CH_2)_zNH_2$ moiety, and y, z are independently integers having a value of 2 or greater.

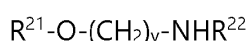
13. The method of claim 10, wherein the fuel further comprises:

one or more carrier fluids comprising an alkyl polyethoxylate defined as follows:



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

one or more amine-based detergents defined as follows:



wherein R^{21} is a hydrocarbyl group having 8 to 20 carbons, R^{22} is hydrogen or $(CH_2)_zNH_2$ moiety, and y, z are independently integers having a value of 2 or greater.

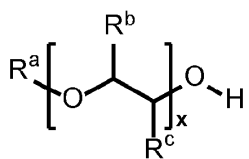
14. The method of claim 10, wherein the hydrocarbon-based fuel comprises a blend of gasoline and ethanol.

15. 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:

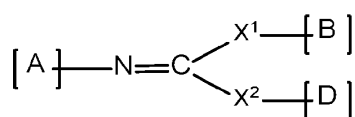
one or more carrier fluids comprising an alkyl polyethoxylate defined as follows:



Formula 1

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

one or more nitrogen-containing detergents defined as follows:



Formula 2

or an acceptable salt thereof;

wherein X^1 and X^2 are independently H, C, N, O, or S and wherein X^1 or X^2 independently includes one or more C_2 - C_{20} alkyl group or one or more aromatic ring;

wherein each A, B and D is selected from hydrogen, monovalent organic groups, and monovalent heterorganic groups in the form of groups or moieties that are bonded through a carbon atom;

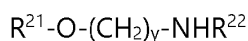
wherein any two or more of A, B and D optionally can be bonded together to form a cyclic structure; and

wherein X^1 and X^2 optionally can be bonded together to form a cyclic structure; or

one or more nitrogen-containing detergents selected from an aliphatic hydrocarbyl-substituted amine or a hydrocarbyl-substituted poly(oxyalkylene)amine.

16. The concentrate composition of claim 15, wherein the composition further comprises:

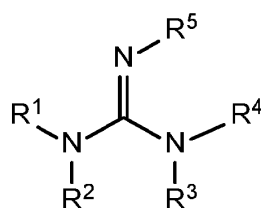
one or more amine-based detergents defined as follows:



wherein R^{21} is a hydrocarbyl group having 8 to 20 carbons, R^{22} is hydrogen or $(CH_2)_zNH_2$ moiety, and y, z are independently integers having a value of 2 or greater.

17. The concentrate composition of claim 15, wherein the one or more nitrogen containing detergents are guanidine, a substituted guanidine, a derivative thereof, or an acceptable salt thereof.

18. The concentrate composition of claim 15, wherein the guanidine, a substituted guanidine, a derivative thereof, or an acceptable salt thereof, is based on the following structure:



wherein R^1, R^2, R^3, R^4 and R^5 are each independently selected from hydrogen, monovalent organic groups and monovalent heterorganic groups in the form of groups or moieties that are bonded through a carbon atom; and wherein any two or more of R^1, R^2, R^3, R^4 and R^5 optionally can be bonded together to form a cyclic structure.

19. The concentrate composition of claim 15, wherein the one or more nitrogen-containing detergents comprises diphenyl guanidine.

20. The concentrate composition of claim 15, wherein the one or more carrier fluids comprise nonylphenol ethoxylate.
21. The concentrate composition of claim 15, wherein the one or more carrier fluids comprise an ethoxylated (C₁₂-C₁₄) secondary alcohol.