FUEL ADDITIVE COMPOSITION

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ABSTRACT

A fuel additive composition including a Mannich product, a polyetheramine, and a friction modifier is disclosed. Also, disclosed are a fuel composition comprising the fuel additive composition, an engine combusting the fuel composition, and a method of preventing and/or forming deposits in an engine.
FUEL ADDITIVE COMPOSITION

FIELD

[0001] The present invention relates to a fuel additive composition comprising a detergent, such as a Mannich product, a dispersant, such as a polyetheramine, and a friction modifier, such as an amide. The fuel additive composition may be useful in compositions such as, e.g., fuel compositions.

Introduction

[0002] Fuels used in internal combustion engines generally contain components that lead to the formation of undesirable engine deposits. It is believed that these deposits can negatively affect engine performance by, for example, clogging fuel induction systems. Considerable research has been devoted to additives for controlling (preventing or reducing) deposit formation in internal combustion engines. The preparation and identification of fuel additives capable of controlling undesirable deposit formation has been a focal point of this research.

[0003] In recent years, several automobile manufacturers jointly created new, voluntary detergent control standards for gasoline. The purpose was to define a new class of commercial gasoline with enhanced detergency called TOP TIER detergent gasoline. A document entitled, “TOP TIER Detergent Gasoline Deposit Control Performance Standards,” was introduced at the American Petroleum Institute’s 33rd Automotive, Petroleum Industry Forum on Apr. 6, 2004, the disclosure of which is hereby incorporated by reference. These standards include the following test methods: intake valve clean initial performance, combustion chamber deposit initial performance, fuel injector fouling initial performance, determination of deposit control additive performance, and intake valve sticking initial performance.

[0004] Thus, there exists a need in the industry for fuels and fuel additive packages that will meet the TOP TIER performance standards.

SUMMARY

[0005] According to various aspects of the disclosure, there is provided a fuel additive composition comprising a Mannich product, a polyetheramine, and a friction modifier; and a process for preparing a fuel additive, comprising providing a Mannich product, a polyetheramine, and a friction modifier to yield a fuel additive.

[0006] It is to be understood that both the foregoing general description and the following description of various embodiments are exemplary and explanatory only and are not restrictive.

DESCRIPTION OF VARIOUS EMBODIMENTS

[0007] The disclosed fuel additive composition may, in one embodiment, comprise a detergent, such as a Mannich product. The Mannich product may be a fuel-soluble reaction product obtained by the reaction of i) an amine; ii) an alkyl-substituted hydroxyaromatic compound; and iii) an aldehyde. In an embodiment, the Mannich product may be a reaction product obtained by the reaction of a low molecular weight alkyl-substituted hydroxyaromatic compound, an aldehyde, and an amino-alcohol as disclosed in U.S. Pat. No. 6,176,886, the disclosure of which is incorporated by reference.

[0008] Amines suitable for use as component i) may comprise at least one primary or secondary amine group and may further comprise at least one hydroxyl group. In other embodiments, the amine reactants may be amino-alcohols; alkoxylated amines; and mixtures thereof. Non-limiting examples of suitable amino-alcohols include ethanolamine and diethanolamine. Non-limiting examples of alkoxylated amines include ethoxylated and propoxylated amines and polyamines. An example of these amines includes, for example, 2-(2-aminoethylamino) ethanol. In another embodiment, diethanolamine may be used.

[0009] Polyamines suitable for use as the amine in the formation of the Mannich may comprise at least two amine groups wherein at least one of the amine groups is a primary or secondary amine. Non-limiting examples of polyamines include alkylen polyamines comprising at least one suitably reactive primary or secondary amine group in the molecule. Other substituents may be present in the polyamine. In an embodiment, the alkylen polyamine may be a polyethylene polyamine. Suitable alkylen polyamine reactants include ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenetetramine, hexaethylenetetramine, heptaethylen etheramine, octaethylenenonamine, nonaethylenedecamine, decaethylenundecamine and mixtures of such amines having nitrogen contents corresponding to alkylen polyamines of the formula H2N-(A-NH-)nH, wherein A may be a divalent ethylene or propylene and n may be an integer of from about 1 to about 10. The alkylen polyamines may be obtained by the reaction of ammonia and dihalo alkanes, such as dichloro alkanes. Thus, the alkylen polyamines obtained from the reaction of about 2 to about 11 moles of ammonia with about 1 to about 10 moles of dichloro alkanes comprising about 2 to about 6 carbon atoms and the chlorines on different carbon atoms may be suitable alkylen polyamine reactants.

[0010] In another embodiment, the amine may be a polyamine comprising at least one primary or secondary amino group and at least one tertiary amino group per molecule. Examples of suitable polyamines include N,N,N',N''-tetraalkyldialkylamidetramines (two terminal tertiary amino groups and one central secondary amino group), N,N,N',N''-tetraalkylamidetramines (two terminal tertiary amino group, two internal tertiary amino groups and one terminal primary amino group), N,N,N',N''-pentaaalkylamidetramines (one terminal tertiary amino group, two internal tertiary amino groups and one terminal secondary amino group), tris(dialkylaminoolalkylamidetramines (three terminal tertiary amino groups and one terminal primary amino group), and like compounds, wherein the alkyl groups may be the same or different and may comprise no more than about 12 carbon atoms each, and which, for example, may comprise from about 1 to about 4 carbon atoms each. For example, these alkyl groups may be methyl and/o or ethyl groups. In certain embodiments, the polyamine reactants include N,N-dimethyl-1,3-propanedi-amine and N-methyl piperazine.

[0011] The ii) alkyl-substituted hydroxyaromatic compounds and iii) aldehydes used in making the Mannich product may be any such compounds known and applied in the art, in accordance with the foregoing limitations.
Representative ii) alkyl-substituted hydroxyaromatic compounds that may be used in forming the Mannich product may include, but are not limited to, polypropylene phenol (formed by alkylating phenol with polypropylene), polybutylphenols (formed by alkylating phenol with polybutenes and/or polyisobutylene), and polybutyl-co-polypolyphenyls (formed by alkylating phenol with a copolymer of butylene and/or butylene and propylene). In an embodiment, the alkyl-substituted hydroxyaromatic compound may be chosen from polyolefin-substituted phenols, such as polybutylene-substituted phenols, polypropylene-substituted phenols, and for example polyisobutylcresols.

Other similar long-chain alkylphenols may also be used. Non-limiting examples include phenols alkylated with copolymers of butylene and/or isobutylene and/or propylene, and at least one mono-olefinic comonomer copolymerizable therewith (e.g., ethylene, 1-pentene, 1-hexene, 1-octene, 1-decene, etc.) where the copolymer molecule comprises at least 50% by weight of butylene and/or isobutylene and/or propylene units. The comonomers polymerized with propylene or such butenes may be aliphatic and can also comprise non-olefinic groups, e.g., styrene, o-methylstyrene, p-methylstyrene, divinyl benzene and the like. Thus, in any case, the resulting polymers and copolymers used in forming the alkyl-substituted hydroxyaromatic compounds may be substantially aliphatic hydrocarbon polymers. In an embodiment, the alkyphenol may be chosen from cresols.

Polybutylphenol (formed by alkylating phenol with polybutylene) may be used. Unless otherwise specified herein, the term “polybutylene” is used in a generic sense to include polymers made from any and all “pure” or “substantially pure” 1-butene or isobutene, and polymers made from mixtures of two or all three of 1-butene, 2-butene and isobutene. Commercial grades of such polymers may also comprise insignificant amounts of other olefins. So-called high reactivity polybutylenes having relatively high proportions of polymer molecules having a terminal vinylidene group, formed by methods as described, for example, in U.S. Pat. No. 4,152,499 and W. German Offenlegungsschrift 29 04 314, the disclosures of both of which are hereby incorporated by reference, may also be suitable for use in forming the long chain alkylated phenol reactant.

The alkylation of the hydroxyaromatic compound may be performed in the presence of an alkylating catalyst at a temperature in the range of about 50 to about 200°C. Acidic catalysts may be generally used for promoting Friedel-Crafts alkylation. Catalysts used in commercial production include, for example, sulphuric acid, BF₃, aluminum phenoxyde, methanesulphonic acid, cationic exchange resin, acidic clays and modified zeolites or other Lewis acids, such as tin halides.

The long chain alkyl substituents on the benzene ring of the phenolic compound may be derived from polyolefin having a number average molecular weight (Mn) of from about 500 to about 3000 (for example from about 500 to about 2100) as determined by gel permeation chromatography (GPC). In some embodiments, the polyolefin may have a polydispersity (weight average molecular weight/ number average molecular weight) in the range of about 1 to about 4 (for example from about 1 to about 2) as determined by GPC.

The Mannich product may be, for example, made from a long chain alkylphenol. However, other phenolic compounds may be used including high molecular weight alkyl-substituted derivatives of resorcinol, hydroquinone, catechol, hydroxydiphenyl, benzylphenol, phenethylyphenol, naphthol, tolylnaphthol, among others. In embodiments, the Mannich product may be prepared from polyalkylphenol reactants, e.g., polypropylene phenol and polybutylphenol whose alkyl group has a number average molecular weight of about 500 to about 2100, wherein the alkyl group may be a polybutyl group derived from polybutylene having a number average molecular weight in the range of about 800 to about 1300.

A configuration of the alkyl-substituted hydroxyaromatic compound may be that of a para-substituted mono-alkylphenol. However, any alkylphenol readily reactive in the Mannich condensation reaction may be employed. The long chain alkyl substituents may contain some residual unsaturation, but in general, may be substantially saturated branched or linear alkyl groups.

Representative iii) aldehydes for use in the preparation of the Mannich product include, but are not limited to, aliphatic aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, caproic aldehyde, heptaldehyde, stearaldehyde. Aromatic aldehydes which may be used include benzaldehyde and salicylaldehyde. Illustrative heterocyclic aldehydes for use herein are furfural and thiophene aldehyde, etc. Also useful may be formaldehyde-producing reagents such as paraformaldehyde, or aqueous formaldehyde solutions such as formalin. In an embodiment, formaldehyde or formalin may be used.

Components i), ii), and iii) may be reacted under suitable Mannich reaction conditions to form a Mannich product. The condensation reaction among the alkyl-substituted hydroxyaromatic compound, the amine, and the aldehyde may be conducted at a temperature in the range of about 40°C to about 200°C. The reaction can be conducted in bulk (no diluent or solvent) or in a solvent or diluent. Water may be evolved and can be removed by azeotropic distillation during the course of the reaction. The Mannich product may be formed, in one embodiment, by reacting the alkyl-substituted hydroxyaromatic compound, the amine, and the aldehyde in the molar ratio of 1.0:0.2-1.8:1.0-4.0, respectively, for example 1.0:5-1.5:1.5-2.5. The aldehyde may be present in a molar amount at least equal to the total molar amount of the amine compound present.

The detergent may be present in the fuel additive composition in any amount sufficient to reduce and/or prevent the formation of deposits, such as intake valve and chamber combustion valves. In an embodiment, the Mannich product may comprise from about 5 pb to about 300 pb, for example from about 25 pb to about 200 pb, and as a further example from about 75 to about 150 pb, of active material in the fuel composition. Commercial examples of a Mannich Product include HITEC® 6416 (Ethyl Corp., Richmond, Va.).

The disclosed fuel additive composition may comprise reaction products of the Mannich product. For example, the fuel additive composition may, in one embodiment, comprise up to 15% by weight of unreacted polyisobutylene phenol, and/or up to 10% by weight of unreacted polyisobutylene.
The fuel additive composition may also comprise a dispersant, such as a polyetheramine or polyether. The disclosed polyetheramine may be represented by the formula $R(OCH_2CH(R'))_nA$ wherein $R$ may be a hydrocarbyl group comprising from $C_1$ to $C_10$, $R'$ may be selected from the group consisting of hydrocarbon, hydrocarbyl groups comprising from about 1 to about 16 carbon atoms, and mixtures thereof; $n$ may be a number from about 2 to about 50; and $A$ may be selected from the group consisting of $-OCH_2CH_2CH_2NR'R^2$ and $-NR'R^2$ wherein each $R'$ may be independently hydrogen or hydrocarbyl comprising from about $C_1$ to $C_10$, and each $R^2$ may be independently hydrogen, hydrocarbyl or $-(R^3N(R^5))_pR^4$ wherein $R^4$ may be $C_1-C_{10}$ alkylene, and $R^3$ and $R^5$ may be independently hydrogen or hydrocarbyl, and $p$ may be a number from about 1 to about 7.

These polyetheramines can be prepared by initially condensing an alcohol or alkylphenol with an alkylene oxide, mixture of alkylene oxides or with several alkylene oxides in sequential fashion in, for example, a 1:2-50 mole ratio of hydric compound to alkylene oxide to form a polyether intermediate. U.S. Pat. No. 5,094,667 provides reaction conditions for preparing a polyether intermediate, the disclosure of which is incorporated herein by reference. U.S. Pat. No. 5,952,261 provides double metal cyanide complex catalysts which can be used to polymerize epoxides to provide polyether polyols having low levels of unsaturation and/or high molecular weights, the disclosure of which is hereby incorporated by reference.

The alcohols can be linear or branched from about 1 to about 30 carbon atoms, for example from about 6 to about 20 carbon atoms, and as a further example from about 10 to about 16 carbon atoms. The alkyl group of the alkylphenols can comprise from about 1 to about 30 carbon atoms, and for example from about 10 to about 20 carbon atoms.

The alkylene oxides may be selected from the group consisting of ethylene oxide, propylene oxide, and butylene oxide. The number of alkylene oxide units in the polyether intermediate may be from about 10 to about 35, and for example from about 18 to about 27.

The polyether intermediate can be converted to a polyetheramine by amination with ammonia, an amine or a polyamine to form a polyetheramine of the type where $A$ may be $-NR'R^2$, wherein $R'$ may be as defined above. Published Patent Application EP310875 provides reaction conditions for the amination reaction, the disclosure of which is incorporated herein by reference. Alternatively, the polyether intermediate can also be converted to a polyetheramine of the type where $A$ may be $-OCH_2CH_2CH_2NR'R^2$, wherein $R^2$ may be as defined above, by reaction with acrylonitrile followed by hydrocyanation. U.S. Pat. No. 5,094,667 provides reaction conditions for the cyanmethylation and subsequent hydrogenation, the disclosure of which is incorporated herein by reference.

In some embodiments, the polyetheramines wherein $A$ may be $-OCH_2CH_2CH_2NRH_2$ may be used. Commercial examples of suitable polyetheramines are the TECCHIRON® series from Chevron, the JEFFAMINE® series from Huntsman, and the HITEC® from Afton Chemical Corp.

The disclosed polyethers may be represented by the formula $R'\text{O}($CH$_2$CH(R$^8$)O)$_q$H wherein $R'$ may be a hydrocarbyl group comprising from about 1 to about 30 carbon atoms, $R^8$ may be selected from the group consisting of hydrogen, hydrocarbyl groups comprising from about 1 to about 16 carbon atoms, and mixtures thereof, and $q$ may be a number from about 2 to about 50. Reaction conditions for preparation as well as some embodiments of the disclosed polyethers were presented above in the poly etheramine description for the polyether intermediate. A commercial example of a polyether is the Bayer ACTACLEAR® series. Suitable samples may also be available from Dow Chemicals, Huntsman, BASF, and ICI.

The dispersant, such as the polyetheramine, may comprise from about 5 pbh to about 300 pbh, for example from about 25 pbh to about 200 pbh, and as a further example from about 75 to about 150 pbh, of active material in the fuel composition. The dispersant may be present in the fuel additive composition in an amount of from about 5 to about 60% by weight of active material relative to the total weight of the composition. The disclosed fuel additive composition may comprise reaction products of the polyetheramine. The fuel additive composition may further comprise up to 25% by weight of unreacted starting material, such as polyether alcohol.

In an embodiment, the polyetheramine disclosed herein may not be a friction modifier.

The disclosed fuel additive composition will also comprise a friction modifier. The friction modifier may be an amide obtained from a reaction of an amine with an acid. Both the amine and the acid may independently be monofunctional or multifunctional. For example, a monoamine may be reacted with a dimer acid to form an amide suitable for use herein. Alternatively, a polyamine may be reacted with a monoaacid to form an amide. One of ordinary skill in the art would readily know all the various types of acids and amines that could be reacted in various permutations and combinations in order to achieve an amide.

In an embodiment, the friction modifier may be an amide, such as a reaction product of a monocarboxylic fatty acid with an amine, such as diethanolamine and its derivatives, to form a monocarboxylic fatty acid amide. Diethanolamine derivatives suitable for use as the amine herein to produce the amide friction modifier include, but are not limited to, fatty acid amines and esters of diethanolamine, and mixtures thereof. The fatty acid amides or esters of diethanolamine can be made by forming a mixture of a fatty acid and diethanolamine and heating the mixture to remove water. Optionally, a water immiscible inert solvent such as toluene or xylene can be included to aid in the removal of water. Optionally, a fatty ester may be substituted for the fatty acid described above and reacted directly with the amine.

In preparing mixtures, according to one embodiment of the present invention, about 1 to about 3 moles of fatty acid may be used per mole of amine, such as diethanolamine. The reaction proceeds to yield mainly amide according to the following equation:
Some of the diethanolamine can react to form an ester according to the following equation:

\[
R\text{--COOH} + \text{HN---C}_2\text{H}_4\text{OH} \rightarrow R\text{--N---C}_2\text{H}_4\text{OH}
\]

wherein R may be a hydrocarbon residue of the fatty acid.

Some of the above reaction products can be separated by distillation and used separately in diesel or gasoline fuel compositions. For example, they may not be separated, but may be used as mixtures. The mixtures can also contain fatty acid ester-amides of diethanolamine. When equal mole mixtures of fatty acid and diethanolamine are reacted, very little ester-amide forms. However, whenever more than one mole of fatty acid is reacted with a mole of diethanolamine, increased amounts of ester-amide can form according to the following equation:

\[
2R\text{--COOH} + \text{HN---C}_2\text{H}_4\text{OH} \rightarrow 2R\text{--N---C}_2\text{H}_4\text{OH}
\]

Such ester-amides are within the scope of the present disclosure.

In some embodiments, the fatty acids used in the diethanolamine derivatives useful in the present disclosure may be those comprising from about 8 to about 20 carbon atoms. Non-limiting examples of these include caprylic acid, pelargonic acid, capric acid, iso-octanoic acid, undecylic acid, lauric acid, tridecanoic acid, myristic acid, stearic acid, arachidic acid, and mixtures thereof.

For example, the fatty acid may be an unsaturated fatty acid such as linoleic acid, oleic acid, erucic acid, Brassidic acid, and the like. As a further example, the fatty acid may be oleic acid. Thus, suitable additives are N,N-bis-(2-hydroxyethyl)oleamide, N-(2-hydroxyethyl)amineoethyl oleate, and mixtures thereof. The diethanolamine derivatives suitable for use herein include those taught in U.S. Pat. No. 4,204,481, the disclosure of which is hereby incorporated by reference.

The friction modifier may be present in the fuel additive composition in a friction modifying amount. Commercial examples of a friction modifier, for use in the disclosed fuel additive, include, but are not limited to HitEC® 4848A, and HitEC® 6457 from Afton Chemical Corp., Richmond, Va. Friction modifying amount as determined by ASTM D 6079, which is a standard method for determining lubricity in a “high-frequency reciprocating rig” (HFRR). In various embodiments, oleo amides may be used. For example, ethamidin, such as N-(hydroxyethyl)-pentacyclo(hexamethylene) oleamide, and schercomids, such as ethoxylated fatty amides, for example schercomid SOA-E (ethoxylated fatty C10 to 18 amide) and SCHREROMID SL-ML, may be used.

The disclosed fuel additive composition may also optionally comprise a fluidizer, such as a polyether alcohol, for example polyethermonol. The polyether alcohol may be present in the fuel additive composition as an unreacted hyproduct of the polyetheramide reaction.

The fuel additive composition of the present disclosure may optionally contain at least one supplemental additive. The at least one supplemental additive may be chosen from, for example, dispersants, detergents, antioxidants, friction modifiers, biocides, antistatic additives, drag-reducing agents, demulsifiers, dehazers, anti-icing additives, anti-knock additives, anti-rust additives, and/or other fuel additive, and lubricity additives, multifunctional additives (e.g., methylcyclopentadienyl manganese tricarbonyl, MMTR, Afton Chemical Corp., Richmond, Va., and/or other cyclopentadienyl manganese tricarbonyl compounds), and combustion improvers. The at least one supplemental additive may be provided in the fuel composition in an amount necessary to achieve the desired effect.

The base fuels used in formulating the fuel compositions according to the present disclosure include any base fuels suitable for use in the operation of spark-ignition internal combustion engines, such as leaded or unleaded motor and aviation gasolines, diesel, and so-called reformulated gasolines which typically contain both hydrocarbons of the gasoline boiling range and fuel-soluble oxygenated blending agents, such as fuels, and other suitable oxygen-containing organic compounds. Suitable oxygenates include, for example, methanol, ethanol, isopropanol, t-butanol, mixed C1 to C5 alcohols, methyl tertiary butyl ether, tertiary amyl methyl ether, ethyl tertiary butyl ether, and mixed ethers. Oxygenates, when used, will normally be present in the base fuel in an amount below about 25% by volume, for example in an amount that provides an oxygen content in the overall fuel in the range of about 0.5 to about 5% by volume.

Fuel compositions may comprise a major amount of a base fuel and a minor amount of a fuel additive composition. A “major amount” may be understood to mean greater than or equal to about 50%. A “minor amount” may be understood to mean less than about 50%.

According to one aspect of the present disclosure, the component product may be used in combination with at least one liquid carrier or induction aid. Such carriers can be of various types such as, for example, liquid poly-α-olefin oligomers, mineral oils, liquid poly(oxyalkylene) compounds, liquid alcohols or polyols, polyalkenes, liquid esters, similar liquid carriers. Mixtures of two or more such carriers can be employed.

The additives used in formulating the fuels disclosed herein can be blended into the base fuel individually
or in various sub-combinations. However, it may be desir-able in some instances to blend all of the components concurrently using an additive concentrate (i.e., additives plus a diluent, such as a hydrocarbon solvent). The use of an additive concentrate takes advantage of the mutual compat-ibility afforded by the combination of ingredients when in the form of an additive concentrate. Also, use of a concen-trate may reduce blending time and may lessen the possi-bility of blending errors.

[0047] The fuel additive composition disclosed herein can contact an actuated injector. Non-limiting examples of an actuated injector include direct-injection gasoline, port-fuel, sequential central port-fuel, and director plate injectors.

[0048] In another embodiment, a fuel additive composition may comprise an aliphatic hydrocarbyl-substituted amine, a polyetheramine as disclosed herein, and a friction modifier as disclosed herein. In various aspects of this embodiment, the polyetheramine may not be a friction modifier.

[0049] The aliphatic hydrocarbyl-substituted amine may be a straight or branched chain hydrocarbyl-substituted amine comprising at least one basic nitrogen atom wherein the hydrocarbyl group has a number average molecular weight of about 700 to about 3,000, for example from about 750 to about 2,200, and as a further example from about 900 to about 1,500. In embodiments, the aliphatic amines may be of sufficient molecular weight so as to be nonvolatile at normal engine intake valve operating temperatures, such as in the range of about 175°C to 300°C.

[0050] When employing a branched-chain hydrocarbyl amine, the hydrocarbyl group may be derived from poly-mers of C₅-C₁₀ olefins. In embodiments, the branched-chain hydrocarbyl groups may be derived from polypropylene and polyisobutylene and the branches may comprise from about 1 to about 2 carbon atoms, for example 1 carbon atom, such as a methyl. The branched-chain hydrocarbyl amines may not be a pure single product, but rather a mixture of compounds having an average molecular weight.

[0051] The amine component of the aliphatic hydrocarbyl-substituted amine may be derived from ammonia, a monoamine or a polyamine. The monoamine or polyamine component may include a broad class of amines having from about 1 to about 12 amine nitrogen atoms and from about 1 to about 40 carbon atoms with a carbon to nitrogen ratio ranging from about 1:1 to 10:1. In most instances, the amine component may not be a pure single product, but rather a mixture of compounds having a major quantity of the designated amine. For the more complicated polyamines, the compositions will be a mixture of amines having as the major product the compound indicated and having minor amounts of analogous compounds. Suitable monoamines and polyamines are described more fully below.

[0052] When the amine component is a polyamine, it may be a polyalkylene polyamine, including alkylenediamine, wherein the alkylene group may comprise from about 2 to about 6 carbon atoms. Non-limiting examples of polyamines include ethylene diamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, ditrimethylene triamine, propylene diamine, dipropylene triamine, tripropy-lene tetramine, and pentaethylenhexamine.

[0053] In an embodiment, the branched-chain hydrocarbyl amines may include, but are not limited to, polyisobuteneyle diamine and polyisobutyl amine, wherein the poly-isobutyl group may be substantially saturated and the amine moiety may be derived from ammonia.

[0054] Hydrocarbyl, as used in describing the amine moi-eity on the aliphatic amine employed in this invention, may denote an organic radical comprising carbon and hydrogen which may be aliphatic, alicyclic, aromatic or combinations thereof, e.g., aralkyl. In embodiments, the hydrocarbyl group may be relatively free of aliphatic unsaturation, i.e., ethynyl and acetylenic, for example acetylenic unsaturation. Non-limiting examples of hydrocarbyl groups and substituted hydrocarbyl groups include alkyils such as methyl, ethyl, propyl, butyl, isobutyl, pentyl, hexyl, octyl, etc., alkenyls such as propenyl, isobutenyl, hexenyl, octenyl, etc., hydroxyalkyls, such as 2-hydroxyethyl, 3-hydroxypropyl, hydroxy-isopropyl, 4-hydroxybutyl, etc., ketoalkyls, such as 2-ketopropyl, 6-ketoctyl, etc., alkoxy and lower alkenoxy alkyls, such as ethoxyethyl, ethoxypropyl, propoxyethyl, propoxypropyl, diethylenoexymethyl, triethylenoxyethyl, tetraethylenoexyethyl, diethylenoexyhexyl, etc.

[0055] The amine component also may be derived from heterocyclic polyamines, heterocyclic substituted amines and substituted heterocyclic compounds, wherein the het-erocycle comprises at least one 5-6 membered rings con-taining oxygen and/or nitrogen. Such heterocyclic rings may be saturated or unsaturated and substituted. The heterocyclic compounds may be exemplified by piperazines, such as 2-methylpiperazine, N-(2-hydroxyethyl)-piperazine, 1,2-bis-(N-piperazinyl)ethane and N,N'-bis-(N-piperazinyl)piper-azine, 2-methylimidazoline, 3-aminopiperidine, 3-ami-nopyridine, and N-(3-aminopropyl)-morpholine, etc.

[0056] The aliphatic hydrocarbyl amines employed may be prepared by conventional procedures known in the art. See U.S. Pat. Nos. 5,993,499; 3,438,757; 3,565,804; 3,574,576; 3,848,056; 3,960,515; and 4,832,702, the disclosures of which are incorporated herein by reference.

[0057] Other aspects of the present invention include methods for reducing the formation or persistence of depo-sits, and the formation of valve deposits and chamber combustion deposits, in an engine and eliminating valve sticking in a spark-ignition engine by fueling and/or operating the engine with the fuel composition disclosed herein.

**EXAMPLE**

[0058] A fuel additive composition comprising 23% by weight of polyetheramine, 23% by weight of a Mannich product from high reactivity polyisobutylene cresol (HiTEC® 6416, Ethyl Corp., Richmond, Va.), 12% by weight of a polyether alcohol (ACTACTER® 2400®, Bayer Corporation, Pittsburgh, Pa.), and 42% by weight of a solvent (A100, Exxon, Paulsboro, N.J.) was blended into a fuel and tested on a SwRI PFI Rig according to ASTM D6421.

[0059] ASTM D6421 is a test method covering a bench test procedure to evaluate the tendency of automotive spark-ignition engine fuel to foul electronic port fuel injectors (PFI). The test method utilizes a bench apparatus equipped with Bosch injectors specified for use in a 1985-1987 Chrysler 2.2-L turbocharged engine. The test method is based on a test procedure developed by the Coordinating
Research Council (CRC) for prediction of the tendency of spark-ignition engine fuel to form deposits in the small metering clearances of injectors in a port fuel injection engine (see CRC Report No. 5922). The test method is applicable to spark-ignition engine fuels, which may contain antioxidants, corrosion inhibitors, metal deactivators, dyes, deposit control additives, demulsifiers, or oxygenates, or a combination thereof.

[0060] The data is as follows:

[0061] Run 1: 80 ptb (0.864 grams/gallon) of the above-identified fuel additive was added to a gasoline.

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[0062] Run 2: 80 ptb (0.864 grams/gallon) of the above-identified fuel additive and 20 ptb (0.216 grams/gallon) of a friction modifier (HiTEC® 6457, Afton Chemical Corp., Richmond, Va.) was added to the same gasoline as in Run 1 in the same set of injectors, but cleaned between tests. The friction modifier was a low molecular weight amide made from a (C18) branched fatty acid reacted with diethanolamine.

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<th>Injector</th>
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[0063] Run 3: Base fuel gasoline with no fuel additive composition.

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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>31.0</td>
<td>33.5</td>
<td>25.1</td>
<td>6.6</td>
</tr>
</tbody>
</table>

Example 2

[0064] The fuel additive composition identified in Example 1 was used in a base fuel with and without the addition of a friction modifier, such as the disclosed amide. The fuel was tested in a model year 2000 to 2002 GM Astro Van with a 4.3-L V-6 engine, which was equipped with sequential central port fuel injection (SCPI). The fuel injector fouling initial performance standard as detailed in the “TOP TIER Detergent Gasoline Deposit Control Performance Standards,” released in April 2004, was used. A pass occurs when the vehicle “sticks” no more than one injector.

[0065] The data is as follows:

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Fuel Additive of Example 1</th>
<th>Friction modifier</th>
<th>No. Stuck Injector</th>
<th>Vehicle Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(not inventive)</td>
<td>80 ptb</td>
<td>0 ptb</td>
<td>2 Fail</td>
</tr>
<tr>
<td>2</td>
<td>(not invention)</td>
<td>80 ptb</td>
<td>0 ptb</td>
<td>2 Fail</td>
</tr>
<tr>
<td>3</td>
<td>(inventive)</td>
<td>80 ptb</td>
<td>20 ptb</td>
<td>0 Pass</td>
</tr>
</tbody>
</table>

[0066] HiTEC® 6457, which is a reaction product of isostearic acid and diethanolamine, was used as the friction modifier.

[0067] As can be seen from the data, a vehicle which uses a fuel composition comprising a fuel additive composition without a friction modifier resulted in a higher percentage of deposits (see Run 1 of Example 1) and more stuck injectors (see Test Nos. 1 and 2 of Example 2) as compared to a fuel composition comprising a fuel additive composition with a friction modifier.

Example 3

[0068] A mileage accumulation test was done on a Chassis Dynamometer, with a mixed highway and city driving cycle. In particular, the driving cycle was 76 miles, for 99.46 minutes, at an average speed of 45.7 mph. Two runs with different formulations were tested. The first one did not comprise a friction modifier. The second run did comprise a friction modifier. For the test, a 2000 Mercury Marquis 4.6-L V8 engine was used. The average intake deposits were measured after a 1500 mile dirty up on a PUL fuel. Moreover, the average chamber head and piston-top deposits were measured after a 5000 mile clean up on the fuel additive in the PUL fuel at treat rates as indicated in the table (ptb).

<table>
<thead>
<tr>
<th>Clean-Up Phase</th>
<th>Dirry-Up Phase</th>
<th>Avg Intake Deposit</th>
<th>Avg Intake Deposit</th>
<th>% IVD Clean Up</th>
<th>Avg Chamber Head Deposit</th>
<th>Avg Piston-Top Deposit</th>
<th>Total Chamber Deposit</th>
<th>Total Deposits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1 (not inventive)</td>
<td>615.9</td>
<td>176.6</td>
<td>71.3%</td>
<td>2004.8</td>
<td>2181.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run 2 (inventive)</td>
<td>856.4</td>
<td>250.6</td>
<td>70.7%</td>
<td>817.9</td>
<td>932.5</td>
<td>1750.4</td>
<td>2001.0</td>
<td></td>
</tr>
</tbody>
</table>
As can be seen, the second run with the formulation comprising a friction modifier exhibited less average chamber head and piston-top deposits, and therefore less total chamber deposits.

For the purposes of this specification and appended claims, unless otherwise indicated, all numbers expressing quantities, percentages or proportions, and other numerical values used in the specification and claims, are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

Notwithstanding that the numerical ranges and parameters set forth the broad scope of the disclosure are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements. Moreover, all ranges disclosed herein are to be understood to encompass any and all subranges subsumed therein. For example, a range of “less than 10” includes any and all subranges between (and including) the minimum value of zero and the maximum value of 10, that is, any and all subranges having a minimum value of equal to or greater than zero and a maximum value of equal to or less than 10, e.g., 1 to 5.

It is noted that, as used in this specification and the appended claims, the singular forms “a,” “an,” and “the,” include plural referents unless expressly and unequivocally limited to one referent. Thus, for example, reference to “a friction modifier” includes two or more different friction modifiers. As used herein, the term “include” and its grammatical variants are intended to be non-limiting, such that recitation of items in a list is not to the exclusion of other like items that can be substituted or added to the listed items.

It will be apparent to those skilled in the art that various modifications and variations can be made to various embodiments described herein without departing from the spirit or scope of the present teachings. Thus, it is intended that the various embodiments described herein cover other modifications and variations within the scope of the appended claims and their equivalents.

What is claimed is:

1. A fuel additive composition comprising:
   a) a Mannich product,
   b) a polyetheramine, and
   c) a friction modifier.

2. The composition of claim 1, wherein the Mannich product is a reaction product of an alkyl-substituted hydroxyaromatic compound, an aldehyde, and an amine.

3. The composition of claim 2, wherein the alkyl-substituted hydroxyaromatic compound is chosen from alkylphenols.

4. The composition according to claim 3, wherein the alkylphenols are chosen from cresols.

5. The composition according to claim 2, wherein the alkyl-substituted hydroxyaromatic compound is chosen from polyolefin-substituted phenols.

6. The composition according to claim 5, wherein the polyolefin-substituted phenols are chosen from polybutylene-substituted phenols and polypropylene-substituted phenols.

7. The composition according to claim 5, wherein the polyolefin-substituted phenols are polyisobutylcresols.

8. The composition according to claim 2, wherein the amine comprises an alkylene polyamine.

9. The composition according to claim 1, further comprising a polyether alcohol.

10. The composition according to claim 2, wherein the aldehyde is formaldehyde or a precursor thereof.

11. The composition according to claim 1, wherein the friction modifier is an amide.

12. The composition according to claim 11, wherein the amide is an alkanolamide.

13. The composition according to claim 11, wherein the amide is a reaction product of an acid and an amine.

14. The composition according to claim 13, wherein the acid is selected from the group consisting of a monofunctional acid and a multifunctional acid.

15. The composition according to claim 13, wherein the amine is selected from the group consisting of a monoamine and a polyamine.

16. The composition according to claim 13, wherein the acid is a monocarboxylic fatty acid and the amine is diethanolamine.

17. The composition according to claim 1, wherein the Mannich product is combined with at least one liquid carrier.

18. A process for preparing a fuel additive, comprising providing a Mannich product, a polyetheramine, and a friction modifier to yield a fuel additive.

19. The process according to claim 18, wherein the friction modifier is present in the fuel additive in a friction modifying amount via ASTM D 6079.
20. A fuel composition comprising:

(A) a fuel in a major amount; and

(B) a fuel additive composition according to claim 1 in a minor amount.

21. The composition according to claim 20, wherein the fuel comprises gasoline.

22. The composition according to claim 20, wherein the Mannich product comprises from about 5 ptb to about 300 ptb of active material in the fuel composition.

23. The composition according to claim 22, wherein the Mannich product comprises from about 25 ptb to about 200 ptb of active material in the fuel composition.

24. The composition according to claim 20, wherein the polyetheramine comprises from about 5 ptb to about 300 ptb of active material in the fuel composition.

25. The composition according to claim 24, wherein the polyetheramine comprises from about 25 to about 200 ptb of active material in the fuel composition.

26. The composition according to claim 20, further comprising at least one additive selected from the group consisting of dispersants, detergents, antioxidants, carrier fluids, metal deactivators, dyes, markers, corrosion inhibitors, biocides, anti-static additives, drag-reducing agents, demulsifiers, dehazers, anti-icing additives, anti-knock additives, anti-valve-seat recession additives, lubricity additives, and combustion improvers.

27. A method for preventing and/or reducing the formation of deposits in an engine, comprising fueling and operating said engine with a fuel composition according to claim 20.

28. The method of claim 27, wherein the deposits are combustion chamber deposits.

29. An engine combusting a fuel additive composition according to claim 1.

30. An engine combusting a fuel composition according to claim 20.

31. An actuated injector contacting a fuel additive composition according to claim 1.

32. An actuated injector contacting a fuel composition according to claim 20.

33. The injector of claim 31, wherein the actuated injector is selected from the group consisting of direct-injection gasoline, port-fuel, sequential central port-fuel, and direct plate injectors.

34. A fuel additive composition comprising:

a) an aliphatic hydrocarbyl-substituted amine,

b) a polyetheramine, and
c) a friction modifier.