

GASOLINE ADDITIVE COMPOSITION FOR IMPROVED ENGINE PERFORMANCE

TECHNICAL FIELD

[0001] This disclosure is directed to fuel additives for spark-ignition engines providing enhanced engine, intake valve, and/or injector performance, to fuel compositions including such additives, and to methods for using such fuel additives in a fuel composition for improved performance.

BACKGROUND

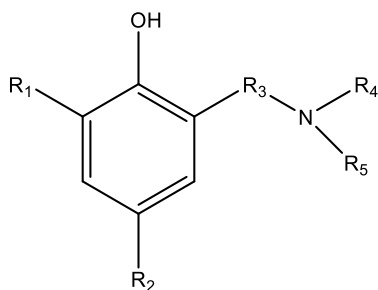
[0002] Fuel compositions for vehicles are continually being improved to enhance various properties of the fuels in order to accommodate their use in newer, more advanced engines including both gasoline port fuel injected engines as well as gasoline direct injected engines. Often, improvements in fuel compositions center around improved fuel additives and other components used in the fuel. For example, friction modifiers may be added to fuel to reduce friction and wear in the fuel delivery systems of an engine. Other additives may be included to reduce the corrosion potential of the fuel or to improve the conductivity properties. Still other additives may be blended with the fuel to improve fuel economy. Engine and fuel delivery system deposits represent another concern with modern combustion engines, and therefore other fuel additives often include various deposit control additives to control and/or mitigate engine deposit problems. Thus, fuel compositions typically include a complex mixture of additives.

[0003] However, there remain challenges when attempting to balance such a complex assortment of additives. For example, some of the conventional fuel additives may be beneficial for one characteristic or one type of engine, but at the same time be detrimental to another characteristic of the fuel. In some instances, fuel additives effective in gasoline port fuel injection engines (PFI) do not necessarily provide comparable performance in gasoline direct injection engines (GDI) and vice versa. In yet other circumstances, fuel additives often require an unreasonably high treat rate to achieve desired effects, which tends to place undesirable limits on the available amounts of other additives in the fuel composition. Yet other fuel additives tend to be expensive and/or difficult to manufacture or incorporate in fuels.

SUMMARY

[0004] In one embodiment or approach, a fuel additive or fuel additive package for a spark-ignition engine is described herein to provide improved engine performance and includes a Mannich detergent including the reaction product of a hydrocarbyl-substituted phenol or cresol, one or more aldehydes, and one or more amines; a succinimide detergent prepared by reacting a hydrocarbyl-substituted succinic acylating agent with an amine, polyamine, or alkyl amine having one or more primary, secondary, or tertiary amino groups; and wherein a weight ratio of the Mannich detergent to the succinimide detergent is from about 15:1 to about 30:1. As discussed more herein, such weight ratios provide a synergistic effect with improved engine and/or injector performance in both port fuel injection (PFI) engines as well as gasoline direct injection (GDI) engines.

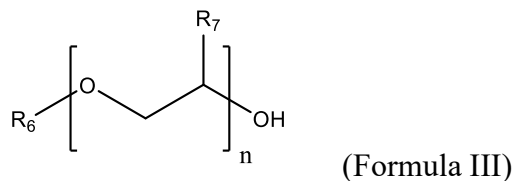
[0005] In other embodiments or approaches, the fuel additive of the previous paragraph may include one or more optional features or embodiments in any combination. The optional features or embodiments may include one or more of the following: wherein the weight ratio of the Mannich detergent to the succinimide detergent is from about 20:1 to about 30:1; and/or wherein the Mannich detergent has the structure of Formula I:



(Formula I)

wherein R₁ of Formula I is hydrogen or a C1 to C4 alkyl group, R₂ of Formula I is a hydrocarbyl group having a molecular weight of about 500 to about 3000, R₃ of Formula I is a C1 to C4 alkylene or alkenyl group (preferably a C1 group), and R₄ and R₅ of Formula I are, independently, hydrogen, a linear or branched C1 to C12 alkyl group, or a mono or di(C1 to C4)alkyl amino C1-C12 alkyl group; and/or wherein R₂ of Formula I is polyisobutenyl having a number average molecular weight of about 500 to about 1500; and/or wherein the succinimide detergent is a hydrocarbyl substituted mono-succinimide detergent, a hydrocarbyl substituted bis-succinimide detergent, or a combination thereof; and/or wherein the hydrocarbyl-substituted succinic acylating agent is a hydrocarbyl-substituted succinic anhydride, wherein the

hydrocarbonyl group has a molecular weight of about 450 to about 3000, and wherein a molar ratio of the hydrocarbonyl-substituted succinic anhydride to the amine, polyamine, or alkyl amine is from about 0.5:1 to about 2:1; and/or wherein the hydrocarbonyl-substituted succinic anhydride is polyisobutylene substituted succinic anhydride, and wherein the polyisobutylene has a number average molecular weight of about 500 to about 1200 as measured by GPC using polystyrene as reference; and/or wherein the amine, polyamine, or alkyl amine is tetraethylene pentamine (TEPA), triethylene tetraamine (TETA), or a polyamine or alkyl amine having the formula $H_2N-((CHR_{20}-(CH_2)_q-NH)_r-H$, wherein R_{20} thereof is hydrogen or an alkyl group having from 1 to 4 carbon atoms, q is an integer of from 1 to 4 and r is an integer of from 1 to 6, and mixtures thereof; and/or wherein the amine, polyamine, or alkyl amine is tetraethylene pentamine (TEPA); and/or further comprising an alkoxyated alcohol, and wherein a weight ratio of the alkoxyated alcohol to the Mannich detergent is about 1.0 or less (preferably 0.8 or less, 0.6 or less, or 0.5 or less); and/or wherein the alkoxyated alcohol is a polyether prepared by reacting an alkyl alcohol or an alkylphenol with an alkylene oxide selected from ethylene oxide, propylene oxide, butylene oxide, copolymers thereof, or combinations thereof; and/or wherein the alkoxyated alcohol is a polyether having the structure of Formula III:



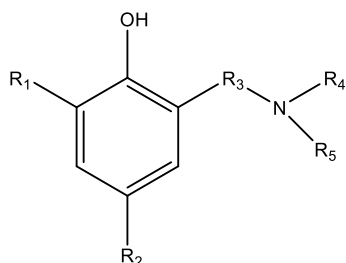
wherein R_6 of Formula III is an aryl group or a linear, branched, or cyclic aliphatic group having 5 to 50 carbons, R_7 of Formula III is a C1 to C4 alkyl group, and n is an integer from 5 to 100; and/or wherein the fuel additive includes about 20 to about 60 weight percent of the Mannich detergent, about 0.5 to about 10 weight percent of the succinimide detergent, and about 5 to about 30 weight percent of an alkoxyated alcohol.

[0006] In another approach or embodiment, a gasoline fuel composition providing improved engine and/or injector performance in both port fuel injection (PFI) engines as well as gasoline direct injection (GDI) engines is described herein. The gasoline fuel composition includes about 15 to about 300 ppmw of a Mannich detergent including the reaction product of a hydrocarbonyl-substituted phenol or cresol, one or more aldehydes, and one or more amines; about 0.5 to about 20 ppmw of a succinimide detergent prepared by reacting a hydrocarbonyl-substituted succinic acylating agent with an amine, polyamine, or alkyl amine having one or more primary,

secondary, or tertiary amino groups; wherein a weight ratio of the Mannich detergent to the succinimide detergent is from about 15:1 to about 30:1; and about 5 to about 150 ppmw of an alkoxyated alcohol. In further embodiments, the gasoline fuel composition may also include any of the optional features or embodiments as described above with respect to the fuel additive.

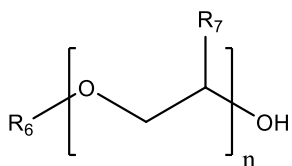
[0007] In yet other approaches or embodiments, a method of reducing deposits in a gasoline engine is described herein. The method includes operating a gasoline engine on a fuel composition containing a major amount of a gasoline fuel and a minor amount of a fuel additive by injecting the gasoline fuel through one or more injectors; wherein the fuel additive includes (i) a Mannich detergent including the reaction product of a hydrocarbyl-substituted phenol or cresol, one or more aldehydes, and one or more amines; (ii) a succinimide detergent prepared by reacting a hydrocarbyl-substituted succinic acylating agent with an amine, polyamine, or alkyl amine having one or more primary, secondary, or tertiary amino groups; and (iii) wherein the fuel additive has a weight ratio of the Mannich detergent to the succinimide detergent of about 15:1 to about 30:1; and wherein the fuel additive reduces deposits in the gasoline engine.

[0008] In other embodiments or approaches, the method described in the previous paragraph may include one or more optional features, method steps, or embodiments in any combination. The optional features, steps, or embodiments may include one or more of the following: wherein the fuel additive reduces deposits in a port fuel injection (PFI) engine, a gasoline direct injection (GDI) engine, or both; and/or wherein the reduced deposits are reduced injector deposits measured by one of injector pulse width, injection duration, injector flow, or combinations thereof; and/or wherein the fuel additive reduces deposits when sprayed from an injector configured to spray droplets of about 10 to about 30 microns, about 120 to about 200 microns, or both; and/or wherein the weight ratio of the Mannich detergent to the succinimide detergent is from about 20:1 to about 30:1; and/or wherein the Mannich detergent has the structure of Formula I:



(Formula I)

wherein one of R₁ and R₂ of Formula I is hydrogen or a C1 to C4 alkyl group, the other of R₁ and R₂ is a hydrocarbyl group having a molecular weight of about 500 to about 3000, R₃ of Formula I is a C1 to C4 alkylene or alkenyl group, and R₄ and R₅ of Formula I are, independently, hydrogen, a C1 to C12 alkyl group, or a mono or di(C1 to C4)alkyl amino C1-C12 alkyl group; and/or wherein R₂ of Formula I is polyisobutenyl having a number average molecular weight of about 500 to about 1500; and/or wherein the succinimide detergent is a hydrocarbyl substituted mono-succinimide detergent, a hydrocarbyl substituted bis-succinimide detergent, or a combination thereof; and/or wherein the hydrocarbyl-substituted succinic acylating agent is a hydrocarbyl-substituted succinic anhydride, wherein the hydrocarbyl group has a molecular weight of about 450 to about 3000, and wherein a molar ratio of the hydrocarbyl-substituted succinic anhydride to the amine, polyamine, or alkyl amine is from about 0.5:1 to about 2:1; and/or wherein the hydrocarbyl-substituted succinic anhydride is polyisobutylene substituted succinic anhydride, and wherein the polyisobutylene has a number average molecular weight of about 500 to about 1200 as measured by GPC using polystyrene as reference; and/or wherein the amine, polyamine, or alkyl amine is tetraethylene pentamine (TEPA), triethylenetetraamine (TETA), or a polyamine or alkyl amine having the formula H₂N-((CHR₂₀-(CH₂)_q-NH)_r-H, wherein R₂₀ thereof is hydrogen or an alkyl group having from 1 to 4 carbon atoms, q is an integer of from 1 to 4 and r is an integer of from 1 to 6, and mixtures thereof; and/or wherein the amine, polyamine, or alkyl amine is tetraethylene pentamine (TEPA); and/or further comprising an alkoxyated alcohol and wherein a weight ratio of the alkoxyated alcohol to the Mannich detergent is about 1.0 or less; and/or wherein the alkoxyated alcohol is a polyether prepared by reacting an alkyl alcohol or an alkylphenol with an alkylene oxide selected from ethylene oxide, propylene oxide, butylene oxide, copolymers thereof, or combinations thereof; and/or wherein the alkoxyated alcohol is a polyether having the structure of Formula III:



(Formula III)

wherein R₆ of Formula III is an aryl group or a linear, branched, or cyclic aliphatic group having 5 to 50 carbons, R₇ of Formula III is a C1 to C4 alkyl group, and n is an integer from 5 to 100; and/or wherein the fuel additive includes about 20 to about 60 weight percent of the Mannich

detergent, about 0.5 to about 10 weight percent of the succinimide detergent, and about 5 to about 30 weight percent of the alkoxylated alcohol.

[0009] In yet other approaches or embodiments, the use of a fuel additive package as described by any embodiment herein or the use of a gasoline fuel as described by any embodiment of the fuel composition herein for improving the injector performance of a port fuel injection (PFI) engine, a gasoline direct injection (GDI) engine, or both the PFI and GDI engine.

[00010] In any embodiment of the fuel additive package, the fuel, the method, or the use herein, the fuel additive package of this disclosure may be free of quaternary ammonium salt detergents, and preferably, free of quaternary ammonium internal salt detergents that are obtained from amines or polyamines and substantially devoid of any free anion species. In this context, free of means less than 0.5 ppmw, less than 0.1 ppmw, less than 0.05 ppmw or, preferably, none.

BRIEF DESCRIPTION OF DRAWING FIGURES

[00011] FIG. 1 is a graph showing GDI dirty-up (DU) and clean-up (CU) of Comparative and Inventive fuel additives; and

[00012] FIG. 2 is a graph showing GDI dirty-up (DU) and clean-up (CU) of Comparative and Inventive fuel additives.

DETAILED DESCRIPTION

[00013] The present disclosure provides fuel additives including combinations of Mannich detergent(s) and succinimide detergent(s) discovered effective in certain weight ratios to provide improved engine and/or injector performance in both port fuel injection (PFI) engines as well as gasoline direct injection (GDI) engines. The fuel additives, in some approaches, may also include alkoxylated alcohols and, when included, certain ratios of the alkoxylated alcohol to the Mannich detergent. Also provided herein are fuel compositions including the novel fuel additive combinations and methods of using or combusting a fuel including the fuel additive combinations herein to achieve improved engine, intake valve, and/or injector performance. As noted more below, the fuel additives herein include a synergistic combination of Mannich detergent(s) and succinimide detergent(s) when used in a weight ratio of the Mannich detergent to the succinimide detergent of about 15:1 to about 30:1. Mannich detergents alone do not

provide any clean-up performance in GDI engines, but surprisingly achieve improved clean-up when combined in certain ratios with succinimide detergents.

[00014] In aspects or embodiments of this disclosure, improved engine, intake valve, and/or injector performance of the fuel additive combinations herein may include one or more of controlling or reducing fuel injector deposits, controlling or reducing intake valve deposits, controlling or reducing combustion chamber deposits and/or controlling or reducing intake valve sticking in PFI engines, GDI engines, or both types of engines. Improved injector performance may also be one or more of improved fuel flow, improved fuel economy, and/or improved engine efficiency as determined via one or more of injector pulse width, injection duration, and/or injector flow.

[00015] Mannich Detergent

[00016] In one aspect, the fuel additives and fuels herein first include one or more Mannich detergent(s). Suitable Mannich detergents include the reaction product(s) of an alkyl-substituted hydroxyaromatic or phenol compound, aldehyde, and amine as discussed more below.

[00017] In one approach, the alkyl substituents of the hydroxyaromatic compound may include long chain hydrocarbyl groups on a benzene ring of the hydroxyaromatic compound and may be derived from an olefin or polyolefin having a number average molecular weight (M_n) from about 500 to about 3000, preferably from about 700 to about 2100, as determined by gel permeation chromatography (GPC) using polystyrene as reference. The polyolefin, in some approaches, may also have a polydispersity (weight average molecular weight/number average molecular weight) of about 1 to about 10 (in other instances, about 1 to about 4 or about 1 to about 2) as determined by GPC using polystyrene as reference.

[00018] The alkylation of the hydroxyaromatic or phenol compound is typically performed in the presence of an alkylating catalyst at a temperature in the range of about 0 to about 200°C, preferably 0 to about 100°C. Acidic catalysts are generally used to promote Friedel-Crafts alkylation. Typical catalysts used in commercial production include sulphuric acid, BF_3 , aluminum phenoxide, methanesulphonic acid, cationic exchange resin, acidic clays and modified zeolites.

[00019] Polyolefins suitable for forming the alkyl-substituted hydroxyaromatic compounds of the Mannich detergents 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 a copolymer molecule contains at least 50% by weight, of butylene and/or isobutylene and/or propylene units. Any comonomers polymerized with propylene or butenes may be aliphatic and can also contain non-aliphatic groups, e.g., styrene, o-methylstyrene, p-methylstyrene, divinyl benzene and the like if needed. Thus, the resulting polymers and copolymers used in forming the alkyl-substituted hydroxyaromatic compounds are substantially aliphatic hydrocarbon polymers.

[00020] Polybutylene is preferred for forming the hydrocarbyl-substituted hydroxyaromatic or phenol compounds herein. 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 polyisobutenes having relatively high proportions of polymer molecules having a terminal vinylidene group are also suitable for use in forming the long chain alkylated phenol reactant. Suitable high-reactivity polyisobutenes include those polyisobutenes that comprise at least about 20% of the more reactive methylvinylidene isomer, preferably at least 50% and more preferably at least 70%. Suitable polyisobutenes include those prepared using BF_3 catalysts. The preparation of such polyisobutenes in which the methylvinylidene isomer comprises a high percentage of the total composition is described in US 4,152,499 and US 4,605,808, which are both incorporated herein by reference.

[00021] The Mannich detergent, in some approaches or embodiments, may be made from an alkylphenol or alkylcresol. However, other phenolic compounds may be used including alkyl-substituted derivatives of resorcinol, hydroquinone, catechol, hydroxydiphenyl, benzylphenol, phenethylphenol, naphthol, tolylnaphthol, among others. Preferred for the preparation of the Mannich detergents are the polyalkylphenol and polyalkylcresol reactants, e.g., polypropyl phenol, polybutylphenol, polypropylcresol and polybutylcresol, wherein the alkyl group has a number average molecular weight of about 500 to about 3000 or about 500 to about 2100 as measured by GPC using polystyrene as reference, while the most preferred alkyl group is a polybutyl group derived from polyisobutylene having a number average molecular weight in the range of about 700 to about 1300 as measured by GPC using polystyrene as reference.

[00022] The preferred configuration of the alkyl-substituted hydroxyaromatic compound is that of a para-substituted mono-alkylphenol or a para-substituted mono-alkyl ortho-cresol. However, any hydroxyaromatic compound readily reactive in the Mannich condensation reaction may be employed. Thus, Mannich products made from hydroxyaromatic compounds having only one ring alkyl substituent, or two or more ring alkyl substituents are suitable for forming this detergent additive. The alkyl substituents may contain some residual unsaturation, but in general, are substantially saturated alkyl groups.

[00023] In approaches or embodiments, representative amine reactants suitable to form the Mannich detergent herein 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 a one embodiment, the alkylene polyamine is a polyethylene polyamine. Suitable alkylene polyamine reactants include ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylene pentamine and mixtures of such amines having nitrogen contents corresponding to alkylene polyamines of the formula $H_2N--(A-NH--)_nH$, where A in this formula is divalent ethylene or propylene and n is an integer of from 1 to 10, preferably 1 to 4. The alkylene polyamines may be obtained by the reaction of ammonia and dihalo alkanes, such as dichloro alkanes.

[00024] 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''-tetraalkyldialkylenetriamines (two terminal tertiary amino groups and one central secondary amino group), N,N,N',N''-tetraalkyltrialkylenetetramines (one terminal tertiary amino group, two internal tertiary amino groups and one terminal primary amino group), N,N,N',N'',N'''-pentaalkyltrialkylenetetramines (one terminal tertiary amino group, two internal tertiary amino groups and one terminal secondary amino group), N,N'-dialkylamine, N,N-dihydroxyalkyl-alpha-, omega-alkylenediamines (one terminal tertiary amino group and one terminal primary amino group), N,N,N'-trihydroxyalkyl-alpha, omega-alkylenediamines (one terminal tertiary amino group and one terminal secondary amino group), tris(dialkylaminoalkyl) 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 preferably contain from 1 to 4 carbon atoms each. Most preferably these alkyl groups are methyl and/or ethyl groups. Preferred

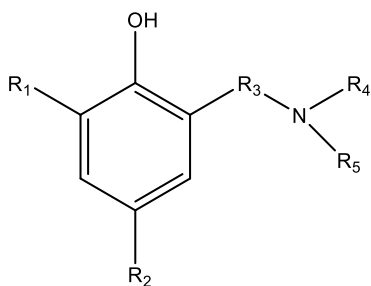
polyamine reactants are N,N-dialkyl-alpha, omega-alkylene diamine, such as those having from 3 to about 6 carbon atoms in the alkylene group and from 1 to about 12 carbon atoms in each of the alkyl groups, which most preferably are the same but which can be different. Exemplary amines may include N,N-dimethyl-1,3-propanediamine and/or N-methyl piperazine.

[00025] 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-propane diamine-, N-(*tert*-butyl)-1-methyl-1,2-ethanediamine, N-(*tert*-butyl)-1-methyl-1,3-propane diamine, and 3,5-di(*tert*-butyl)aminoethylpiperazine.

[00026] In approaches or embodiments, representative aldehydes for use in the preparation of the Mannich detergents herein 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 heterocyclic aldehydes for use herein are furfural and thiophene aldehyde, etc. Also useful are formaldehyde-producing reagents such as paraformaldehyde, or aqueous formaldehyde solutions such as formalin. Most preferred is formaldehyde or formalin.

[00027] The condensation reaction among the alkylphenol, the specified amine(s) and the aldehyde may be conducted at a temperature typically 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 is evolved and can be removed by azeotropic distillation during the course of the reaction. Typically, the Mannich reaction products are formed by reacting the alkyl-substituted hydroxyaromatic compound, the amine and aldehyde in the molar ratio of 1.0:0.5-2.0:1.0-3.0, respectively. Suitable Mannich base detergents include those detergents taught in US 4,231,759; US 5,514,190; US 5,634,951; US 5,697,988; US 5,725,612; and 5,876,468, the disclosures of which are incorporated herein by reference.

[00028] In other approaches or embodiments, suitable Mannich detergents for the fuel additives herein may have a structure of Formula I below:



(Formula I)

wherein one of R₁ and R₂ of Formula I is hydrogen or a C1 to C4 alkyl group, the other of R₁ and R₂ is a hydrocarbyl group having a molecular weight of about 500 to about 3000, R₃ of Formula I is a C1 to C4 alkylene or alkenyl linking group, and R₄ and R₅ of Formula I are, independently, hydrogen, a C1 to C12 alkyl group, or a mono or di(C1 to C4)alkyl amino C1-C12 alkyl group. In one aspect, R₁ of Formula I is hydrogen or a C1 to C4 alkyl group, R₂ of Formula I is a hydrocarbyl group having a molecular weight of about 500 to about 3000 (or about 500 to about 2100, or about 500 to about 1800, or about 500 to about 1500). In another aspect, R₁ of Formula I is hydrogen or a C1 to C4 alkyl group, and R₂ of Formula I is a polyisobutenyl group having a number average molecular weight of about 500 to about 1500.

[00029] A fuel additive or additive package may include about 20 to about 60 weight percent of the above-described Mannich detergent, about 25 to about 50 weight percent of the Mannich detergent, or about 30 to about 45 weight percent of the Mannich detergent (based on the total weight of the active Mannich detergent in the fuel additive). When blended into a gasoline fuel, the fuel composition may include about 15 ppmw to about 300 ppmw of the above-described Mannich detergent, about 25 ppmw to about 155 ppmw, or about 55 ppmw to about 125 ppmw of the Mannich detergent in the fuel composition (active Mannich detergent treat rates). In some embodiments, the fuel additives herein includes a single type of Mannich detergents.

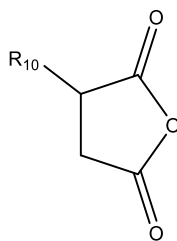
[00030] Succinimide Detergents

[00031] The fuel additives or fuels herein may also include one or more hydrocarbyl-substituted dicarboxylic anhydride derivatives, and preferably, one or more hydrocarbyl-substituted succinimide detergents. In one approach, this additive may be prepared by reacting a hydrocarbyl-substituted succinic acylating agent with an amine, polyamine, or alkyl amine having one or more primary, secondary, or tertiary amino groups. In some embodiments, the hydrocarbyl substituted dicarboxylic anhydride derivative includes hydrocarbyl succinimides, succinamides, succinimide-amides and succinimide-esters. These nitrogen-containing

derivatives of hydrocarbyl succinic acylating agents may be prepared by reacting a hydrocarbyl-substituted succinic acylating agent with an amine, polyamine, or alkyl amine having one or more primary, secondary, or tertiary amino groups. The succinimide detergents may be mono-succinimides, bis-succinimides, or combinations thereof.

[00032] In some approaches or embodiments, the hydrocarbyl substituted dicarboxylic anhydride derivative may include a hydrocarbyl substituent having a molecular weight or a number average molecular weight ranging from about 450 to about 3000 as measured by GPC using polystyrene as reference. The derivative may be selected from a diamide, acid/amide, acid/ester, diacid, amide/ester, diester, and imide. Such derivative may be made from reacting a hydrocarbyl substituted dicarboxylic anhydride with ammonia, a polyamine, or an alkyl amine having one or more primary, secondary, or tertiary amino groups. In some embodiments, the polyamine or alkyl amine may be tetraethylene pentamine (TEPA), triethylenetetramine (TETA), and the like amines. In other approaches, the polyamine or alkyl amine may have the formula $\text{H}_2\text{N}-((\text{CHR}_{20}-\text{(CH}_2)_q-\text{NH})_r-\text{H}$, wherein R_{20} thereof is hydrogen or an alkyl group having from 1 to 4 carbon atoms, q is an integer of from 1 to 4 and r is an integer of from 1 to 6, and mixtures thereof. In other approaches, a molar ratio of the hydrocarbyl substituted dicarboxylic anhydride reacted with the ammonia, polyamine, or alkyl amine may be from about 0.5:1 to about 2:1, in other approaches about 1:1 to about 2:1, or in other approaches, about 1:1 to about 1.6:1.

[00033] In other approaches, the hydrocarbyl substituted dicarboxylic anhydride may be a hydrocarbyl carbonyl compound of the Formula IV:



(Formula IV)

where R_{10} of Formula IV is a hydrocarbyl group derived from a polyolefin. In some aspects, the hydrocarbyl carbonyl compound may be a polyalkylene succinic anhydride reactant wherein R_{10} is a hydrocarbyl moiety, such as for example, a polyalkenyl radical having a number average molecular weight of from about 450 to about 3000 as measured by GPC using polystyrene as reference. For example, the number average molecular weight of R_{10} may range from about 600

to about 2500, or from about 700 to about 1500 or about 850 to about 1000, as measured by GPC using polystyrene as reference. A particularly useful R_{10} of Formula IV has a number average molecular weight of about 900 to about 1000 Daltons (as measured by GPC using polystyrene as reference) and comprises polyisobutylene. Unless indicated otherwise, molecular weights in the present specification are number average molecular weights as measured by GPC using polystyrene as reference.

[00034] The R_{10} hydrocarbyl moiety of Formula IV may include one or more polymer units chosen from linear or branched alkenyl units. In some aspects, the alkenyl units may have from about 2 to about 10 carbon atoms. For example, the polyalkenyl radical may comprise one or more linear or branched polymer units chosen from ethylene radicals, propylene radicals, butylene radicals, pentene radicals, hexene radicals, octene radicals and decene radicals. In some aspects, the R_{10} polyalkenyl radical may be in the form of, for example, a homopolymer, copolymer or terpolymer. In one aspect, the polyalkenyl radical is isobutylene. For example, the polyalkenyl radical may be a homopolymer of polyisobutylene comprising from about 10 to about 60 isobutylene groups, such as from about 20 to about 30 isobutylene groups. The polyalkenyl compounds used to form the R_{10} polyalkenyl radicals may be formed by any suitable methods, such as by conventional catalytic oligomerization of alkenes.

[00035] In some aspects, high reactivity polyisobutenes having relatively high proportions of polymer molecules with a terminal vinylidene group may be used to form the R_{10} group. In one example, at least about 60%, such as about 70% to about 90%, of the polyisobutenes comprise terminal olefinic double bonds. High reactivity polyisobutenes are disclosed, for example, in US 4,152,499, the disclosure of which is herein incorporated by reference in its entirety.

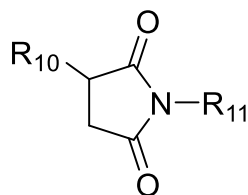
[00036] In some aspects, approximately one mole of maleic anhydride may be reacted per mole of polyalkylene, such that the resulting polyalkenyl succinic anhydride has about 0.8 to about 1 succinic anhydride group per polyalkylene substituent. In other aspects, the molar ratio of succinic anhydride groups to polyalkylene groups may range from about 0.5 to about 3.5, such as from about 1 to about 1.1.

[00037] The hydrocarbyl carbonyl compounds may be made using any suitable method. One example of a method for forming a hydrocarbyl carbonyl compound comprises blending a polyolefin and maleic anhydride. The polyolefin and maleic anhydride reactants are heated to temperatures of, for example, about 150°C to about 250°C, optionally, with the use of a catalyst,

such as chlorine or peroxide. Another exemplary method of making the polyalkylene succinic anhydrides is described in US 4,234,435, which is incorporated herein by reference in its entirety.

[00038] In the hydrocarbyl substituted dicarboxylic anhydride derivative, the polyamine reactant may be an alkylene polyamine. For example, the polyamine may be selected from ethylene polyamine, propylene polyamine, butylenes polyamines, and the like. In one approach, the polyamine is an ethylene polyamine that may be selected from ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, and N, N'- (iminodi-2,1,ethanediyl) bis-1,3- propanediamine. A particularly useful ethylene polyamine is a compound of the formula $H_2N-((CHR_1-(CH_2)_q-NH)_r-H$, wherein R_1 thereof is hydrogen, q is 1 and r is 4.

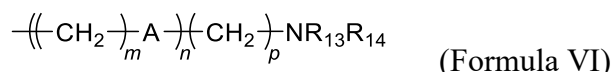
[00039] In yet further approaches, the hydrocarbyl substituted dicarboxylic anhydride derivative is a compound of Formula V



(Formula V)

wherein R_{10} of Formula V is a hydrocarbyl group (such as polyisobutylene and/or the other above described R_{10} moieties) and R_{11} of Formula V is a hydrogen, an alkyl group, an aryl group, -OH, -NHR₁₂, or a polyamine, or an alkyl group containing one or more primary, secondary, or tertiary amino groups. In some approaches, R_{11} of Formula V is derived from ethylene diamine, diethylene triamine, triethylene tetraamine, tetraethylene pentamine, pentaethylene hexamine, N,N'-(iminodi-2,1,ethanediyl)bis-1,3-propanediamine and combinations thereof. In some embodiments, R_{10} of Formula V is a hydrocarbyl group and R_{11} is hydrogen, an alkyl group, an aryl group, -OH, -NHR₁₂, or a polyamine and wherein R_{12} thereof is a hydrogen or an alkyl group. In other embodiments, the additive of Formula V includes a hydrocarbyl substituted succinimide derived from ethylene diamine, diethylene triamine, triethylene tetraamine, tetraethylene pentamine, pentaethylene hexamine, N,N'-(iminodi-2,1,ethanediyl)bis-1,3-propanediamine and combinations thereof. In still other embodiments, R_{10} in the compound of Formula V is a hydrocarbyl group having a number average molecular weight from about 450 to about 3,000 and R_{11} is derived from tetraethylene pentamine and derivatives thereof.

[00040] In yet other approaches, R₁₁ is a radical of Formula VI



wherein A is NR₁₂ or an oxygen atom, R₁₂, R₁₃, and R₁₄ of Formula VI are independently a hydrogen atom or an alkyl group, m and p are integers from 2 to 8; and n is an integer from 0 to 4. In some approaches, R₁₃ and R₁₄ of Formula VI, together with the nitrogen atom to which they are attached, form a 5 membered ring.

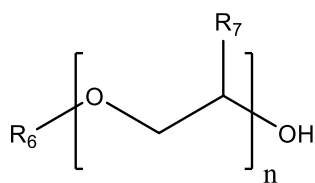
[00041] In approaches or embodiments, the succinimide detergent herein is a hydrocarbyl substituted mono-succinimide detergent, a hydrocarbyl substituted bis-succinimide detergent, or a combination thereof. In one approach or embodiment, the succinimide detergent may be derived from polyisobutylene succinic anhydride and the amine in a 1:1 to a 1:6 molar ratio.

[00042] A fuel additive or the fuel herein may include about 0.5 to about 10 weight percent of the active succinimide detergent, about 0.5 to about 8 weight percent of the succinimide detergent, or about 1 to about 5 weight percent of the succinimide detergent (based on the total weight of the active succinimide within the fuel additive). When blended into a gasoline fuel, the fuel may include about 0.5 ppmw to about 20 ppmw of the active succinimide detergent, about 1 ppmw to about 10 ppmw, or about 2 ppmw to about 5 ppmw of the succinimide detergent in the fuel (based on total weight of the active succinimide).

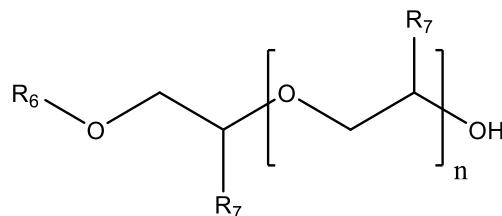
[00043] As discussed more below, the fuel additive and fuels herein include a select weight ratio of the Mannich detergent to the succinimide detergent.

[00044] Alkoxyated Alcohol

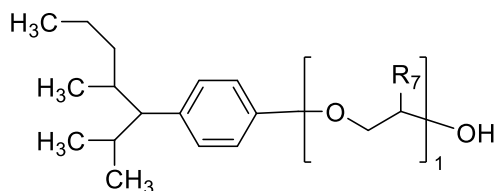
[00045] The fuel additives or fuels of the present disclosure may also include one or more optional alkoxyated alcohols. The alkoxyated alcohol is preferably a polyether prepared by reacting an long chain alkyl alcohol or alkylphenol with an alkylene oxide. By one approach, the alkoxyated alcohol may be one or more hydrocarbyl-terminated or hydrocarbyl-capped poly(oxyalkylene) polymers. The hydrocarbyl moieties thereof may be aryl or aliphatic groups, and preferably, aliphatic chains that are linear, branched or cyclic, and most preferably are linear aliphatic chains. In one approach, the alkoxyated alcohols may have the structure of Formula IIIa, IIIb, and/or IIIc below:



(Formula IIIa)



(Formula IIIb)



(Formula IIIc)

wherein R_6 of the Formula III structures above is an aryl group or a linear, branched, or cyclic aliphatic group and preferably having 5 to 50 carbons (or 5 to 30 carbons) or may be a $-C_mH_{2m+1}$ group where m is an integer of 12 or more, R_7 of the Formula III structures above is a C1 to C4 alkyl group, and n is an integer from 5 to 100 (or as further discussed below).

[00046] In some approaches, suitable alkoxyated alcohols are derived from lower alkylene oxides selected from the group consisting of ethylene oxide, propylene oxide, butylene oxide, copolymers thereof, and combinations thereof. Preferably, the lower alkylene oxides are propylene oxide or butylene oxide or copolymers of ethylene oxide, propylene oxide, and butylene oxide (as well as any combinations thereof). In another approach, the alkylene oxides are propylene oxide. Any copolymers of such alkylene oxides may be random or block copolymers. In one approach, the alkoxyated alcohols may be terminated or capped with an aryl, alkyl, or hydrocarbyl group and may include one or more aryl or linear, branched, or cyclic aliphatic C5 to C30 terminated alkoxyated alcohols, and in other approaches, a C16 to C18 (or blend thereof) terminated alkoxyated alcohol having 5 to 100, 10 to 80, 20 to 50, or 22 to 32 repeating units of the alkylene oxide therein (that is, n integer of the formula above). In some approaches, the alkoxyated alcohols may have a weight average molecular weight of about 1300 to about 2600 and, in other approaches, about 1600 to about 2200.

[00047] In some approaches, the aliphatic hydrocarbyl terminated alkoxyated alcohols may include about 20 to about 70 weight percent (in another approach, about 30 to about 50 weight percent) of an aliphatic C16 alkoxyated alcohol having 24 to 32 repeating units of alkoxyene oxide and/or may include about 80 to about 30 weight percent (in another approach, about 50 to

about 70 weight percent) of an aliphatic C18 alkoxyated alcohol having 24 to 32 repeating units of alkoxyene oxide. In other approaches, the fuel additives herein, if including an alkoxyated alcohol, may also have about 8 percent or less (in other approaches, about 6 percent or less, and in yet other approaches, about 4 percent or less) of C20 or greater alkoxyated alcohols and/or about 4 weight percent or less (in or other approaches about 2 weight percent or less, and in yet other approaches, about 1 percent or less) of C14 or lower alkoxyated alcohols.

[00048] The aryl or hydrocarbyl-capped poly(oxyalkylene) alcohols may be produced by the addition of lower alkylene oxides, such as ethylene oxide, propylene oxide, or the butylene oxides, to a desired hydroxy compound R-OH (that is, a starter alcohol) under polymerization conditions, wherein R is the aryl or hydrocarbyl group having either 5 to 30 carbons or other chain length as noted above and which caps the poly(oxyalkylene) chain. The alkoxyated alcohols can be prepared by any starter alcohol that provides the desired polyol distribution. By one approach, the alkoxyated alcohol can be prepared by reacting a saturated linear or branched alcohol of the desired hydrocarbon size with the selected alkylene oxide and a double metal or basic catalyst. In one approach, the alkoxyated alcohol may be nonylphenol alkyxylated alcohol such as nonylphenol propoxylated alcohol.

[00049] In other approaches, in the polymerization reaction a single type of alkylene oxide may be employed, e.g., propylene oxide, in which case the product is a homopolymer, e.g., a poly(oxyalkylene) propanol. However, copolymers are equally satisfactory and random or block copolymers are readily prepared by contacting the hydroxyl-containing compound with a mixture of alkylene oxides, such as a mixture of ethylene, propylene, and/or butylene oxides. Random polymers are more easily prepared when the reactivities of the oxides are relatively equal. In certain cases, when ethylene oxides is copolymerized with other oxides, the higher reaction rate of ethylene oxide makes the preparation of random copolymers difficult. In either case, block copolymers can be prepared. Block copolymers are prepared by contacting the hydroxyl-containing compound with first one alkylene oxide, then the others in any order, or repetitively, under polymerization conditions. In one example, a particular block copolymer may be represented by a polymer prepared by polymerizing propylene oxide on a suitable mono-hydroxy compound to form a poly(oxypropylene) alcohol and then polymerizing butylene oxide on the poly(oxyalkylene) alcohol.

[00050] A fuel additive or fuel herein, when included, may include about 5 to about 30 weight

percent of the alkoxyated alcohol, about 8 to about 20 weight percent of the alkoxyated alcohol, or about 10 to about 15 weight percent of the alkoxyated alcohol (based on the active alkoxyated alcohol in the fuel additive). When blended into a gasoline fuel, the fuel may include about 2 ppmw to about 150 ppmw of the active alkoxyated alcohol, about 5 to about 150 ppmw, about 8 ppmw to about 50 ppmw, or about 15 ppmw to about 40 ppmw of the alkoxyated alcohol in the fuel.

[00051] Fuel Additive:

[00052] When formulating the fuel compositions of this application, the above described additives (including at least the Mannich detergent(s) and the succinimide detergent(s)) may be employed in amounts sufficient to reduce or inhibit deposit formation in a fuel system, a combustion chamber of an engine and/or crankcase, and/or within fuel injectors and within a gasoline direct injection engine and/or a port fuel injection engine. Such additives may also be provided in amounts to improve injector performance as described herein. In some aspects, the fuel additive or fuel additive package herein may include at least the above described Mannich detergent, the succinimide detergent, and the optional alkoxyated alcohol. The fuel additives herein may also include other optional additives as needed for a particular application and may include as needed one or more of a demulsifier, a corrosion inhibitor, an antiwear additive, an antioxidant, a metal deactivator, an antistatic additive, a dehazer, an antiknock additive, a lubricity additive, and/or a combustion improver.

[00053] In some approaches or embodiments, the fuel additive or additive package herein may include about 20 to about 60 weight percent of the Mannich detergent and about 0.5 to about 10 weight percent of the succinimide detergent. In other approaches, the fuel additive or additive package may also include about 5 to about 30 weight percent of the alkoxyated alcohol. Other ranges of the Mannich detergent, the succinimide detergent, and the optional alkoxyated alcohol may also be used in the fuel additive, the additive package, or the fuel as described above in this disclosure.

[00054] In other approaches, a gasoline fuel composition may include about 40 to about 750 ppmw of the fuel additive or the additive package herein, in other approaches, about 60 to about 380 ppmw, or about 135 to about 310 ppmw of the above noted fuel additive package and which provides about 15 to about 300 ppmw of the Mannich detergent and about 0.5 to about 20 ppmw

of the succinimide detergent to the fuel (or other ranges as noted above). In other embodiments, the fuel may also include about 2 to about 90 ppmw of the optional alkoxyated alcohol (or other ranges as noted above). It will also be appreciated that any endpoint between the above described ranges are also suitable range amounts as needed for a particular application. The above-described amounts reflects additives on an active ingredient basis, which means the additives noted above excludes the weight of (i) unreacted components associated with and remaining in the product as produced and used, and (ii) solvent(s), if any, used in the manufacture of the product either during or after its formation.

[00055] In other approaches, the fuel additive package or fuel thereof also has a certain weight ratio of the alkoxyated alcohol to the Mannich detergent of about 1.0 or less (i.e., about 1.0:1 or less), about 0.8 or less (i.e., 0.8:1 or less), about 0.6 or less, about 0.5 or less, about 0.4 or less, or about 0.3 or less, and about 0.1 or more (i.e., 0.1:1 or more), about 0.2 or more, or about 0.3 or more.

[00056] In yet other approaches, the fuel additive package or fuel thereof may also have a weight ratio of the Mannich detergent to the succinimide detergent of about 15:1 to about 30:1, or about 20:1 to about 30:1 or about 22:1 to about 30:1 (wherein the weight ratios are active Mannich detergent to the active succinimide detergent). In other approaches, the fuel additive package or fuel thereof may have a weight ratio of the Mannich detergent to the succinimide detergent from about 15:1 to about 25:1, or from about 20:1 to from about 25:1 (wherein the weight ratios are active Mannich detergent to the active succinimide detergent). In yet other approaches, the fuel additive package or fuel thereof may have a weight ratio of the Mannich detergent to the succinimide detergent from about 25:1 to about 30:1, or from about 26:1 to about 30:1 (wherein the weight ratios are active Mannich detergent to the active succinimide detergent). As shown in the Examples below, such weight ratios achieve a surprising synergy of the detergent additives in engine performance.

[00057] Other Additives

[00058] One or more optional compounds may be present in the fuel compositions of the disclosed embodiments. For example, the fuels may contain conventional quantities of cetane improvers, octane improvers, corrosion inhibitors, cold flow improvers (CFPP additive), pour point depressants, solvents, demulsifiers, lubricity additives, friction modifiers, amine stabilizers,

combustion improvers, detergents, dispersants, antioxidants, heat stabilizers, conductivity improvers, metal deactivators, marker dyes, organic nitrate ignition accelerators, cyclomatic manganese tricarbonyl compounds, carrier fluids, 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 optional additives. Similarly, the fuels may contain suitable amounts of conventional fuel blending components such as methanol, ethanol, dialkyl ethers, 2-ethylhexanol, and the like.

[00059] In some aspects of the disclosed embodiments, organic nitrate ignition accelerators that include aliphatic or cycloaliphatic nitrates 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, isoamyl nitrate, 2-amyl nitrate, 3-amyl nitrate, hexyl nitrate, heptyl nitrate, 2-heptyl nitrate, octyl nitrate, isooctyl nitrate, 2-ethylhexyl nitrate, nonyl nitrate, decyl nitrate, undecyl nitrate, dodecyl nitrate, cyclopentyl nitrate, cyclohexyl nitrate, methylcyclohexyl nitrate, cyclododecyl nitrate, 2-ethoxyethyl nitrate, 2-(2-ethoxyethoxy)ethyl nitrate, tetrahydrofuranyl nitrate, and the like. Mixtures of such materials may also be used.

[00060] Examples of suitable optional metal deactivators useful in the compositions of the present application are disclosed in U.S. Pat. No. 4,482,357, the disclosure of which is herein incorporated by reference in its entirety. Such metal deactivators include, for example, salicylidene-o-aminophenol, disalicylidene ethylenediamine, disalicylidene propylenediamine, and N,N'-disalicylidene-1,2-diaminopropane.

[00061] 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 and U.S. Pat. No. 3,015,668 both of which disclosures are herein incorporated by reference in their entirety.

[00062] Other commercially available detergents may be used in combination with the

reaction products described herein. Such detergents include but are not limited to succinimides, Mannich base detergents, PIB amine, quaternary ammonium detergents, bis-aminotriazole detergents as generally described in U.S. patent application Ser. No. 13/450,638, and a reaction product of a hydrocarbyl substituted dicarboxylic acid, or anhydride and an aminoguanidine, wherein the reaction product has less than one equivalent of amino triazole group per molecule as generally described in U.S. patent application Ser. Nos. 13/240,233 and 13/454,697.

[00063] The additives of the present application and optional additives used in formulating the fuels of this invention 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.

[00064] Fuels

[00065] The fuels of the present application may be applicable to the operation of diesel, jet, or gasoline engines, and preferably, spark-ignition or gasoline engines. The engines may include both stationary engines (e.g., engines used in electrical power generation installations, in pumping stations, etc.) and ambulatory engines (e.g., engines used as prime movers in automobiles, trucks, road-grading equipment, military vehicles, etc.). For example, the fuels may include any and all middle distillate fuels, diesel fuels, biorenewable fuels, biodiesel fuel, fatty acid alkyl ester, gas-to-liquid (GTL) fuels, gasoline, jet fuel, alcohols, ethers, kerosene, 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 petcoke), genetically engineered biofuels and crops and extracts therefrom, and natural gas. Preferably, the additives herein are used in spark-ignition fuels or gasoline. “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 can comprise monohydroxy alcohols, such as those comprising from 1 to about 5 carbon atoms.

Non-limiting examples of suitable monohydroxy alcohols include methanol, ethanol, propanol, n-butanol, isobutanol, t-butyl alcohol, amyl alcohol, and isoamyl alcohol. Preferred fuels include diesel fuels.

[00066] Accordingly, aspects of the present application are directed to methods of or the use of the noted fuel additive package for controlling or reducing fuel injector deposits, controlling or reducing intake valve deposits, controlling or reducing combustion chamber deposits, and/or controlling or reducing intake valve sticking in one of port-injection engines, direct-injection engines, and preferably both engine types. In some approaches, the fuel additives and fuels herein are configured to reduce deposits when sprayed from an injector in droplets of about 10 to about 30 microns, when sprayed from an injector in droplets of about 120 to about 200 microns, or both. As such, the fuel additives and fuels herein surprisingly provide improved engine performance as defined herein in both port fuel injected engines (PFI) as well as gasoline direct injection engines (GDI). In some aspects, the method may also comprise mixing into the fuel at least one of the optional additional ingredients described above. The improved engine performance may be evaluated pursuant to the test protocols of ASTM D6201 or by the methods as set forth in the following two SAE publications: Smith, S. and Imoehl, W., "Measurement and Control of Fuel Injector Deposits in Direct Injection Gasoline Vehicles," SAE Technical Paper 2013-01-2616, 2013, doi:10.4271/2013-01-2616 and/or Shanahan, C., Smith, S., and Sears, B., "A General Method for Fouling Injectors in Gasoline Direct Injection Vehicles and the Effects of Deposits on Vehicle Performance," SAE Int. J. Fuels Lubr. 10(3):2017, doi:10.4271/2017-01-2298, both of which are incorporated herein by reference. Intake valve sticking may be evaluated using the test protocols at Southwest Research Institute (SWRI, San Antonio Texas) or similar test house.

[00067] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having a predominantly hydrocarbon character. Each hydrocarbyl group is independently selected from hydrocarbon substituents, and substituted hydrocarbon substituents containing one or more of halo groups, hydroxyl groups, alkoxy groups, mercapto groups, nitro groups, nitroso groups, amino groups, pyridyl groups, furyl groups, imidazolyl groups, oxygen and nitrogen, and wherein no more than two non-hydrocarbon substituents are present for every ten carbon atoms

in the hydrocarbyl group.

[00068] As used herein, the term "percent by weight" or "wt%", unless expressly stated otherwise, means the percentage the recited component represents to the weight of the entire composition. All percent numbers herein, unless specified otherwise, is weight percent.

[00069] The term "alkyl" as employed herein refers to straight, branched, cyclic, and/or substituted saturated chain moieties from about 1 to about 200 carbon atoms. The term "alkenyl" as employed herein refers to straight, branched, cyclic, and/or substituted unsaturated chain moieties from about 3 to about 30 carbon atoms. The term "aryl" as employed herein refers to single and multi-ring aromatic compounds that may include alkyl, alkenyl, alkylaryl, amino, hydroxyl, alkoxy, halo substituents, and/or heteroatoms including, but not limited to, nitrogen, and oxygen.

[00070] As used herein, the molecular weight is determined by gel permeation chromatography (GPC) using commercially available polystyrene standards (with a Mp of about 162 to about 14,000 as the calibration reference). The molecular weight (Mn) for any embodiment herein may be determined with a gel permeation chromatography (GPC) instrument obtained from Waters or the like instrument and the data processed with Waters Empower Software or the like software. The GPC instrument may be equipped with a Waters Separations Module and Waters Refractive Index detector (or the like optional equipment). The GPC operating conditions may include a guard column, 4 Agilent PLgel columns (length of 300×7.5 mm; particle size of 5 μ, and pore size ranging from 100-10000 Å) with the column temperature at about 40 °C. Un-stabilized HPLC grade tetrahydrofuran (THF) may be used as solvent, at a flow rate of 0.38 mL/min. The GPC instrument may be calibrated with commercially available polystyrene (PS) standards having a narrow molecular weight distribution ranging from 500 – 380,000 g/mol. The calibration curve can be extrapolated for samples having a mass less than 500 g/mol. Samples and PS standards can be dissolved in THF and prepared at concentration of 0.1-0.5 weight percent and used without filtration. GPC measurements are also described in US 5,266,223, which is incorporated herein by reference. The GPC method additionally provides molecular weight distribution information; *see, for example*, W. W. Yau, J. J. Kirkland and D. D. Bly, "Modern Size Exclusion Liquid Chromatography", John Wiley and Sons, New York, 1979, also incorporated herein by reference.

[00071] As used herein and unless the context suggests otherwise, a major amount refers to

greater than 50 weight percent (greater than 60 weight percent, greater than 70 weight percent, greater than 80 weight percent or greater than 90 weight percent), and a minor amount refers to less than 50 weight percent (less than 40 weight percent, less than 30 weight percent, less than 20 weight percent, or less than 10 weight percent).

[00072] It is to be understood that throughout the present disclosure, the terms "comprises," "includes," "contains," etc. are considered open-ended and include any element, step, or ingredient not explicitly listed. The phrase "consists essentially of" is meant to include any expressly listed element, step, or ingredient and any additional elements, steps, or ingredients that do not materially affect the basic and novel aspects of the invention. The present disclosure also contemplates that any composition described using the terms, "comprises," "includes," "contains," is also to be interpreted as including a disclosure of the same composition "consisting essentially of" or "consisting of" the specifically listed components thereof.

EXAMPLES

[00073] The following examples are illustrative of exemplary embodiments of the disclosure. In these examples as well as elsewhere in this application, all ratios, 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. The specifications for base fuels A, B, and C used in the Examples are below in Table 1.

[00074] Table 1: Fuel Specifications.

FUEL PROPERTY	BASE FUEL A	BASE FUEL B	BASE FUEL C
API Gravity	64.8-50.9	60.3	58.5
Specific Gravity	0.7207-0.7758	0.7377	0.7447
Density	0.7200-0.7750	0.7370	0.7440
% Benzene	<0.8	0.47	<0.10
Bromine No.	n.a.	9.7	<0.5
BTU Gross (btu/lb)	n.a.	18711	19614
BTU Net (btu/lb)	n.a.	17477	18409
Unwashed Gum (ASTM D-381)	<30	3	3.5
Washed Gum (ASTM D-381)	<5	<0.5	<0.5
ASTM D-525 Oxidation (minutes)	<480	960	960+
RVP (ASTM D-5191)	n.a.	9.46	8.76
%Carbon	n.a.	82.63	86.79
%Hydrogen	n.a.	13.53	13.21
Aromatics (vol-%)	<35	27.9	29.1
Olefins (vol-%)	<15	4.7	1.2
Saturates (vol-%)	n.a.	67.4	69.7
Ethanol (vol-%)	n.a.	9.3	<0.10
Oxygen Content	<2.7	3.84	<0.02
Sulfur (ppm)	<10	8.4	30

RON	89-95	98.2	97.4
MON		87.5	89
Octane (R+M)/2	84-90	92.85	93.2
ASTM D-86 (Temperature °F)			
Initial Boiling Point	n.a.	87	84.6
5%	n.a.	99.9	108
10%	158	110.5	121.5
20%	n.a.	125.2	104.6
30%	n.a.	140.3	163
40%	n.a.	152.5	191.4
50%	230	165.6	215.8
60%	n.a.	228.4	228.4
70%	n.a.	250.5	237.3
80%	n.a.	276	254
90%	374	316	337.5
95%	n.a.	343.6	338.4
End Point	401	398.5	398.7
% Recovery	n.a.	96.1	97.3
Residue	<2	1.1	1.1
Loss	n.a.	2.8	1.6

[00075] EXAMPLE 1

[00076] Inventive and Comparative fuel additive packages of Table 2 below were prepared. The Mannich detergent was prepared from a high reactivity polyisobutylene cresol, dibutylamine, and formaldehyde according to a known method (see, e.g., US 6,800,103, which is incorporated herein by reference); the propoxylated alcohol was a blend of commercially available C16-C18 propoxylated alcohols; and the succinimide detergents were derived from polyisobutylene succinic anhydride (PIBSA) and tetraethylene pentamine (TEPA) in a 1:1 to 1.6:1 molar ratio, where the polyisobutylene had an about 950 molecular weight.

[00077] Table 2

Ingredients*	Inventive							Comparative		
	I-1				I-2			C-1	C-2	C-3
	a	b	c	d	a	b	c			
Mannich Detergent, ppmw	63.8	69.1	73.4	183.4	79.6	164.1	183.4	183.4	-	-
Propoxylated alcohol, ppmw	19.1	20.7	22.3	55.0	23.9	49.2	55.0	55.0	55.0	55.0
Polyisobutenyl mono-succinimide detergent, ppmw	-	-	-	-	2.7	5.6	8.0	-	-	5.6
Polyisobutenyl bis-Succinimide, ppmw	2.8	3.0	3.2	8.0	-	-	-	-	8.0	-
Mannich detergent to PIBSI ratio	23.0	23.0	22.9	22.9	29.5	29.3	22.9	N/A	N/A	N/A

Alkoxylated alcohol to Mannich detergent ratio	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	-	-
--	-----	-----	-----	-----	-----	-----	-----	-----	---	---

* The additive package also contained other non-detergent ingredients, such as demulsifier and solvent.

[00078] Each of the additives of Table 2 above were blended into Base Fuel A, B, or C as specified in the footnotes of Table 3 below. Each fuel was then evaluated for intake valve deposits and/or injector deposits as set forth in Table 3 below.

[00079] Table 3

	I-1				I-2			C-1	C-2	C-3
	a	b	c	d	a	b	c			
GB/T 19230 ** (M111), IVD, mg	28	14	5	--	--	--	--	--	--	--
ASTM 6201 ** Ford 2.3L, IVD, mg	--	--	--	--	86.9	--	--	--	--	--
IVD improvement over average base fuel, %	88.3	94.2	97.9	--	93.1	--	--	--	--	--
GDI by Afton RIFT method***, clean up (CU), %	--	--	--	59.9	--	79.9	88.0	-60.8 ¹	24.8	62.6

** Base fuel IVD: 240 mg for M111 engine in Base Fuel A and 1263 mg for Ford 2.3L engine in Base Fuel B.

*** LHU GDI testing method, refer to the following SAE papers, testing in Base Fuel C: (1) Smith, S. and Imoehl, W., "Measurement and Control of Fuel Injector Deposits in Direct Injection Gasoline Vehicles," SAE Technical Paper 2013-01-2616, 2013, doi:10.4271/2013-01-2616; and/or (2) Shanahan, C., Smith, S., and Sears, B., "A General Method for Fouling Injectors in Gasoline Direct Injection Vehicles and the Effects of Deposits on Vehicle Performance," SAE Int. J. Fuels Lubr. 10(3):2017, doi:10.4271/2017-01-2298, both of which are incorporated herein by reference.

¹No clean-up observed as sample continued a dirty-up phase as shown in FIGS. 1 and 2.

[00080] In the context of GDI engines, a series of tests were run to evaluate the impact that the additive packages had on fuel inject deposits in a gasoline direct injection engine (GDI). All tests were run with a consistent Base Fuel C during a Dirty-up (DU), Clean-up (CU) and/or Keep Clean (KC) phases of the respective test. The additive packages of Table 2 above were tested to evaluate the ability of each fuel additive to improve injector performance by reducing injector deposits in the GDI engine. Results are shown in Table 3 as well as FIGS. 1 and 2.

[00081] Base fuel C was investigated for a DU level by indirect measurements of injector fouling, such as by pulse width or long term fuel trim (LTFT), on a gasoline direct injection GM LHU engine pursuant to the RIFT methods as set forth in Smith, S. and Imoehl, W., "Measurement and Control of Fuel Injector Deposits in Direct Injection Gasoline Vehicles," SAE Technical Paper 2013-01-2616, 2013, doi:10.4271/2013-01-2616 and/or Shanahan, C.,

Smith, S., and/or Sears, B., “A General Method for Fouling Injectors in Gasoline Direct Injection Vehicles and the Effects of Deposits on Vehicle Performance,” SAE Int. J. Fuels Lubr. 10(3):2017, doi:10.4271/2017-01-2298, both of which are incorporated by reference herein.

[00082] In order to accelerate the DU phase of the Base Fuel, a combination of di-tert-butyl disulfide (DTBDS, 406 ppmw) and tert-butyl hydrogen peroxide (TBHP, 286 ppmw) were added to the base fuel and the DU was accelerated to provide the fouling in the range of 5 to 12%.

Percent of fouling is calculated as:

$$\text{Percent of fouling} = \frac{\text{Injector pulse width} - \text{injector pulse width at start of testing}}{\text{injector pulse at start of testing}} * 100\%$$

[00083] GDI clean up (CU) deposit tests were conducted to demonstrate the removal of deposits that had been formed in the fuel injectors during the dirty-up (DU) phase. The Additive packages of Table 2 were blended into the Base Fuel C that was used for DU. The test procedure consisted of a 114 hour cycle at 2000 rpm and 100 Nm torque with continuous monitoring of injection pulse width to maintain stoichiometric Air/Fuel ratio on the GM LHU engine. After 66 hours of test operation, the fuel was changed to an additized formulation that is designed to have a clean-up effect. The percentage of injector pulse width increase, and subsequent decrease, after completion of the 114 hour cycle is one parameter for evaluating the fouling or cleaning effect of the fuel candidate. CU is calculated as in the following equation:

$$CU = \frac{\text{Injector pulse width at end of DU} - \text{injector pulse width at end of testing}}{\text{Injector pulse width at end of DU} - \text{injector pulse width at starting of testing}} * 100\%$$

[00084] As shown in Table 3 above and in FIGS. 1 and 2, Inventive samples with both the Mannich and succinimide detergents at ratios from 15:1 to 30:1 exhibited improved injector clean-up relative to the comparative examples with either the Mannich or succinimide detergents alone. FIG. 1 shows the DU phase (open symbols) and CU phase (closed symbols) of Comparative additive packages C-1 and C-2 relative to Inventive additive package I-1d. As shown in Table 3 and FIG. 1, the Comparative sample C-1 with only the Mannich detergent continued a dirty-up phase in the GDI engine (that is, no clean-up performance), but Inventive sample I-1d demonstrated improved clean-up with both the Mannich and the succinimide detergents in the noted ratios. Given that a fuel additive with only a Mannich detergent (e.g., C-1) had no clean-up performance in a GDI engine (and rather continued the dirty up phase),

Inventive sample I-1d with both the Mannich detergent and the succinimide detergent demonstrated an unexpected synergy in performance. That is, it would not have been expected that the clean-up performance with both the succinimide and the Mannich detergents would have been better than the clean-up performance of comparative sample C-2 including only the succinimide detergent given that the Mannich detergent alone provided no clean-up performance (but rather continues DU). Table 3 and FIG. 2 shows a similar pattern of an unexpected synergy with inventive sample I-2c (both Mannich and succinimide detergents) compared to C-1 (Mannich detergent only) and C-2 (succinimide detergent only).

[00085] 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 “an antioxidant” includes two or more different antioxidants. 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

[00086] 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.

[00087] It is to be understood that each component, compound, substituent or parameter disclosed herein is to be interpreted as being disclosed for use alone or in combination with one or more of each and every other component, compound, substituent or parameter disclosed herein.

[00088] It is further understood that each range disclosed herein is to be interpreted as a disclosure of each specific value within the disclosed range that has the same number of

significant digits. Thus, for example, a range from 1 to 4 is to be interpreted as an express disclosure of the values 1, 2, 3 and 4 as well as any range of such values.

[00089] It is further understood that each lower limit of each range disclosed herein is to be interpreted as disclosed in combination with each upper limit of each range and each specific value within each range disclosed herein for the same component, compounds, substituent or parameter. Thus, this disclosure is to be interpreted as a disclosure of all ranges derived by combining each lower limit of each range with each upper limit of each range or with each specific value within each range, or by combining each upper limit of each range with each specific value within each range. That is, it is also further understood that any range between the endpoint values within the broad range is also disclosed herein. Thus, a range from 1 to 4 also means a range from 1 to 3, 1 to 2, 2 to 4, 2 to 3, and so forth.

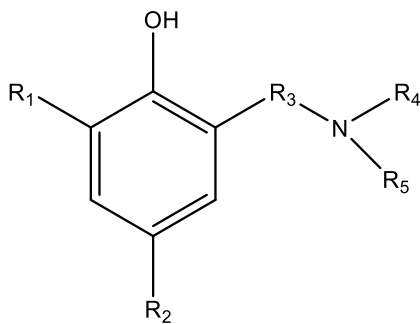
[00090] Furthermore, specific amounts/values of a component, compound, substituent or parameter disclosed in the description or an example is to be interpreted as a disclosure of either a lower or an upper limit of a range and thus can be combined with any other lower or upper limit of a range or specific amount/value for the same component, compound, substituent or parameter disclosed elsewhere in the application to form a range for that component, compound, substituent or parameter.

CLAIMS

WHAT IS CLAIMED IS:

1. A fuel additive for a spark-ignition engine comprising:
a Mannich detergent including the reaction product of a hydrocarbyl-substituted phenol or cresol, one or more aldehydes, and one or more amines;
a succinimide detergent prepared by reacting a hydrocarbyl-substituted succinic acylating agent with an amine, polyamine, or alkyl amine having one or more primary, secondary, or tertiary amino groups; and
wherein a weight ratio of the Mannich detergent to the succinimide detergent is from about 15:1 to about 30:1.

2. The fuel additive of claim 1, wherein the weight ratio of the Mannich detergent to the succinimide detergent is from about 20:1 to about 30:1; and/or wherein the Mannich detergent has the structure of Formula I:



(Formula I)

wherein R₁ is hydrogen or a C1 to C4 alkyl group, R₂ is a hydrocarbyl group having a molecular weight of about 500 to about 3000, R₃ is a C1 to C4 alkylene or alkenyl group, and R₄ and R₅ are, independently, hydrogen, a C1 to C12 alkyl group, or a mono or di(C1 to C4)alkyl amino C1-C12 alkyl group.

3. The fuel additive of claim 2, wherein R₂ is polyisobutenyl having a number average molecular weight of about 500 to about 1500.

4. The fuel additive of claim 1, wherein the succinimide detergent is a hydrocarbyl substituted mono-succinimide detergent, a hydrocarbyl substituted bis-succinimide detergent, or

a combination thereof; and/or wherein the hydrocarbyl-substituted succinic acylating agent is a hydrocarbyl-substituted succinic anhydride, wherein the hydrocarbyl group has a molecular weight of about 450 to about 3000, and wherein a molar ratio of the hydrocarbyl-substituted succinic anhydride to the amine, polyamine, or alkyl amine is from about 0.5:1 to about 2:1.

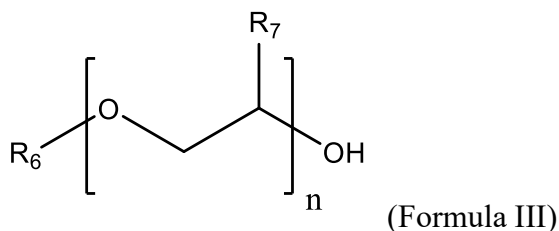
5. The fuel additive of claim 4, wherein the hydrocarbyl-substituted succinic anhydride is polyisobutylene substituted succinic anhydride, and wherein the polyisobutylene has a number average molecular weight of about 500 to about 1200 as measured by GPC using polystyrene as reference.

6. The fuel additive of claim 5, wherein the amine, polyamine, or alkyl amine is tetraethylene pentamine (TEPA), triethylenetetraamine (TETA), or a polyamine or alkyl amine having the formula $H_2N-((CHR_{20}-(CH_2)_q-NH)_r-H$, wherein R_{20} thereof is hydrogen or an alkyl group having from 1 to 4 carbon atoms, q is an integer of from 1 to 4 and r is an integer of from 1 to 6, and mixtures thereof.

7. The fuel additive of claim 6, wherein the amine, polyamine, or alkyl amine is tetraethylene pentamine (TEPA).

8. The fuel additive of claim 1, further comprising an alkoxyated alcohol, and wherein a weight ratio of the alkoxyated alcohol to the Mannich detergent is about 1.0 or less; and/or wherein the alkoxyated alcohol is a polyether prepared by reacting an alkyl alcohol or an alkylphenol with an alkylene oxide selected from ethylene oxide, propylene oxide, butylene oxide, copolymers thereof, or combinations thereof.

9. The fuel additive of claim 8, wherein the alkoxyated alcohol is a polyether having the structure of Formula III:



wherein R₆ of Formula III is an aryl group or a linear, branched, or cyclic aliphatic group having 5 to 50 carbons, R₇ of Formula III is a C1 to C4 alkyl group, and n is an integer from 5 to 100.

10. The fuel additive of claim 1, wherein the fuel additive includes about 20 to about 60 weight percent of the Mannich detergent, about 0.5 to about 10 weight percent of the succinimide detergent, and about 5 to about 30 weight percent of an alkoxyated alcohol.

11. A gasoline fuel composition comprising
about 15 to about 300 ppmw of a Mannich detergent including the reaction product of a hydrocarbyl-substituted phenol or cresol, one or more aldehydes, and one or more amines;
about 0.5 to about 20 ppmw of a succinimide detergent prepared by reacting a hydrocarbyl-substituted succinic acylating agent with an amine, polyamine, or alkyl amine having one or more primary, secondary, or tertiary amino groups;
wherein a weight ratio of the Mannich detergent to the succinimide detergent is about from 15:1 to about 30:1; and
about 5 to about 150 ppmw of an alkoxyated alcohol.

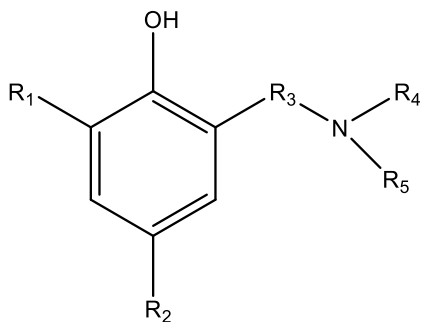
12. A method of reducing deposits in a gasoline engine, the method comprising:
operating a gasoline engine on a fuel composition containing a major amount of a gasoline fuel and a minor amount of a fuel additive by injecting the gasoline fuel through one or more injectors;
wherein the fuel additive includes (i) a Mannich detergent including the reaction product of a hydrocarbyl-substituted phenol or cresol, one or more aldehydes, and one or more amines;
(ii) a succinimide detergent prepared by reacting a hydrocarbyl-substituted succinic acylating agent with an amine, polyamine, or alkyl amine having one or more primary, secondary, or tertiary amino groups; and (iii) wherein the fuel additive has a weight ratio of the Mannich detergent to the succinimide detergent of from about 15:1 to about 30:1; and
wherein the fuel additive reduces deposits in the gasoline engine.

13. The method of claim 12, wherein the fuel additive reduces deposits in a port fuel injection (PFI) engine, a gasoline direct injection (GDI) engine, or both; and/or wherein the

reduced deposits are reduced injector deposits measured by one of injector pulse width, injection duration, injector flow, or combinations thereof.

14. The method of claim 12, wherein the fuel additive reduces deposits when sprayed from an injector configured to spray droplets of about 10 to about 30 microns, about 120 to about 200 microns, or both.

15. The method of claim 12, wherein the weight ratio of the Mannich detergent to the succinimide detergent is from about 20:1 to about 30:1; and/or wherein the Mannich detergent has the structure of Formula I:



(Formula I)

wherein R₁ is hydrogen or a C1 to C4 alkyl group, R₂ is a hydrocarbyl group having a molecular weight of about 500 to about 3000, R₃ is a C1 to C4 alkylene or alkenyl group, and R₄ and R₅ are, independently, hydrogen, a C1 to C12 alkyl group, or a mono or di(C1 to C4)alkyl amino C1-C12 alkyl group.

16. The method of claim 12, further comprising an alkoxyated alcohol and wherein a weight ratio of the alkoxyated alcohol to the Mannich detergent is about 1.0 or less; and/or wherein the alkoxyated alcohol is a polyether prepared by reacting an alkyl alcohol or an alkylphenol with an alkylene oxide selected from ethylene oxide, propylene oxide, butylene oxide, copolymers thereof, or combinations thereof; and/or wherein the fuel additive includes about 20 to about 60 weight percent of the Mannich detergent, about 0.5 to about 10 weight percent of the succinimide detergent, and about 5 to about 30 weight percent of the alkoxyated alcohol.