A fuel, fuel additive concentrate, and method for removing and/or preventing the occurrence of deposits in a fuel injector of an injection engine are provided. The additive concentrate contains at least one hexahydro triazine.
COMPOSITIONS AND METHODS INCLUDING HEXAHYDROTRIAZINES USEFUL AS DIRECT INJECTION FUEL ADDITIVES

TECHNICAL FIELD

[0001] The disclosure is directed to certain fuel additives, fuel additive concentrates, and fuels that include a hexahydrotriazine. In particular the disclosure is directed to a fuel additive that is effective to reduce deposits in fuel injectors useful in diesel and/or gasoline direct injection engines.

BACKGROUND

[0002] It has long been desired to maximize fuel economy, power, and drivability of vehicles while enhancing acceleration, reducing emissions, and preventing hesitation. While it is known to enhance engine performance by employing dispersants to keep valves and fuel injectors clean, such dispersants may be only minimally effective.

[0003] Dispersants are suitable for keeping soot and sludge suspended in a fluid, however dispersants are not particularly effective for cleaning surfaces once deposits have formed on the surfaces. Hence, fuel compositions that include dispersants often still produce undesirable deposits on diesel engine injectors. Accordingly, improved compositions that can prevent deposit build up, maintaining “as new” cleanliness for the vehicle life are desired. Ideally, the same composition that can clean dirty fuel injectors restoring performance to the previous “as new” condition would be equally desirable and valuable in the attempt to reduce airborne exhaust emissions.

SUMMARY

[0004] In accordance with the disclosure, exemplary embodiments provide a fuel, a fuel additive concentrate, a fuel soluable deposit control additive, and a method for improving the performance of fuel injectors for a direct injection engine. The additive comprises at least one hexahydrotriazine.

[0005] In an embodiment, a fuel suitable for use in a fuel injection engine may comprise a major amount of a fuel, and a minor amount of an additive concentrate comprising a hexahydrotriazine.

[0006] In some embodiments, an alkyl group is attached to at least one nitrogen in the hexahydro triazine ring. In some embodiments, the alkyl group is linear. In some embodiments, the alkyl group is branched at a position after the beta position to the at least one nitrogen.

[0007] In some embodiments, the hexahydro triazine comprises the product combining, mixing, admixing, or contacting one or more primary amine(s) and a formaldehyde.

[0008] In some embodiments, the hexahydro triazine has a molecular weight of from about 100 to about 700. In some embodiments, the hexahydro triazine has a molecular weight of from about 400 to about 600.

[0009] In some embodiments, the hexahydro triazine is selected from the group consisting of at least one of dodecyamine hexahydro triazine and octyl hexahydro triazine.

[0010] In some embodiments, the hexahydro triazine is selected from the group consisting of at least one of the following structures:
In some embodiments, the hexahydro triazine is present in an amount sufficient to remove and/or prevent the occurrence of deposits in a fuel injector of an injection engine.

In some embodiments, the hexahydro triazine is present in the fuel in an amount from about 1 ppm to about 100 ppm. In some embodiments, the hexahydro triazine is present in the fuel in an amount from about 5 ppm to about 20 ppm.

In some embodiments, the additive concentrate further comprises a dispersant/detergent.

In some embodiments, the dispersant/detergent comprises at least one of an amine dispersant/detergent, an alkenyl succinimide dispersant, an alkenyl succinic acid ester dispersant, an alkenyl succinic ester-amide dispersant, a polyisobutylene amine dispersant, or a Mannich base dispersant.

In some embodiments, the fuel is selected from the group consisting of middle distillate fuels, diesel fuels, gasoline, biorenewable fuels, biodiesel fuels, gas-to-liquid (GTL) fuels, jet fuels, aviation fuels, marine fuels, burner fuels, alcohols, ethers, esters, kerosene, home heating oils (for example, home heating oil no. 6), low sulfur fuels, synthetic fuels, such as Fischer-Tropsch fuels, liquid petroleum gas, bunker oils, coal to liquid (CTL) fuels, biomass to liquid (BTL) fuels, high asphaltene fuels, fuels derived from coal (natural, cleaned, and pet coke), genetically engineered biofuels and crops and extracts therefrom, natural gas, a Group I base oil, a Group II base oil, a Group III base oil, and a Group IV base oil.

In another embodiment, a method for removing and/or preventing the occurrence of deposits in a fuel injector of a fuel injection engine may comprise adding to and operating in an injection engine having fuel injectors a fuel composition comprising (a) a major amount of fuel and (b) a minor amount of an additive concentrate comprising a hexahydro triazine.

In some embodiments, an alkyl group is attached to at least one nitrogen in the hexahydro triazine ring.

In some embodiments, the alkyl group is linear.

In some embodiments, the alkyl group is branched at a position after the beta position to the at least one nitrogen.

In some embodiments, the hexahydro triazine comprises the product combing, mixing, admixing, or contacting one or more primary amine(s) and a formaldehyde.

In some embodiments, the hexahydro triazine has a molecular weight of from about 100 to about 700. In some embodiments, the hexahydro triazine has a molecular weight of from about 400 to about 600.
In some embodiments, the hexahydro triazine is selected from the group consisting of at least one of dodecylamine hexahydro triazine and octyl hydroxytriazine.

In some embodiments, the hexahydro triazine is selected from the group consisting of at least one of the structures I to XX, disclosed herein.

In some embodiments, the hexahydro triazine is present in an amount sufficient to remove and/or prevent the occurrence of deposits in a fuel injector of an injection engine.

In some embodiments, the hexahydro triazine is present in the fuel in an amount from about 1 ppm to about 100 ppm. In some embodiments, the hexahydro triazine is present in the fuel in an amount from about 5 ppm to about 20 ppm.

In some embodiments, the additive concentrate further comprises a dispersant/detergent.

In some embodiments, the dispersant/detergent comprises at least one of an amine dispersant/detergent, an alkyl succinimide dispersant, an alkyl succinic acid ester dispersant, an alkyl succinic ester-amide dispersant, polyisobutylene amine dispersant, or a Mannich base dispersant.

The fuel compositions of the present application may be suitable for use in a fuel injection engine. The fuel...
composition may comprise a major amount of a fuel and a minor amount of an additive concentrate comprising a hexahydro triazine, wherein the hexahydro triazine is present in an amount sufficient to remove and/or reduce the occurrence of deposits in a fuel injector of an injection engine. Suitable hexahydro triazines may be oil soluble and thermally stable.

[0047] The hexahydro triazine ring may be the reaction product of or the product of combining an alkylamine and formaldehyde or a mixture of amines and formaldehyde. Suitable amines may comprise any primary amines. The hexahydro triazine may, but is not limited to, be alkylated or alkoxylated. At least one nitrogen on the hexahydro triazine ring may be un hindered. The hexahydro triazine ring may be saturated. Suitable hexahydro triazines include but are not limited to octyl hexahydro triazine and dodecyl hexahydro triazine. In some embodiments, a triazine suitable for use in present embodiments is free of or substantially free of triazines made from diamines. Embodiments may include, but are not limited to the following structures:
[0048] Suitable hexahydro triazines may be unhindered. For example, hexahydro triazines may lack steric hindrance. For example, an alkyl group attached to a ringed nitrogen may be branched at a position after the beta position to the ringed nitrogen. In the Comparative Structures I and II, below, there is branching at the beta position to at least one ringed nitrogen.

[0049] In some embodiments the hexahydro triazine has a molecular weight of from about 100 to about 700. In another embodiment, the hexahydro triazine has a molecular weight of from about 400 to about 600.

[0050] The hexahydro triazine additive components may be added to a fuel composition in an amount sufficient to provide control, including removal or prevention of, deposits. For example, the hexahydro triazine additive components may be added to a fuel in proportions effective to reduce the volume of injector deposits in a direct injection gasoline engine operated on said fuel containing said hexahydro triazine additive components to below the volume of injector deposits in said engine operated in the same manner on the same fuel except that it is devoid of said hexahydro triazine additive components. Economically, it is desirable to use the least amount of additive effective for the desired purpose.

[0051] In some embodiments, one or more hexahydro triazine additive component(s) may be present in a fuel in an amount from about 1 ppm to about 100 ppm. In other embodiments, one or more hexahydro triazine additive component(s) may be present in a fuel in an amount from about 5 ppm to about 20 ppm.

Additional Components

[0052] One or more additional optional compounds may be present in the fuel compositions of the disclosed embodiments. For example, the fuels may contain conventional quantities of cetane improvers, corrosion inhibitors, cold flow improvers (CFPP additive), pour point depressants, solvents, demulsifiers, emulsifiers, lubricity additives, friction modifiers, amine stabilizers, combustion improvers, dispersant/detergents, antioxidants, heat stabilizers, conductivity improvers, metal deactivators, markers, dyes, organic nitrate ignition accelerators, cyclomeric manganese tricarbonyl compounds, carrier fluids, biocides, antistatic additives, drag reducing agents, dehazers, anti-icing additives, antiknock additives, anti-valve-seat recession additives, surfactants, and the like.

In some aspects, the compositions described herein may contain about 10 weight percent or less, or in other aspects, about 5 weight percent or less, based on the total weight of the additive concentrate, of one or more of the above additives. Similarly, the fuels may contain suitable amounts of conventional fuel blending components such as methanol, ethanol, dialkyl ethers, and the like.

Dispersants/Detergents

[0053] In some embodiments, the fuel additive concentrate may comprise a dispersant/detergent. The dispersant/detergent may comprise an ashless dispersant, a metal-containing dispersant, or a Mannich dispersant. A suitable dispersant/detergent may include at least one oil-soluble ashless dispersant having a basic nitrogen and/or at least one hydroxyl group...
in the molecule. Other suitable dispersants/detergents include alkyl succinimides, alkyl succinic acid esters, alkyl succinic ester-amides, and Mannich bases. For example, suitable dispersants/detergents may comprise, but are not limited to ethylene diamine or dibutyl amine Mannich base dispersants. An example of a dibutyl amine Mannich base dispersant is HTEC® 6416 Performance Additive Package (available from Alton Chemical Corporation). In some embodiments, a suitable dispersant may have a molecular weight of from about 750 to about 3000.

[0054] Suitable amine detergents include those well known in the art for use in fuels for MPI engines to control intake valve deposits. Suitable amine detergents include nitrogen-containing derivatives of hydrocarbyl succinic acylating agents, Mannich condensation products, hydrocarboxylic acids, and polyethers. When used, the amine detergents are typically present in an amount sufficient to control intake valve deposits and are typically present in an amount of from about 5 to about 100 pounds by weight of additive per thousand barrels by volume of fuel.

[0055] The nitrogen-containing derivatives of hydrocarbyl succinic acylating agents suitable for use in the present embodiments may include hydrocarboxyl succinimides, succinamides, succinimide-amides and succinimide-esters. The nitrogen-containing derivatives of hydrocarbyl succinic acylating agents are typically prepared by reacting a hydrocarbyl-substituted succinic acylating agent with a polyamine.

[0056] The hydrocarbyl-substituted succinic acylating agents include the hydrocarboxyl-substituted succinic acids, the hydrocarboxyl-substituted succinic acid halides (especially the acid fluorides and acid chlorides), the esters of the hydrocarboxyl-substituted succinic acids and lower alcohols (e.g., those containing up to 7 carbon atoms), that is, hydrocarboxyl-substituted compounds which can function as carboxylic acylating agents, and mixtures of hydrocarboxyl-substituted succinic acids and hydrocarboxyl-substituted succinic anhydrides.

[0057] Amines which may be reacted with the alkyl succinimide anhydride to form the hydrocarboxyl-succinimide include any that have at least one primary amine group that can react to form an imide group. A few representative examples are: methylenamine, 2-ethylhexylamine, n-dodecylamine, stearylamine, N,N-dimethyl-propanediamine, N-(triminopropyl)morpholine, N-dodecyl propaneamine, N-aminoethylpiperazine ethanamine, N-ethyl ethylene diamine and the like. Suitable amines include the alkylene polyamines such as propylene diamine, diethylene triamine, di-(1,2-butylen) triamine, tetra-(1,2-propylene) pentaamine.

[0058] Further suitable amines are the ethylene polyamines which have the formula H₂N(CH₂CH₂NH₂)ₙ wherein n is an integer from one to ten. These ethylene polyamines include ethylene diamine, diethylene triamine, triethylene tetrarime, tetraethylene pentamine, pentethylene hexamine, and the like, including mixtures thereof in which case n is the average value of the mixture. These ethylene polyamines have a primary amine group at each end so can form mono-alkylsuccinimides and bis-alkylsuccinimides. Thus suitable hydrocarboxyl succinimides may include the products of reaction of a polyethylene polyamine, e.g. triethylene tetramine or tetraethylene pentamine, with a hydrocarbon substituted carboxylic acid or anhydride made by reaction of a polyol, for example polysorbate, having a molecular weight of 500 to 2,000, especially 700 to 1500, with an unsaturated polycarboxylic acid or anhydride, e.g. maleic anhydride.

[0059] Suitable Mannich base detergents include the reaction products of a high molecular weight alkyl-substituted hydroxyaromatic compound, aldehydes, and amines. The alkyl-substituted hydroxyaromatic compound, aldehydes, and amines used in making the Mannich reaction products may be any suitable such compounds.

[0060] The high molecular weight alkyl substituents on the benzene ring of the hydroxyaromatic compound may be derived from polyolefin having a number average molecular weight (M₇) of from about 500 to about 3000, or from about 700 to about 2100, as determined by gel permeation chromatography (GPC). 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.

[0061] The alkylation of the hydroxyaromatic compound is typically performed in the presence of an alkylation catalyst at a temperature in the range of about 0 to about 200°C, for example from 0 to 100°C. Acidic catalysts are generally used to promote Friedel-Crafts alkylation. Typical catalysts used in commercial production include sulphuric acid, BF₃, alumino phenoxy, methanesulphon acid, cationic exchange resin, acidic clays, and modified zeolites.

[0062] Polyolefins suitable for forming the high molecular weight alkyl-substituted hydroxyaromatic compounds include polypropylene, polybutenes, polyisobutylene, copolymers of butylene and/or butylene and propylene, copolymers of butylene and/or isobutylene and/or propylene, and one or more mono-olefinic comonomers copolymerizable therewith (e.g., ethylene, 1-pentene, 1-hexene, 1-octene, 1-decene, etc.) where the copolymer molecule contains 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 contain non-aliphatic groups, e.g., styrene, o-methylstyrpene, p-methylstyrene, divinyl benzene, and the like. Thus in any case the resulting polymers and copolymers used in forming the high molecular weight alkyl-substituted hydroxyaromatic compounds are substantially aliphatic hydrocarbons.

[0063] Unless otherwise specified herein, the term “polybutylene” is used in a generic sense to include polymers made from “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 contain insignificant amounts of other olefins. So-called high reactivity polysobutenes having relatively high proportions of polymer molecules having a terminal vinylidene group are also suitable for use in forming the high molecular weight alkyl-substituted hydroxyaromatic compounds. Suitable high-reactivity polysobutenes include those polysobutenes that comprise at least about 20% of the more reactive methylvinylidene isomer, for example at least 50%, and as a further example at least 70%. Suitable polysobutenes include those prepared using BF₃ catalysts. The preparation of such polysobutenes in which the methylvinylidene isomer comprises a high percentage of the total composition is described in U.S. Pat. Nos. 4,152,499 and 4,605,808.

[0064] The Mannich detergent may be made from a high molecular weight alkylphenol or alkylkerosol. However, other phenolic compounds may be used including high molecular weight alkyl-substituted derivatives of resorcinol, hydroquinone, catechol, hydroxypiphenol, benzylphenol, phenethylphenol, naphthol, tolylnaphthol, among others. In the preparation of the Mannich detergents are the polylalkylphenol and polylalkylkerosol reactants, e.g., polylpropylphenol, polybutylphenol, polypropylkerosol and polylbutylkerosol, wherein the alkyl group has a number average molecular weight of about 500 to about 2100, and as another example, the alkyl group is a polybutyl group derived from polysobutene.
ethylene having a number average molecular weight in the range of about 700 to about 1300.

A suitable configuration of the high molecular weight alkyl-substituted hydroxycaromatic compound is that of a para-substituted mono-alkylphenol or a para-substituted mono-alkyl ortho-cresol. However, any hydroxycaromatic compound readily reactive in the Mannich condensation reaction may be employed. Thus, Mannich products made from hydroxycaromatic compounds having only one ring alkyl substituent, or two or more ring alkyl substituents are suitable. The long chain alkyl substituents may contain some residual unsaturation, but in general, are substantially saturated alkyl groups.

Representative amine reactants include, but are not limited to, alkylene polyamines having at least one suitably reactive primary or secondary amino group in the molecule. Other substituents such as hydroxyl, cyano, amido, etc., can be present in the polyamine. In an embodiment, the alkylene polyamine is a polyethylene polyamine. Suitable alkylene polyamine reactants include ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, and mixtures of such amines having nitrogen contents corresponding to alkylene polyamines of the formula \( H_2N-(A-NH-)_nH \), where \( A \) is divalent ethylene or propylene and \( n \) is an integer of from 1 to 10, or as another example, from 1 to 4. The alkylene polyamines may be obtained by the reaction of ammonia and dihalo alkanes, such as dichloro alkanes.

The amine may also be an aliphatic diamine having one primary or secondary amino group and at least one tertiary amino group in the molecule. Examples of suitable polyamines include \( N,N,N',N' \)-tetraalklyldialkylentriamines (two terminal tertiary amino groups and one central secondary amino group), \( N,N,N',N' \)-tetraalklylalkylentetramines (one terminal tertiary amino group, two internal tertiary amino groups and one terminal primary amino group), \( N,N,N',N' \)-pentalklylalkylentetramines (one terminal tertiary amino group and one terminal primary amino group), \( N,N' \)-di(hydroxy)alkyl-alpha, omega-alkylenediamines (one terminal tertiary amino group and one terminal primary amino group), \( N,N',N' \)-tri(hydroxy)alkyl-alpha, omega-alkylenediamines (one terminal tertiary amino group and one terminal secondary amino group), tris(dialkylenoalkyl)aminoalkylmethanes (three terminal tertiary amino groups and one terminal primary amino group), and similar compounds wherein the alkyl groups are the same or different and typically contain no more than about 12 carbon atoms each, and which may contain from 1 to 4 carbon atoms each. These alkyl groups may be methyl and/or ethyl groups. Suitable polyamine reactants are \( N,N \)-dialkyl-alpha, omega-alkylenediamine, such as those having from 3 to about 6 carbon atoms in the alkylene group and from 1 to about 12 carbon atoms in each of the alkyl groups, which may be the same but which can be different. Suitable examples include \( N,N \)-dimethyl-1,3-propanediamine and \( N \)-methylpiperazine.

Examples of polyamines having one reactive primary or secondary amino group that can participate in the Mannich condensation reaction, and at least one sterically hindered amino group that cannot participate directly in the Mannich condensation reaction to any appreciable extent include \( N \)-(tert-butyl)-1,3-propanediamine, \( N \)-neopentyl-1,3-propanediamine, \( N \)-(tert-butyl)-1-methyl-1,2-ethenediamine, \( N \)-(tert-butyl)-1-methyl-1,3-propanediamine, and 3,5-di(tert-butyl)aminoethylpiperazine.

Representative aldehydes for use in the preparation of the Mannich base products include the aliphatic aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, caproaldehyde, heptaldehyde, stearaldehyde. Aromatic aldehydes which may be used include benzaldehyde and salicylaldehyde. Illustrative hetero cyclic aldehydes for use herein are furfural and thiophene aldehyde, etc. Also useful are formyl aldehyde-formaldehyde, or aqueous formaldehyde solutions such as formalin.

Suitable Mannich base detergents may include those detergents taught in U.S. Pat. Nos. 4,231,759; 5,514,190; 5,634,951; 5,697,988; 5,725,612; and 5,876,468, the disclosures of which are incorporated herein by reference.

Carriers

In some embodiments, the additive concentrates may comprise a fuel soluble carrier. Such carriers may be of various types, such as liquids or solids, e.g., waxes. Examples of liquid carriers include, but are not limited to, mineral oil and oxygenates, such as liquid polyalkoxyxylated ethers (also known as polyalkylglycol ethers or polyalkylene ethers), liquid polyalkoxyxylated phenols, liquid polyalkoxyxylated esters, liquid polyalkoxyxylated amines, and mixtures thereof. Examples of the oxygenate carriers may be found in U.S. Pat. No. 5,752,989, issued May 19, 1998 to Henly et al., the description of which carriers is herein incorporated by reference in its entirety. Additional examples of oxygenate carriers include alkyl-substituted aryl polyalkoxylates described in U.S. Patent Publication No. 2003/0130157, published Jul. 17, 2003 to Colacei et al., the description of which is herein incorporated by reference in its entirety.

Suitable carriers can be of various types, such as for example liquid poly-alpha-olefin oligomers, mineral oils, liquid poly(oxyalkylene) compounds, liquid alcohol or polyols, polyalkenes, liquid esters, and similar liquid carriers. Mixtures of two or more such carriers can be employed.

Suitable liquid carriers may include 1) a mineral oil or a blend of mineral oils that have a viscosity index of less than about 120, 2) or one or more poly-alpha-olefin oligomers, 3) one or more poly(oxyalkylene) compounds having an average molecular weight in the range of about 500 to about 3000, 4) polyalkenes, 5) polyalkyl-substituted hydroxyxaromatic compounds, or 6) mixtures thereof. The mineral oil carrier fluids that can be used include paraffinic, naphthenic, and asphaltic oils, and can be derived from various petroleum crude oils and processed in any suitable manner. For example, the mineral oils may be solvent extracted or hydroprocessed oils. Reclaimed mineral oils can also be used. The mineral oil used may have a viscosity at 40°C of less than about 1600 SUS, and as another example between about 300 and 1500 SUS at 40°C. Paraffinic mineral oils may have viscosities at 40°C in the range of about 475 SUS to about 700 SUS. In some embodiments, the mineral oil may have a viscosity index of less than about 100, as a further example, less than about 70, or, as an even further example, in the range of from about 30 to about 60.

When the carrier fluids are used in combination with the amine detergents, the ratio (wt/wt) of detergent to carrier fluid(s) is typically in the range of from 1:0.1 to 1:3.

In other aspects, compositions of the present application may not contain a carrier. For example, some compositions of the present application may not contain mineral oil or oxygenates, such as those oxygenates described above.

Ignition Accelerators

In some aspects of the disclosed embodiments, organic nitrate ignition accelerators that include aliphatic or cycloaliphatic nitrate in which the aliphatic or cycloaliphatic
group is saturated, and that contain up to about 12 carbons may be used. Examples of organic nitrate ignition accelerators that may be used are methyl nitrate, ethyl nitrate, propyl nitrate, isopropyl nitrate, allyl nitrate, butyl nitrate, isobutyl nitrate, sec-butyl nitrate, tert-butyl nitrate, amyl nitrate, isomyl nitrate, 2-ethyl nitrate, 3-ethyl nitrate, hexyl nitrate, heptyl nitrate, 2-heptyl nitrate, octyl nitrate, 2-ethylhexyl nitrate, nonyl nitrate, decyl nitrate, undecyl nitrate, dodecyl nitrate, cyclopentyl nitrate, cyclohexyl nitrate, methylcyclohexyl nitrate, cyclooctodicycyl nitrate, 2-ethoxyethyl nitrate, 2-(2-ethoxyethoxy)ethyl nitrate, tetrahydrofuran nitrate, and the like. Mixtures of such materials may also be used.

Metal Deactivators

Examples of suitable optional metal deactivators useful in the compositions of the present application are disclosed in U.S. Pat. No. 4,482,357, issued Nov. 13, 1984, the disclosure of which is herein incorporated by reference in its entirety. Such metal deactivators include, for example, salicyldieneaminophenol, disalicyldiene ethylenediamine, disalicyldiene propylenediamine, and N,N′-disalicyldiene-1,2-diaminopropane.

Manganese Tricarbonyl Compounds

Suitable optional cyclomatic manganese tricarbonyl compounds which may be employed in the compositions of the present application include, for example, cyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese tricarbonyl, indenyl manganese tricarbonyl, and ethylcyclopentadienyl manganese tricarbonyl. Yet other examples of suitable cyclomatic manganese tricarbonyl compounds are disclosed in U.S. Pat. No. 5,575,823, issued Nov. 19, 1996, and U.S. Pat. No. 3,015,668, issued Jan. 2, 1962, both of which disclosures are herein incorporated by reference in their entirety.

Base Fuel

The base fuels suitable for use in formulating the fuel compositions of embodiments described herein may include any base fuels suitable for use in the operation of direct injection engines such as leaded or unleaded motor gasolines, and so-called reformulated gasolines which typically contain both hydrocarbons of the gasoline boiling range and fuel-soluble oxygenated blending agents ("oxygenates"), such as alcohols, ethers, and other suitable oxygen-containing organic compounds. The fuel may be a mixture of hydrocarbons boiling in the gasoline boiling range. The fuel may consist of straight chain or branch chain paraffins, cycloparaffins, olefins, aromatic hydrocarbons, or any mixture of these. The fuel may be a gasoline derived from straight run naphtha, polymer gasoline, natural gasoline or from catalytically reformed stocks boiling in the range from about 80 to about 450° F. The octane level of the gasoline is not critical and any conventional gasoline may be employed. In embodiments where the fuel comprises a diesel fuel, the diesel fuel may be applicable to the operation of both stationary diesel engines (e.g., engines used in electrical power generation installations, in pumping stations, etc.) and ambulatory diesel engines (e.g., engines used as prime movers in automobiles, trucks, road-grading equipment, military vehicles, etc.).

Suitable fuels may include any known hydrocarbon fuel or mixture thereof. Suitable fuels include, but are not limited to, any and all middle distillate fuels, diesel fuels, gasolines, biorenewable fuels, biodiesel fuels, gas-to-liquid (GTL) fuels, jet fuels, aviation fuels, marine fuels, burner fuels, alcohols, ethers, esters, kerosene, home heating oils (for example, home heating oil no. 6), low sulfur fuels, synthetic fuels, such as Fischer-Tropsch fuels, liquid petroleum gas, bunker oils, coal to liquid (CTL) fuels, biomass to liquid (BTL) fuels, high asphaltene fuels, fuels derived from coal (natural, cleaned, and pet coke), genetically engineered biofuels and crops and extracts therefrom, natural gas, a Group I base oil, a Group II base oil, a Group III base oil, and a Group IV base oil. "Biorenewable fuels" as used herein is understood to mean any fuel which is derived from resources other than petroleum. Such resources include, but are not limited to, corn, maize, soybeans and other crops; grasses, such as switchgrass, miscanthus, and hybrid grasses; algae, seaweed, vegetable oils; natural fats; and mixtures thereof. In an aspect, the biorenewable fuel may comprise monohydroxy alcohols, such as those comprising from 1 to about 5 carbon atoms. Non-limiting examples of suitable monohydroxy alcohols include methanol, ethanol, bioethanol, biobutanol, propanol, n-butanol, isobutanol, t-butyl alcohol, amyl alcohol, and isoamyl alcohol.

Suitable oxygenates include methanol, ethanol, iso-propanol, 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 30% by volume, and in an amount that provides an oxygen content in the overall fuel in the range of about 0.5 to about 5 percent by volume.

When formulating the fuel compositions of this application, the additives may be employed in amounts sufficient to remove, reduce, inhibit, and/or prevent deposit formation in an injection engine. In some aspects, the fuels may contain minor amounts of the above described hexahydro triazine compound that removes, reduces, inhibits, or prevents the formation of deposit, for example injector deposits. For example, the fuels of this application may contain, on an active ingredient basis, an amount of the hexahydro triazine compound in the range of about 1 ppm to about 100 ppm in a fuel. As a further example, a fuel may contain from about 5 ppm to about 20 ppm of the hexahydro triazine.

The additives of the present application, including the hexahydro triazine compound described above, and optional additives used in formulating the fuels of this disclosure may be blended into the base fuel individually or in various sub-combinations. In some embodiments, the additive components of the present application may be blended into the fuel concurrently using an additive concentrate, as this takes advantage of the mutual compatibility and convenience afforded by the combination of ingredients when in the form of an additive concentrate. Also, use of a concentrate may reduce blending time and lessen the possibility of blending errors. In some embodiments, the hexahydro triazine may be combined with one or more additives, such as a dispersant, to form a top treat. The top treat may be added directly to a fuel that either does or does not contain a separate additive concentrate. The top treat or after-market additive may be added to a fuel in the vehicle or to a fuel storage facility.

Accordingly, aspects of the present application are directed to methods for removing, reducing, inhibiting, and/or preventing the occurrence of and/or amount of injector deposits in an injection engine. In another aspect, the improvements may also be observed in direct fuel injectors. In some aspects, the methods comprise injecting a hydrocarbon-based compression ignition fuel comprising the hexahydro triazine compound additive of the present application,
through the injectors of the engine. In some aspects, the method may also comprise mixing into the fuel at least one of the optional additional ingredients described above. In some embodiments the additive concentrate may be provided as a top treat, or after-market additive package, that may be added to a fuel in the vehicle, at a fuel storage facility, to a fuel storage receptacle, or the like.

EXAMPLES

[0085] The following examples are illustrative of exemplary embodiments of the disclosure. In these examples as well as elsewhere in this application, all parts and percentages are by weight unless otherwise indicated. It is intended that these examples are being presented for the purpose of illustration only and are not intended to limit the scope of the invention disclosed herein.

[0086] Inventive and comparative samples were prepared and tested to demonstrate the effectiveness of the inventive additive concentrations in reducing deposits in injection versus unadditized fuel (Test 1), versus fuel containing a dispersant package (Test 2), and versus a comparative triazine (Test 4). As shown in Test 1, a base fuel without any additive caused injector plugging at an average of 7.5%. A fluid containing only an additive package at 292 ppm (wt) resulted in injector plugging of 9%, as shown in Test 2. However, when the presently disclosed chemical structures were added at only 11.4 ppm (wt) on top of the additive package in the fuel, injector plugging dropped to 0.75% and 0.24%, as shown in Tests 3 and 5, respectively. A comparative chemical structure added to the fuel at the same rate led to injector plugging of 1.93%, which was less effective than the presently disclosed chemical structures.

[0090] The comparative example demonstrates less than desirable performance when relatively hindered triazines, with branching only one carbon away from the ring-nitrogen, are used. That feature appears to negatively impact performance, as the nitrogen of the ring is not exposed and therefore less available to keep clean or clean injectors. Further, it seems that the hindrance of the triazine ring overrides the polarity effect.

<table>
<thead>
<tr>
<th>Test</th>
<th>Additive package*</th>
<th>PPM (wt) additive package</th>
<th>Chemical Structure</th>
<th>Chemical name</th>
<th>PPM (wt) chemical structure</th>
<th>Plugging average, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>no</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.5</td>
</tr>
<tr>
<td>2</td>
<td>Yes</td>
<td>292</td>
<td>Structure I</td>
<td>Dodecyl hexahydrotriazine</td>
<td>11.4</td>
<td>0.75</td>
</tr>
<tr>
<td>3</td>
<td>Yes</td>
<td>292</td>
<td>Structure I</td>
<td>Ethyl-hexyl hexahydrotriazine</td>
<td>11.4</td>
<td>1.93</td>
</tr>
<tr>
<td>4</td>
<td>Yes</td>
<td>292</td>
<td>Structure II</td>
<td>Octyl hexahydrotriazine</td>
<td>11.4</td>
<td>0.24</td>
</tr>
</tbody>
</table>

*Additive package is a dibutyl amine polyisobutylene cresol Mannich

[0096] 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 dispersant" includes one, two, or more different dispersants. 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.

[0097] 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 can vary depending upon the desired properties sought to be obtained by the present disclosure. 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.

[0098] While particular embodiments have been described, alternatives, modifications, variations, improvements, and substantial equivalents that are or can be presently unforeseen can arise to applicants or others skilled in the art. Accordingly, the appended claims as filed and as they can be amended are intended to embrace all such alternatives, modifications, variations, improvements, and substantial equivalents.
What is claimed is:
1. A fuel suitable for use in a fuel injection engine comprising:
   a major amount of a fuel; and
   a minor amount of an additive concentrate comprising a
   hexahydro triazine.
2. The fuel of claim 1, wherein an alkyl group is attached to
   at least one nitrogen in the hexahydro triazine ring.
3. The fuel of claim 2, wherein the alkyl group is linear.
4. The fuel of claim 2, wherein the alkyl group is branched at
   a position after the beta position to the at least one nitrogen.
5. The fuel of claim 1, wherein the hexahydro triazine
   comprises the product combining, mixing, admixing, or con-
   tacting one or more primary amine(s) and a formaldehyde.
6. The fuel of claim 1, wherein the hexahydro triazine has
   a molecular weight of from about 100 to about 700.
7. The fuel of claim 1, wherein the hexahydro triazine has
   a molecular weight of from about 400 to about 600.
8. The fuel of claim 1, wherein the hexahydro triazine is
   selected from the group consisting of at least one of dodecyl-
   amine hexahydro triazine and octyl hexahydro triazine.
9. The fuel of claim 1, wherein the hexahydro triazine is
   selected from the group consisting of at least one of the
   following structures:
10. The fuel of claim 1, wherein the hexahydro triazine is present in an amount sufficient to remove and/or prevent the occurrence of deposits in a fuel injector of an injection engine.

11. The fuel of claim 1, wherein the hexahydro triazine is present in the fuel in an amount from about 1 ppm to about 100 ppm.

12. The fuel of claim 1, wherein the hexahydro triazine is present in the fuel in an amount from about 5 ppm to about 20 ppm.

13. The fuel of claim 1, wherein the additive concentrate further comprises a dispersant/detergent.

14. The fuel of claim 13, wherein the dispersant/detergent comprises at least one of an amine dispersant/detergent, an alkenyl succinimide dispersant, an alkenyl succinic acid ester dispersant, an alkenyl succinic ester-amide dispersant, a poly-isobutylene amine dispersant, or a Mannich base dispersant.

15. The fuel of claim 1, wherein the fuel is selected from the group consisting of middle distillate fuels, diesel fuels, gaso-

16. A method for removing and/or preventing the occurrence of deposits in a fuel injector of a fuel injection engine comprising:

- adding to and operating in an injection engine having fuel injectors a fuel composition comprising (a) a major amount of fuel and (b) a minor amount of an additive concentrate comprising a hexahydro triazine.

17. The method of claim 16, wherein an alkyl group is attached to at least one nitrogen in the hexahydro triazine ring.

18. The method of claim 17, wherein the alkyl group is linear.

19. The method of claim 17, wherein the alkyl group is branched at a position after the beta position to the at least one nitrogen.

20. The method of claim 16, wherein the hexahydro triazine comprises the product combining, mixing, admixing, or contacting one or more primary amine(s) and a formaldehyde.

21. The method of claim 16, wherein the hexahydro triazine has a molecular weight of from about 100 to about 700.

22. The method of claim 16, wherein the hexahydro triazine has a molecular weight of from about 400 to about 600.

23. The method of claim 16, wherein the hexahydro triazine is selected from the group consisting of at least one of dodecylamine hexahydro triazine and octyl hexahydro triazine.

24. The fuel of claim 16, wherein the hexahydro triazine is selected from the group consisting of at least one of the following structures:
25. The method of claim 16, wherein the hexahydro triazine is present in an amount sufficient to remove and/or prevent the occurrence of deposits in a fuel injector of an injection engine.

26. The method of claim 16, wherein the hexahydro triazine is present in the fuel in an amount from about 1 ppm to about 100 ppm.

27. The method of claim 16, wherein the hexahydro triazine is present in the fuel in an amount from about 5 ppm to about 20 ppm.

28. The method of claim 16, wherein the additive concentrate further comprises a dispersant/detergent.

29. The method of claim 16, wherein the dispersant/detergent comprises at least one of an amine dispersant/detergent, an alkyl succinimide dispersant, an alkyl succinic acid ester dispersant, an alkyl succinic ester-amide dispersant, polyisobutylene amine dispersant, or a Mannich base dispersant.

30. The method of claim 16, wherein the fuel is selected from the group consisting of middle distillate fuels, diesel fuels, gasolines, biorenewable fuels, biodiesel fuels, gas-to-liquid (GTL) fuels, jet fuels, aviation fuels, marine fuels, burner fuels, alcohols, ethers, esters, kerosene, home heating oils (for example, home heating oil no. 6), low sulfur fuels, synthetic fuels, such as Fischer-Tropsch fuels, liquid petroleum gas, bunker oils, coal to liquid (CTL) fuels, biomass to liquid (HTL) fuels, high asphaltene fuels, fuels derived from coal (natural, cleaned, and pet coke), genetically engineered biofuels and crops and extracts therefrom, natural gas, a Group I base oil, a Group II base oil, a Group III base oil, and a Group IV base oil.

31. The method of claim 16, wherein the injection engine comprises a direct injection engine.

32. A fuel additive concentrate for removing and/or preventing the occurrence of deposits in a fuel injector of an injection engine comprising a hexahydro triazine.

33. The additive concentrate of claim 32, wherein the hexahydro-triazine is a member of the group consisting of octyl hexahydro triazine and dodecylamine hexahydro triazine.

34. The additive concentrate of claim 33, wherein the hexahydro-triazine is selected from the group consisting of at least one of the following structures: