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(54) **COMBUSTION MODIFIERS FOR WATER-BLENDED FUELS**

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(57) **ABSTRACT**

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Related U.S. Application Data

(60) Provisional application No. 60/272,209, filed on Feb. 28, 2001. Provisional application No. 60/317,222,

A combustion modifier for an aqueous hydrocarbon fuel emulsion that reduces nitrogen oxides (NOx), hydrocarbons, carbon monoxide (CO) and particulate matter from the emissions of internal combustion engines. A class of combustion modifiers used in this invention contain nitrogen. The nitrogen-containing combustion modifiers are nitro compounds, hydroxylamines or salts thereof, nitrogen compounds having at least one strained ring group containing from 3 to 5 ring atoms, nitrites, nitramines and mixtures thereof. The non nitrogen-containing combustion modifier comprises compounds containing at least one strained ring compound.

COMBUSTION MODIFIERS FOR WATER-BLENDED FUELS

[0001] This is filed from U.S. provisional application Ser. No. 60/272,209, filed Feb. 28, 2001, and U.S. provisional application Ser. No. 60/317,222, filed Sep. 5, 2001, and U.S. provisional application Ser. No. 60/317,205, filed Sep. 5, 2001.

TECHNICAL FIELD

[0002] The invention relates to combustion improving additives for aqueous hydrocarbon fuel emulsions. More particularly, the invention relates to combustion modifiers for aqueous hydrocarbon fuel emulsions that reduces nitrogen oxides (NO_x), hydrocarbons (HC), carbon monoxide (CO) and particulate matter (PM) from the emissions of internal combustion engines.

BACKGROUND OF THE INVENTION

[0003] Internal combustion engines, especially diesel engines, that employ water mixed with the fuel in the combustion chamber can produce lower nitrogen oxides, hydrocarbons and particulate emissions per unit of power output. The reduction of harmful emissions is an environmental issue because the emissions contribute to smog and air pollution. Governmental regulations and environmental concerns have driven the need to reduce harmful emissions from engines.

[0004] Water is inert toward combustion and lowers the peak combustion temperature resulting in reduced particulates and NO_x formation. Water-blended fuels are being employed to reduce NO_x and particulate matter emissions from internal combustion engines. It would be advantageous to improve the efficiency and utilization of aqueous hydrocarbon fuels and further reduce the harmful emissions of such fuels by also reducing hydrocarbons and carbon monoxide emissions.

[0005] U.S. Pat. No. 5,591,237 discloses a fuel additive concentrate package comprising detergent/dispersant, an organic nitrate combustion improver and a corrosion inhibitor such as nitric acid/hydrochloric acid to provide enhanced shelf-life ability.

[0006] U.S. Pat. No. 5,669,938 discloses a fuel composition which comprises a water in oil emulsion comprising hydrocarbonaceous middle distillate fuel, water and an emission reducing amount of at least one fuel soluble organic nitrate ignition improver such as 2-ethylhexyl nitrate providing reduction of exhaust emissions from diesel engines.

[0007] Combustion improvers of this invention improve the combustion characteristics of aqueous hydrocarbon fuels. The improved combustion characteristics include reduced NO_x emissions, reduced CO emissions, reduced hydrocarbon emissions and reduced particulate matter emissions, as well as greater power output which can be expressed as an improved fuel efficiency.

[0008] The term "NO_x" is used herein to refer to any of the nitrogen oxides, NO, NO₂, N₂O, or mixtures of two or more thereof. The terms "aqueous hydrocarbon fuel emulsion" and "water fuel emulsion" and "aqueous hydrocarbon fuel" and "water fuel blend" are interchangeable.

SUMMARY OF THE INVENTION

[0009] This invention relates to an aqueous hydrocarbon fuel emulsion comprising, a liquid hydrocarbon based fuel, water, at least one emulsifier and a combustion modifier. A class of combustion modifiers used in this invention contain nitrogen. The nitrogen-containing combustion modifier comprises:

[0010] (a) a nitro compound;

[0011] (b) a hydroxylamine or a salt thereof wherein each hydroxylamino group of the hydroxylamine or salt thereof contains no more than one tertiary substituent;

[0012] (c) a nitrogen compound having at least one strained ring group containing from 3 to 5 ring atoms;

[0013] (d) organic nitrites;

[0014] (e) nitramines; and

[0015] (f) mixtures thereof.

[0016] The non nitrogen-containing combustion modifier comprises compounds containing at least one strained ring compound.

[0017] The invention is further directed to a method for improving the combustion characteristics of an aqueous hydrocarbon fuel comprising incorporating a combustion improving amount of a nitrogen containing compound in the fuel wherein the nitrogen containing compound comprises:

[0018] (a) a nitro compound;

[0019] (b) a hydroxylamine or a salt thereof wherein each hydroxylamino group of the hydroxylamine or salt thereof contains no more than one tertiary substituent;

[0020] (c) a nitrogen compound having at least one strained ring group containing from 3 to 5 ring atoms;

[0021] (d) organic nitrites;

[0022] (e) nitramines; and

[0023] (f) mixtures thereof.

[0024] The non nitrogen-containing combustion modifier comprises compounds containing at least one strained ring compound

DETAILED DESCRIPTION OF THE INVENTION

[0025] The aqueous hydrocarbon fuel emulsion composition of this invention comprises at least compound which acts as a combustion improver. The nitrogen containing combustion improver compounds are selected from the group consisting of:

[0026] (a) a nitro compound;

[0027] (b) a hydroxylamine or a salt thereof wherein each hydroxylamino group of the hydroxylamine or salt thereof contains no more than one tertiary substituent;

[0028] (c) a nitrogen compound having at least one strained ring group containing from 3 to 5 ring atoms;

[0029] (d) organic nitrites;

[0030] (e) nitramines; and

[0031] (f) mixtures thereof.

[0032] The non nitrogen-containing combustion modifier comprises of compounds containing at least one strained ring compound

[0033] The preferred nitrogen containing combustion improver compound is hydroxy ammonium nitrate (HAN).

[0034] The nitrogen containing compounds are used in the amount ranging in one embodiment from about 0.01 to about 5 percent per weight, in one embodiment from about 0.02 to about 2 percent per weight, in one embodiment from about 0.04 to about 1.5 per weight, and in one embodiment from about 0.05 to about 1.0 per weight of the aqueous hydrocarbon fuel emulsion.

[0035] Suitable emulsifiers comprise:

[0036] (i) at least one fuel-soluble product made by reacting at least one hydrocarbyl-substituted carboxylic acid acylating agent with ammonia or an amine, the hydrocarbyl substituent of said acylating agent having about 50 to about 500 carbon atoms;

[0037] (ii) at least one of an ionic or a nonionic compound having a hydrophilic-lipophilic balance (HLB) of about 1 to about 40;

[0038] (iii) a mixture of (ii) with (i);

[0039] (iv) a water-soluble compound selected from the group consisting of amine salts, ammonium salts, azide compounds, nitrate esters, nitramine, nitro-compounds, alkali metal salts, alkaline earth metal salts, in combination with (i), (ii), (iii), (v), (vii) or combinations thereof;

[0040] (v) the reaction product of polyacidic polymer with at least one fuel soluble product made by reacting at least one hydrocarbyl-substituted carboxylic acid acylating agent with ammonia, an amine, a polyamine, alkanol amine, or hydroxy amines;

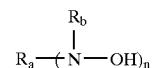
[0041] (vi) an amino alkylphenol which is made by reacting an alkylphenol, an aldehyde and an amine resulting in an amino alkylphenol, or

[0042] (vii) the combination of (vi) and (i), (ii), (iii), (iv), (v) or combination thereof.

[0043] Hydroxylamines and Salts Thereof

[0044] The hydroxylamine or a salt thereof is a combustion modifier for the aqueous hydrocarbon fuel. The hydroxylamine or salt thereof can be a hydroxylamino group of the hydroxylamine or salt thereof containing no more than one tertiary alkyl substituent.

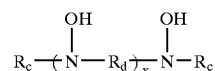
[0045] In one embodiment the hydroxylamine has the general formula



[0046] wherein each of R_a and R_b is, independently, a member selected from the group consisting of H, a primary hydrocarbyl group and a secondary hydrocarbyl group, particularly, H or a hydrocarbyl group containing from 1 to about 25 carbon atoms, and especially a lower alkyl group, and n ranges from 1 to about 30, preferably, from 1 to about 4, and most preferably, 1. Of course, it is obvious that when R_a is H, then n equals 1.

[0047] Particularly preferred is where each hydrocarbyl group is, independently, a primary alkyl group, especially one containing from 1 to about 6 carbon atoms.

[0048] In another embodiment, the hydroxylamine has the general formula



[0049] wherein each R_c is, independently, H or a hydrocarbyl group, particularly, H or a lower alkyl group, each R_d is, independently, a lower alkylene group, preferably an ethylene or propylene group, most preferably, an ethylene group, and x ranges from 1 to about 29, preferably, from 1 to about 5. In another embodiment the general formula above has at least one of the N with an R_c group substituted for the OH group.

[0050] Methods for preparing hydroxylamines are known in the art.

[0051] In another preferred embodiment, the combustion modifiers comprises a hydroxylamine salt. Hydroxylamines from which the hydroxylamine salts are derived are the same as the hydroxylamines described hereinabove. Typically, the salt is at least one member of the group consisting of nitrates, sulfates, sulfonates, carbonates and carboxylates. Nitrates and carbonates are preferred with nitrates being particularly preferred. The salts are generally obtained by contacting a hydroxylamine with an appropriate acid, optionally, in the presence of a diluent. Many of these salts are commercially available, for example, from chemical supply houses such as Aldrich Chemical Company, Milwaukee, Wis., USA.

[0052] Nitro Compounds

[0053] At least one nitro compound hydrocarbon fuel can be used as a combustion modifier for the aqueous hydrocarbon fuel. The nitro compounds can be aliphatic or aromatic and may be mono- or polynitro-compounds. Polynitro compounds are preferred. Useful nitro compounds include purely hydrocarbon and substituted hydrocarbon nitro compounds. Examples of aromatic nitro compounds include nitrobenzene, dinitrotoluene, trinitrotoluene, nitrated phenols, for example butyl-dinitrophenol, and aliphatic compounds, preferably alkyl compounds, including substituted alkyl compounds, preferably purely alkyl compounds and more preferably, lower alkyl compounds. Examples include

nitromethane, nitropropane, dinitropropane, hydroxymethyl nitropropane, 1,3-dimorpholino-2-nitropropane, 1,2-dinitropropane, 2-methyl-2-nitropropane, bis(2-nitropropyl)methane and the like.

[0054] Compounds Containing Strained Ring

[0055] At least one compound having at least one strained ring group containing from 3 to 5 ring atoms can be used as a combustion modifier for the aqueous hydrocarbon fuel. The compounds can be monocyclic or polycyclic compounds, having fused ring systems and/or ring systems connected directly or via a bridge group, and/or spiro-compounds which polycyclic compounds have, for example, from two to four rings and which are unsubstituted or substituted and can contain heteroatoms (such as, for example, O, S, or N in one or more rings and/or can contain fused thereto aromatic or heteroaromatic rings, for example o-phenylene, o-naphthylene, o-pyridinylene or o-pyrimidinylene. The individual strained cyclic rings contain from 3 to 5, preferably 3 to 4, more often 3, ring members. These include cyclopropyl groups, cyclobutyl groups and cyclopentyl groups as well as heteroatom-containing analogues thereof.

[0056] As defined herein, 'strained ring' compounds include 3 and 4 membered rings containing olefinic unsaturation, but do not include olefinically unsaturated 5-membered rings. Preferably, the strained ring compounds used in this invention are substantially saturated and most preferably are free of olefinic unsaturation. 'Substantially saturated' means no more than 5% of the strained ring compounds contain ring unsaturated bonds. The expression 'free of olefinic unsaturation' means the strained ring compounds contain no more than an impurity amount of unsaturated ring components.

[0057] In one embodiment, the ring group is a hydrocarbon group substantially free of heteroatoms. Examples include cyclopropyl methanol, cyclobutyl amine and cyclobutyl hydroxylamine.

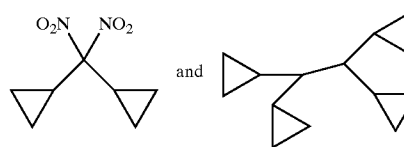
[0058] In another embodiment, the ring contains one or more heteroatoms as mentioned hereinabove. Such heteroatom containing compounds may be illustrated by, for example, furans, dioxolanes, oxetanes, epoxides, aziridines, and thio-analogues thereof and compounds containing one or more of these groups.

[0059] Heterocyclic ring groups contain at least 2 carbon atoms and preferably no more than 2 heteroatoms, often but one heteroatom.

[0060] Preferred heteroatoms are oxygen and nitrogen, although compounds containing sulfur heteroatoms are also useful. Examples of preferred oxygen containing compounds or groups are dioxolane, epoxide, oxetane and furan. Specific examples include 3,3-dimethyloxetane, 1-methoxy-2-methylpropylene oxide, 2-methoxydioxolane and 2,5-dimethoxytetrahydrofuran, preferably, 3,3-dimethyloxetane

[0061] As noted hereinabove, the compound may contain more than one strained ring group, which groups may be present as fused, linked, Spiro- etc groups. Preferably, such compounds contain 2 strained ring groups.

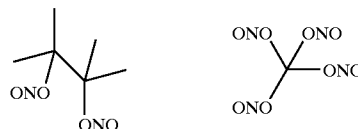
[0062] In one preferred embodiment, the compounds containing two or more strained ring groups are substantially free of heteroatoms. Examples include dicyclopropyl ketone, dicyclobutyl ketone and compounds of the formula



[0063] The strained ring group containing compound is typically used in amounts ranging from about 50 to about 50,000 parts by weight per million parts by weight (ppm) of fuel, more often from about 500 to about 20,000 ppm, typically about 5,000 ppm and in another embodiment, about 2500 ppm.

[0064] Nitrites

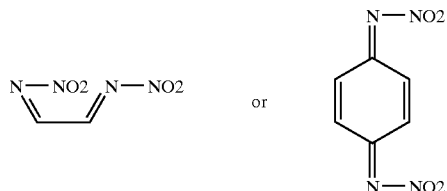
[0065] The nitrites are combustion modifiers for the aqueous hydrocarbon fuel. At least one nitrite compound can be used as a combustion modifier for the aqueous hydrocarbon fuel. The nitrite compounds can be aliphatic or aromatic and may be mono- or polynitrite compounds or combinations thereof. Polynitrite compounds are preferred. Useful nitrite compounds include but are not limited to purely hydrocarbon and substituted hydrocarbon nitrite compounds or combinations thereof. Examples of aromatic nitrite compounds include but are not limited to benzyl nitrite, toluene dinitrite and aliphatic compounds and the like; in one embodiment alkyl compounds, including but not limited to substituted alkyl compounds and the like; in one embodiment purely alkyl compounds; and in one embodiment, lower alkyl compounds; combinations thereof. Examples of the nitrites as combustion modifiers include but are not limited to methyl nitrite, propyl dinitrite, hydroxymethyl propyl nitrite and, 1,3-dimorpholino-2-nitrite propane and combinations thereof. The nitrites are combustion modifiers for the aqueous hydrocarbon fuel and include but are not limited to 2,3-dimethyl-2,3 dinitrite butane nitrite, pentaerythritol tetra nitrite, and nitrite compounds of the formula:



[0066] Nitramines

[0067] At least one nitramine compound can be used as a combustion modifier for the aqueous hydrocarbon fuel. The nitramine compounds can be aliphatic or aromatic and may be mono- or polynitramine-compounds. Polynitramine compounds are preferred. Useful nitramine compounds include but are not limited to purely hydrocarbon and substituted hydrocarbon nitramine compounds. Examples of aromatic nitro compounds include benzyl nitramine, phenyl nitramines, and aliphatic compounds, preferably alkyl compounds, including substituted alkyl compounds, preferably purely alkyl compounds and more preferably, lower alkyl compounds. Examples include but are not limited to methyl nitramine 2-propyl nitramine and more preferable the dinit-

ramines, for example ammonium dinitramine and ethylene dinitramine. And dinitramines for example



[0068] molecules with two or more different functional groups.

[0069] At least one compound can be used as a combustion modifier that has more than one functional group for the aqueous hydrocarbon fuel. The disubstituted compounds can be aliphatic or aromatic and may be mono- or polynitramine-compounds in combination with a mono- or polynitro-compound. Useful disubstituted compounds include purely hydrocarbon and substituted hydrocarbon nitramine compounds with nitro or nitrate groups. Examples of disubstituted compounds include but are not limited to 2-nitrophenol-3-nitramine, and aliphatic compounds, preferably alkyl compounds, including substituted alkyl compounds, preferably purely alkyl compounds and more preferably, lower alkyl compounds. Examples include but are not limited to 2,2-, nitro-nitramine propane. More preferable would be 2,4,6-trinitrophenylnitraminoethyl nitrate.

[0070] The Hydrocarbon Fuel

[0071] The liquid hydrocarbon fuel comprises hydrocarbonaceous petroleum distillate fuel, non-hydrocarbonaceous materials that include but are not limited to water, oils, liquid fuels derived from vegetables, liquid fuels derived from minerals and mixtures thereof. Hydrocarbon based fuels are those fuels that contain hydrocarbon groups, and especially those that are substantially hydrocarbon, that is, those fuels derived from mineral oil sources such as gasoline and middle distillate oils, for example, diesel oil and heating oils, synthetic hydrocarbon fuels such as polyolefins, alkylated aromatic hydrocarbon group containing fuels, hydrocarbon fuels obtained by the Fischer-Tropsch process, and others. Mixtures of hydrocarbon based fuels and oxygenates include mixtures of any of the aforementioned hydrocarbon based fuels with any of alkanols, especially lower alkanols, and ethers, for example, methyl-t-butyl ether, methyl-t-amyl ether, dimethoxymethane and diethoxymethane, and particularly, lower alkanols such as ethanol. The liquid hydrocarbon fuel may be any and all hydrocarbonaceous petroleum distillate fuels including not limited to motor gasoline as defined by ASTM Specification D439 or diesel fuel or fuel oil as defined by ASTM Specification D396 or the like (kerosene, naphtha, aliphatics and paraffinics). The liquid hydrocarbon fuels comprising non-hydrocarbonaceous materials include but are not limited to alcohols such as methanol, ethanol and the like, ethers such as diethyl ether, methyl ethyl ether and the like, organo-nitro compounds and the like; liquid fuels derived from vegetable or mineral sources such as corn, alfalfa, shale, coal and the like. The liquid hydrocarbon fuels also include mixtures of one or more hydrocarbonaceous fuels and one or more non-hydrocarbonaceous materials. Examples of such mixtures are

combinations of gasoline and ethanol and of diesel fuel and ether. In one embodiment, the liquid hydrocarbon fuel is any gasoline. Generally, gasoline is a mixture of hydrocarbons having an ASTM distillation range from about 60° C. at the 10% distillation point to about 205° C. at the 90% distillation point. In one embodiment, the gasoline is a chlorine-free or low-chlorine gasoline characterized by a chlorine content of no more than about 10 ppm.

[0072] In one embodiment, the liquid hydrocarbon fuel is any diesel fuel. Diesel fuels typically have a 90% point distillation temperature in the range of about 300° C. to about 390° C., and in one embodiment about 330° C. to about 350° C. The viscosity for these fuels typically ranges from about 1.3 to about 24 centistokes at 40° C. The diesel fuels can be classified as any of Grade Nos. 1-D, 2-D or 4-D as specified in ASTM D975. The diesel fuels may contain alcohols and esters. In one embodiment the diesel fuel has a sulfur content of up to about 0.05% by weight (low-sulfur diesel fuel) as determined by the test method specified in ASTM D2622-87. In one embodiment, the diesel fuel is a chlorine-free or low-chlorine diesel fuel characterized by chlorine content of no more than about 10 ppm.

[0073] The liquid hydrocarbon fuel is present in the aqueous hydrocarbon fuel emulsion at a concentration of about 50% to about 95% by weight, and in one embodiment about 60% to about 95% by weight, and in one embodiment about 65% to about 85% by weight, and in one embodiment about 80% to about 90% by weight of the aqueous hydrocarbon fuel emulsion.

[0074] The Water

[0075] The water used in the aqueous hydrocarbon fuel emulsion may be taken from any source. The water includes but is not limited to tap, deionized, demineralized, purified, for example, using reverse osmosis or distillation, and the like. The water includes water mixtures that further includes antifreeze such as alcohols and glycols, ammonium salts such as ammonium nitrate, ammonium maleate, ammonium acetate and the like, and combinations thereof.

[0076] The water may be present in the aqueous hydrocarbon fuel emulsions at a concentration of about 1% to about 50% by weight, and in one embodiment about 5% to about 50% by weight, and in one embodiment about 5% to about 40% by weight, and in one embodiment about 5% to about 25% by weight, and in one embodiment about 10% to about 20% water.

[0077] The Emulsifier

[0078] The emulsifier is any suitable emulsifier for emulsifying the aqueous hydrocarbon fuel emulsion so that there is a discontinuous aqueous phase having a mean diameter droplets of 1.0 micron or less in a continuous hydrocarbon fuel phase. Preferred emulsifiers for the aqueous hydrocarbon fuel comprise:

[0079] (i) at least one fuel-soluble product made by reacting at least one hydrocarbyl-substituted carboxylic acid acylating agent with ammonia or an amine, the hydrocarbyl substituent of said acylating agent having about 50 to about 500 carbon atoms;

[0080] (ii) at least one of an ionic or a nonionic compound having a hydrophilic-lipophilic balance (HLB) of about 1 to about 40;

- [0081] (iii) a mixture of (ii) with (i);
- [0082] (iv) a water-soluble compound selected from the group consisting of amine salts, ammonium salts, azide compounds, nitrate esters, nitramine, nitro-compounds, alkali metal salts, alkaline earth metal salts, in combination with (i), (ii), (iii), (v), (vii) or combinations thereof;
- [0083] (v) the reaction product of polyacidic polymer with at least one fuel soluble product made by reacting at least one hydrocarbyl-substituted carboxylic acid acylating agent with ammonia, an amine, a polyamine, alkanol amine, or hydroxy amines;
- [0084] (vi) an amino alkylphenol which is made by reacting an alkylphenol, an aldehyde and an amine resulting in an amino alkylphenol, or
- [0085] (vii) the combination of (vi) and (i), (ii), (iii), (iv), (v) or combination thereof.
- [0086] The emulsifier may be present in the aqueous hydrocarbon fuel emulsion at a concentration of about 0.05% to about 20% by weight, in another embodiment about 0.05% to about 10% by weight, in another embodiment about 0.1% to about 5% by weight, and in a further embodiment of about 0.01% to about 3% by weight of the aqueous hydrocarbon fuel emulsion.
- [0087] Fuel Soluble Product (i)
- [0088] The fuel-soluble product (i) may be at least one fuel-soluble product made by reacting at least one hydrocarbyl-substituted carboxylic acid acylating agent with ammonia or an amine including but not limited to alkanol amines, hydroxy amines, and the like, the hydrocarbyl substituent of said acylating agent having about 50 to about 500 carbon atoms, and is described in greater detail in U.S. Ser. No. 09/761,482, An Emulsifier For An Aqueous Hydrocarbon Fuel, incorporated by reference herein.
- [0089] The hydrocarbyl-substituted carboxylic acid acylating agents may be carboxylic acids or reactive equivalents of such acids. The reactive equivalents may be acid halides, anhydrides, or esters, including partial esters and the like. The hydrocarbyl substituents for these carboxylic acid acylating agents may contain from about 50 to about 500 carbon atoms, and in one embodiment about 50 to about 300 carbon atoms, and in one embodiment about 60 to about 200 carbon atoms. In one embodiment, the hydrocarbyl substituents of these acylating agents have number average molecular weights of about 700 to about 3000, and in one embodiment about 900 to about 2300.
- [0090] In one embodiment, the hydrocarbyl-substituted carboxylic acid acylating agent is a polyisobutene-substituted succinic anhydride, the polyisobutene substituent having a number average molecular weight of about 1,500 to about 3,000, in one embodiment about 1,800 to about 2,300, in one embodiment about 700 to about 1300, in one embodiment about 800 to about 1000, said first polyisobutene-substituted succinic anhydride being characterized by about 1.3 to about 2.5, and in one embodiment about 1.7 to about 2.1 In one embodiment, the hydrocarbyl-substituted carboxylic acid acylating agent is a polyisobutene-substituted succinic anhydride, the polyisobutene substituent having a number average molecular weight of about 1,500 to about

3,000, and in one embodiment about 1,800 to about 2,300, said first polyisobutene-substituted succinic anhydride being characterized by about 1.3 to about 2.5, and in one embodiment about 1.7 to about 2.1, in one embodiment about 1.0 to about 1.3, and in one embodiment about 1.0 to about 1.2 succinic groups per equivalent weight of the polyisobutene substituent.

[0091] The fuel-soluble product (i) may be formed using ammonia, an amine and/or metals such as Na, K, Ca, and the like. The amines useful for reacting with the acylating agent to form the product (i) including but are not limited to, monoamines, polyamines, alkanol amines, hydroxy amines, and mixtures thereof, and amines may be primary, secondary or tertiary amines.

[0092] Examples of primary and secondary monoamines include ethylamine, diethylamine, n-butylamine, di-n-butylamine, allylamine, isobutylamine, cocoamine, stearylamine, laurylamine, methyl laurylamine, oleylamine, N-methyl octylamine, dodecylamine, and octadecylamine. Suitable examples of tertiary monoamines include trimethylamine, triethylamine, tripropylamine, tributylamine, monoethyl dimethylamine, dimethylpropylamine, dimethylbutylamine, dimethylpentylamine, dimethylhexylamine, dimethylheptylamine, and dimethyloctylamine.

[0093] The amines include but are not limited to hydroxy-alkylamines, such as mono-, di-, and triethanolamine, dimethylethanol amine, diethylethanol amine, di-(3-hydroxy propyl) amine, N-(3-hydroxybutyl) amine, N-(4-hydroxy butyl) amine, and N,N-di-(2-hydroxypropyl) amine; alkylene polyamines such as methylene polyamines, ethylene polyamines, butylene polyamines, propylene polyamines, pentylene polyamines, and the like. Specific examples of such polyamines include ethylene diamine, diethylene triamine, triethylene tetramine, propylene diamine, trimethylene diamine, tripropylene tetramine, tetraethylene pentamine, hexaethylene heptamine, pentaethylene hexamine, or a mixture of two or more thereof; ethylene polyamine; or a polyamine bottoms or a heavy polyamine. The fuel-soluble product (i) may be a salt, an ester, an ester/salt, an amide, an imide, or a combination of two or more thereof.

[0094] The Ionic or Nonionic Compound (ii)

[0095] The ionic or nonionic compound (ii) has a hydrophilic-lipophilic balance (HLB, which refers to the size and strength of the polar (hydrophilic) and non-polar (lipophilic) groups on the surfactant molecule) in the range of about 1 to about 40, and in one embodiment about 4 to about 15 and is described in greater detail in U.S. Ser. No. 09/761,482, An Emulsifier For An Aqueous Hydrocarbon Fuel, incorporated by reference herein. Examples of these compounds are disclosed in *McCutcheon's Emulsifiers and Detergents*, 1998, North American & International Edition. Pages 1-235 of the North American Edition and pages 1-199 of the International Edition are incorporated herein by reference for their disclosure of such ionic and nonionic compounds having an HLB in the range of about 1 to about 40, in one embodiment about 1 to about 30, in one embodiment about 1 to 20, and in another embodiment about 1 to about 10. Useful compounds include alkanolamides, carboxylates including amine salts, metallic salts and the like, alkylaryl-sulfonates, amine oxides, poly(oxyalkylene) compounds, including block copolymers comprising alkylene oxide repeat units, carboxylated alcohol ethoxylates, ethoxylated

alcohols, ethoxylated alkylphenols, ethoxylated amines and amides, ethoxylated fatty acids, ethoxylated fatty esters and oils, fatty esters, fatty acid amides, including but not limited to amides from tall oil fatty acids and polyamides, glycerol esters, glycol esters, sorbitan esters, imidazoline derivatives, lecithin and derivatives, lignin and derivatives, monoglycerides and derivatives, olefin sulfonates, phosphate esters and derivatives, propoxylated and ethoxylated fatty acids or alcohols or alkylphenols, sorbitan derivatives, sucrose esters and derivatives, sulfates or alcohols or ethoxylated alcohols or fatty esters, sulfonates of dodecyl and tridecyl benzenes or condensed naphthalenes or petroleum, sulfosuccinates and derivatives, and tridecyl and dodecyl benzene sulfonic acids. In the preferred embodiment of an amine salt, it is a C₈-C₂₀ alkenyl succinic ester amine salts such as the reaction product of an alkenyl succinic anhydride with alkanol amine such as N,N-dimethylethanol amine, N,N-diethylethanol amine or the like.

[0096] Emulsifier Mixture (iii)

[0097] A mixture of (i) and (ii) is described in greater detail in U.S. Ser. No. 09/761,482, An Emulsifier For An Aqueous Hydrocarbon Fuel, incorporated by reference herein. The mixture of (i) and (ii) is useful as an emulsifier for the aqueous hydrocarbon fuel.

[0098] The Water-Soluble Compound (iv)

[0099] The water-soluble compound may be an amine salt, ammonium salt, azide compound, nitro compound, alkali metal salt, alkaline earth metal salt, or mixtures of two or more thereof and is described in greater detail in U.S. Ser. No. 09/761,482, An Emulsifier For An Aqueous Hydrocarbon Fuel, incorporated by reference herein. These compounds are distinct from the fuel-soluble product (i) and the ionic or nonionic compound (ii) discussed above. These water-soluble compounds include organic amine nitrates, nitrate esters, azides, nitramines and nitro compounds. Also included are alkali and alkaline earth metal carbonates, sulfates, sulfides, sulfonates, and the like.

[0100] Particularly useful are the amine or ammonium salts such as ammonium nitrate, ammonium acetate, methylammonium nitrate, methylammonium acetate, ethylene diamine diacetate; urea nitrate; urea; guanidinium nitrate; and combinations thereof.

[0101] Emulsifier (v)

[0102] In one embodiment the emulsifier (v) is the reaction product of A) a polyacidic polymer, B) at least one fuel soluble product made by reacting at least one hydrocarbyl-substituted carboxylic acid acylating agent, and C) a hydroxy amine and/or a polyamine and is described in greater detail in U.S. Ser. No. 09/761,482, An Emulsifier For An Aqueous Hydrocarbon Fuel, incorporated by reference herein.

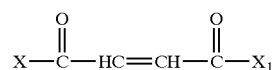
[0103] The fuel soluble product is made by reacting at least one hydrocarbyl-substituted carboxylic agent with a hydroxy amine and/or polyamine and is described earlier in the specification.

[0104] The polyacidic polymers used in the reaction include but are not limited to C₄ to C₃₀, preferably C₈ to C₂₀ olefin/maleic anhydride copolymers. The alpha-olefins include 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene,

1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-eicosene, 1-docosene, 1-triacontene, and the like. the alpha olefin fractions that are useful include C₁₅₋₁₈ alpha-olefins, C₁₂₋₁₆ alpha-olefins, C₁₄₋₁₆ alpha-olefins, C₁₄₋₁₈ alpha-olefins, C₁₆₋₁₈ alpha-olefins, C₁₈₋₂₄ alpha-olefins, C₁₈₋₃₀ alpha-olefins, and the like. Mixtures of two or more of any of the foregoing alpha-olefins or alpha-olefin fractions may be used.

[0105] Other polyacidic polymers suitable for reaction include but are not limited to maleic anhydride/styrene copolymers; poly-maleic anhydride; acrylic and methacrylic acid containing polymers; poly-(alkyl)acrylates; reaction products of maleic anhydride with polymers with multiple double bonds; and combinations thereof. The preferred is polyacidic polymer C₁₈ [1-octadecene]/maleic anhydride copolymer.

[0106] In another embodiment the polyacidic polymer is a copolymer of an olefin and a monomer having the structure:



[0107] wherein X and X₁ are the same or different provided that at least one of X and X₁ is such that the copolymer can function as a carboxylic acylating agent.

[0108] The olefin includes a polymerizable olefin characterized by the presence of one or more ethylenically unsaturated groups. The olefin monomers include but are not limited to 1-hexene, octadecene-1 and diisobutylene. The olefin preferably is a C₄-C₃₀ olefin.

[0109] The emulsifier produced from the reaction product of the polyacidic polymer with the fuel soluble product (i) comprises about 25% to about 95% of fuel soluble product and about 0.1% to about 50% of the polyacidic polymer; preferably about 50% to about 92% fuel soluble product and about 1% to about 20% of the polyacidic polymer, and most preferably about 70% to about 90% of fuel soluble product and about 5% to about 10% of the polyacidic polymer. In one embodiment the emulsifier is described as a polyalkenyl succinimide crosslinked with an olefin/maleic anhydride copolymer.

[0110] Amino Alkylphenol Emulsifier (vi) and (vii)

[0111] The amino alkyl emulsifier is comprised of the reaction product of an alkylphenol, an aldehyde, and an amine resulting in amino alkylphenol and is described in greater detail in U.S. Ser. No. 09/977,742, A Continuous Process for Making an Aqueous Hydrocarbon Emulsion, incorporated by reference herein. The amino alkylphenol can be made by (a) the reaction of alkylphenol directly with an aldehyde and an amine resulting in an alkylphenol monomer connected by a methylene group to an amine, (b) the reaction of an alkylphenol with an aldehyde resulting in an oligomer wherein the alkylphenols are bridged with methylene groups, the oligomer is then reacted with more aldehyde and an amine to give a Mannich product, or (c) a mixture of (a) and (b)

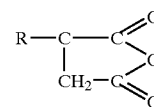
[0112] The alkylphenols have an alkyl group selected from C₁ to C₂₀₀, preferably C₆ to C₁₇₀ wherein the alkyl group is either linear, branched or a combination thereof. The alkylphenols include, but are not limited to, polypropylphenol, polybutylphenol, poly(isobutenyl)phenol, polyamylphenol, tetrapropylphenol, similarly substituted phenols and the like. The preferred alkylphenols are tetrapropenylphenol and poly(isobutenyl)phenol. For example, in place of the phenol, alkyl-substituted compounds of resorcinol, hydroquinone, catechol, cresol, xylene, amyl phenol, hydroxydiphenyl, benzylphenol, phenylethylphenol, methylhydroxydiphenyl, alpha and beta naphthol, alpha and beta methylnaphthol, tolylnaphthol, xylylnaphthol, benzylnaphthol, anthranol, phenylmethylnaphthol, phenanthrol, monomethyl ether of catechol, phenoxyphenol, chlorophenol, hydroxyphenyl sulfides and the like may be used.

[0113] The aldehydes include, but are not limited to, aliphatic aldehydes, such as formaldehyde; acetaldehyde; aldol (β -hydroxy butyraldehyde); aromatic aldehydes, such as benzaldehyde; heterocyclic aldehydes, such as furfural, and the like. The aldehyde may contain a substituent group such as hydroxyl, halogen, nitro and the like; in which the substituent does not take a major part in the reaction. The preferred aldehyde is formaldehyde.

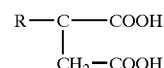
[0114] The amines are those which contain an amino group characterized by the presence of at least one active hydrogen atom. The amines may be primary amino groups, secondary amino groups, or combinations of primary and secondary amino groups.

[0115] The amines include, but are not limited to, alkanolamines such as monoethanol amine, diethanolamine, N-(2-aminoethyl) ethanolamine and the like; di- and polyamine (polyalkylene amines) such as dimethylaminopropylamine, 3-aminopropyl morpholine, ethylenediamine, diethylenetriamine, triethylene tetramine, tetraethylene pentamine and the like including distillation bottoms such as HPAX (commercially available from The Union Carbide Corporation), E-100 (commercially available from Dow Chemical Co.), and the like; polyalkyl polyamines; propylenediamine, the aromatic amines such as o-, m- and p-phenylene diamine, diamino naphthalenes; the acid-substituted polyalkylpolyamines, such as N-acetyl tetraethylenepentamine, and the corresponding formyl-, propionyl-, butyryl-, and the like N-substituted compounds; and the corresponding cyclized compounds formed therefrom, such as the N-alkyl amines of imidazolidine and pyrimidine. (Secondary heterocyclic amines that are suitable are those characterized by attachment of a hydrogen atom to a nitrogen atom in the heterocyclic group such as morpholine, thiomorpholine, pyrrole, pyrrolidine, indole, pyrazole, pyrazoline, pyrazolidine, imidazole, imidazoline, imidazolidine, piperidine, phenoxazine, phentiazine and their substituted analogs. Substituent groups attached to the carbon atoms of these amines are typified by alkyl, aryl, alkaryl, aralkyl, cycloalkyl, and amino compounds referred to above.)

[0116] The "amine" includes, but is not to be limited, to the product obtained by reacting an alkenyl succinic anhydride such as succinic anhydride of the formula



[0117] or alkenyl succinic acid such as succinic acids of the formula



[0118] with the amines of the foregoing paragraph.

[0119] In the above formulae, R is an alkylene group. The alkenyl radical can be straight-chain or branched-chain; and it can be saturated at the point of unsaturation by the addition of a substance that adds to olefinic double bonds, such as hydrogen, sulfur, bromine, chlorine, or iodine. There must be at least two carbon atoms in the alkenyl radical, but there is no real upper limit to the number of carbon atoms therein. The alkenyl succinic acid anhydrides and the alkenyl succinic acids are interchangeable for the purposes of the present invention. Nonlimiting examples of the alkenyl succinic acid anhydride component are ethenyl succinic acid anhydride; ethenyl succinic acid; ethyl succinic acid anhydride; propenyl succinic acid anhydride; sulfurized propenyl succinic acid anhydride; butenyl succinic acid; 2-methylbutenyl succinic acid anhydride; 1,2-dichloropentyl succinic acid anhydride; hexenyl succinic acid anhydride; hexyl succinic acid; sulfurized 3-methylpentyl succinic acid anhydride; 2,3-dimethylbutenyl succinic acid anhydride; 3,3-dimethylbutenyl succinic acid; 1,2-dibromo-2-ethylbutyl succinic acid; heptenyl succinic acid anhydride; 1,2-diiodooctyl succinic acid; octenyl succinic acid anhydride; diisobutenyl succinic acid anhydride; 2-methylheptenyl succinic acid anhydride; 4-ethylhexenyl succinic acid; 2-isopropylpentenyl succinic acid anhydride; nonenyl succinic acid anhydride; 2-propylhexenyl succinic acid anhydride; decenyl succinic acid; decenyl succinic acid anhydride; 5-methyl-2-isopropyl-hexenyl succinic acid anhydride; 1,2-dibromo-2-ethyloctenyl succinic acid anhydride; decyl succinic acid anhydride; undecenyl succinic acid anhydride; 1,2-dichloroundecyl succinic acid; 3-ethyl-2-t-butylpentenyl succinic acid anhydride; tetrapropenyl succinic acid anhydride; tetrapropenyl succinic acid; triisobutenyl succinic acid anhydride, 2-propyl-nonenyl succinic acid anhydride, 3-butyloctenyl succinic acid anhydride; tridecenyl succinic acid anhydride; tetradecenyl succinic acid anhydride; hexadecenyl succinic acid anhydride; sulfurized octadecenyl succinic acid; octadecyl succinic acid anhydride; 1,2-dibromo-2-methylpentadecenyl succinic acid anhydride; 8-propylpentadecyl succinic acid anhydride; eicosenyl succinic acid anhydride; 1,2-dichloro-2-methylnonadecenyl succinic acid anhydride; 2-octyldodecenyl succinic acid; 1,2-diiodotetracosenyl succinic acid anhydride; hexacosenyl succinic acid; hexacosenyl succinic acid anhydride; hentriacontenyl succinic acid anhydride and combinations thereof. In general, alkenyl succinic acid anhydrides having from about 8 to about 35, and preferably, from about 9 to

about 18 carbon atoms in the alkenyl group. Methods for preparing the alkenyl succinic acid anhydrides are known to those familiar with the art, the most feasible method comprising the reaction of an olefin with maleic acid anhydride.

[0120] The reaction is prepared by any known method such as an emulsion, a solution, a suspension, a continuous additive bulk process or the like. The reaction is carried out under conditions that provide for the formation of the desired product.

[0121] Additional Additives

[0122] In addition to the foregoing materials, other fuel additives that are known to those of skill in the art may be used in the aqueous hydrocarbon fuel emulsions of the invention. These include but are not limited to dyes, rust inhibitors such as alkylated succinic acids and anhydrides, bacteriostatic agents, gum inhibitors, metal deactivators, upper cylinder lubricants, and the like.

[0123] The water fuel compositions of the present invention may contain other additives that are known to those skilled in the art. These can include combustion modifiers, such as octane number enhancers for gasoline, for example, anti-knock agents such as tetra-alkyl lead compounds and certain ethers, cetane number improvers for diesel fuels such as alkyl nitrates, lead scavengers such as halo-alkanes, dyes, antioxidants such as hindered phenols, lubricity agents, cold flow improvers, dispersants, surfactants, rust inhibitors such as alkylated succinic acids and anhydrides and derivatives thereof, bacteriostatic agents, auxiliary dispersants and detergents, gum inhibitors, fluidizers, metal deactivators, demulsifiers, anti-icing agents and the like. The fuel compositions of this invention may be lead-containing or lead-free fuels. Preferred are lead-free fuels.

[0124] The total concentration of additives, including the emulsifiers, in the aqueous hydrocarbon fuel emulsions of the invention may range from about 0.05 to about 30% by weight, and in one embodiment about 0.1 to about 20% by weight, and in one embodiment about 0.1 to about 15% by weight, and in one embodiment about 0.1 to about 10% by weight, and in one embodiment about 0.1 to about 5% by weight.

[0125] Antifreeze Agent

[0126] The water-fuel emulsions of the invention may additionally contain an antifreeze agent. The antifreeze agent is typically an alcohol. Examples include but are not limited to ethylene glycol, propylene glycol, methanol, ethanol, glycerol and mixtures of two or more thereof. The

antifreeze agent is typically used at a concentration sufficient to prevent freezing of the water used in the water-fuel emulsions. The concentration is therefore dependent upon the temperature at which the fuel is stored or used. In one embodiment, the concentration is at a level of up to about 20% by weight based on the weight of the water-fuel emulsion, and in one embodiment about 0.1 to about 20% by weight, and in one embodiment about 1 to about 10% by weight.

[0127] The Engines

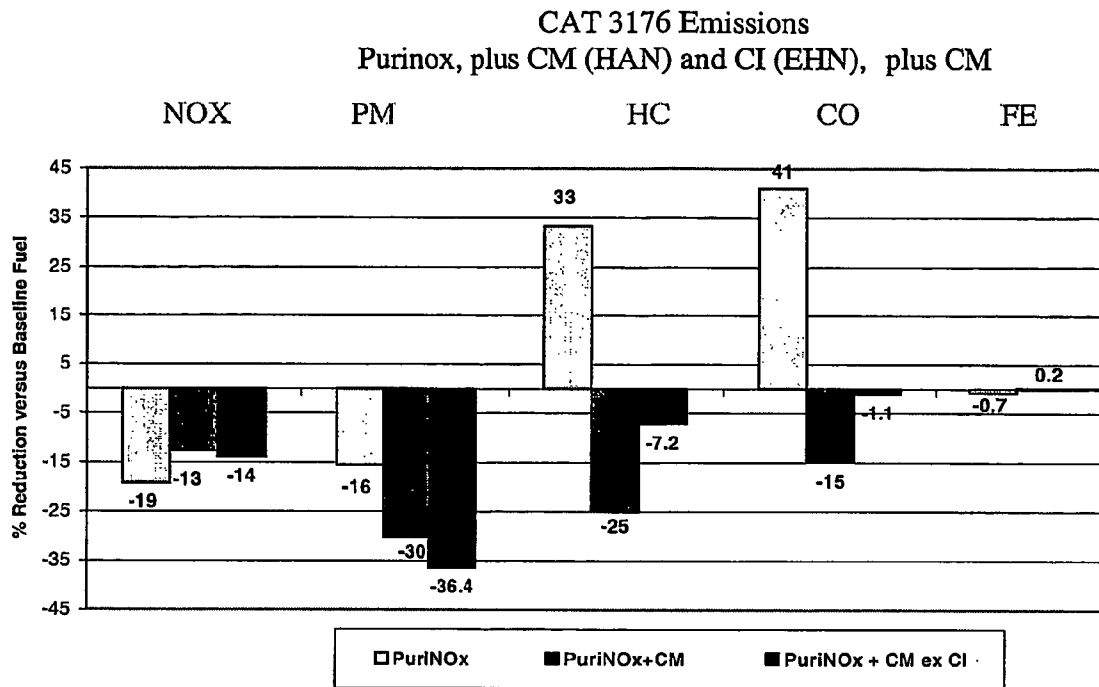
[0128] The engines that may be operated in accordance with the invention include all compression-ignition (internal combustion) engines for both mobile (including locomotive and marine) and stationary power plants. These include engines that use diesel, gasoline, and the like. The engines that can be used include but are not limited to those used in automobiles, trucks such as all classes of truck, buses such as urban buses, locomotives, light and heavy duty diesel engines, stationary engines and the like. Included are on- and off-highway engines, including new engines as well as in-use engines. These include diesel engines of the two-stroke-per-cycle and four-stroke-per-cycle types.

Specific Embodiment

[0129] The following examples demonstrate the advantages of the present invention.

EXAMPLE 1

[0130] A fuel composition (Purinox) contains 86% diesel fuel, 20% water, 3% of an emulsifier packages containing 0.28% N,N-diethylhydroxylamine hexadecyl substituted succinic ester-salt prepared by reacting one mole each of hexadecyl substituted succinic anhydride with dimethylethanolamine, 0.75% 2-ethylhexy nitrate, 1.2% % N,N-diethylhydroxylamine hexadecyl substituted succinic ester-salt prepared by reacting one mole each of 2000 MW Polyisobutylene hexadecyl substituted succinic anhydride with dimethylethanolamine, 0.5% ammonium nitrate, and 0.6% substituted succinimide by reacting one mole each of 2000 MW Polyisobutylene and hexadecyl substituted succinic anhydrides with N,N-triethyltetramine; to which emulsion is added 1 part hydroxylamine nitrate (as sufficient 82% aqueous solution to provide 0.85 parts, the remaining water contributing to the 18% total water). This above fuel was tested in a Caterpillar 3176 at South West Research Institute. The engine was operated at an 8 mode steady state test simulating the Federal test procedure for heavy-duty engines. The results on the emission test are shown below.



[0131] The above example demonstrates the emission result on three fuels as shown. The first fuel Purinox yielded a 19% reduction in NOX as compared to base fuel. Purinox also yielded a 16% decrease in Particulate Matter (PM) emissions. However, Purinox cause a 33% increase in Hydrocarbons (HC) as well as a 41% increase in carbon monoxide as compared to the base fuel. The second fuel labeled Purinox+CM is the Purinox fuel plus a 1% solution of Hydroxy Ammonium Nitrate (HAN) (82% concentrate in 18% water). This fuel yielded a 13% reduction in NOX, a 30% reduction in PM, a 25% decrease in HC and a 15 reduction in CO.

[0132] The third fuel had the same formulation as the second except 0.75% of 2-ethylhexyl nitrate was removed. It yielded a 14% reduction in NOX, a 36.4% reduction in PM, a 7.2% reduction in HC and a 1.1% reduction in CO.

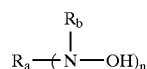
[0133] From the above descriptions and examples of the invention, those skilled in the art will perceive improvements, changes and modifications in the invention. Such improvements, changes and modifications within the skill in the art are intended to be covered by the appended claims.

What is claimed is:

1. An aqueous hydrocarbon fuel emulsion comprising, a liquid hydrocarbon fuel, water, at least one emulsifier and a nitrogen containing combustion modifier, wherein the nitrogen containing combustion modifier comprises:

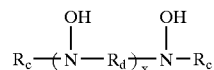
- (a) a nitro compound;
- (b) a hydroxylamine or a salt thereof wherein each hydroxylamino group of the hydroxylamine or salt thereof contains no more than one tertiary substituent;
- (c) a compound having at least one strained ring group containing from 3 to 5 ring atoms;
- (d) organic nitrites;
- (e) nitramines; and
- (f) mixtures thereof.

2. The fuel composition of claim 1 comprising a hydroxylamine wherein the hydroxylamine has the general formula



wherein each R_a and R_b is, independently, a member selected from the group consisting of H, a primary hydrocarbyl group and a secondary hydrocarbyl group containing from 1 to about 25 carbon atoms, and n ranges from 1 to about 30.

3. The fuel composition of claim 1 comprising a hydroxylamine wherein the hydroxylamine has the general formula



wherein each R_c is, independently, H or a hydrocarbyl group, each R_d is, independently, a lower alkylene group and x ranges from 1 to about 29.

4. The fuel composition of claim 1 comprising a hydroxylamine salt and wherein the salt is at least one member of the group consisting of nitrates, sulfates, sulfonates, carbonates and carboxylates.

5. The fuel composition of claim 1 wherein the nitro compounds are selected from the group consisting of aliphatic and aromatic nitro compounds.

6. The fuel composition of claim 1 wherein the nitro compound comprises at least one member of the group consisting of nitromethane, dinitrobutyl phenol, dinitropropane, nitromethane, nitropropane, trinitrotoluene, dinitrotoluene, 1,2-dinitropropanol and hydroxymethyl nitropropane.

7. The fuel composition of claim 1 wherein the ring group is a hydrocarbyl group substantially free of heteroatoms.

8. The fuel composition of claim 1 wherein the ring contains both carbon atoms and heteroatoms, said heteroatoms being selected from the group consisting of O, S and N.

9. The fuel composition of claim 7 wherein the ring contains at least two carbon atoms.

10. The fuel composition of claim 9 wherein the ring contains no more than 2 heteroatoms.

11. The fuel composition of claim 7 wherein the hydrocarbyl group is a cyclopropyl group, a cyclobutyl group or a cyclopentyl group.

12. The composition of claim 10 wherein the ring is an epoxy group, an oxetane group or a furan group.

13. The fuel composition of claim 1 wherein the compound comprises at least two strained ring groups.

14. The fuel composition of claim 11 wherein the compound comprises cyclopropyl methanol, cyclobutyl amine and cyclobutyl hydroxylamine.

15. The fuel composition of claim 12 wherein the compound is selected from the group consisting of 3,3-dimethyl-oxetane, 1-methoxy-2-methylpropylene oxide and 2,5-dimethoxytetrahydrofuran.

16. The fuel composition of claim 1 further comprising at least one component selected from the group consisting of (a) dispersants, (b) lubricity agents, (c) cold flow improvers, (d) fluidizers, (e) surfactants, (f) corrosion inhibitors and (g) mixtures thereof.

17. The fuel composition of claim 1 comprising a nitramine selected from the group consisting of benzyl nitramine, phenyl nitramine, methyl nitramine 2-propyl nitramine, ammonium dinitramine, ethylene dinitramine and combinations thereof.

18. A method from improving the combustion characteristics of an aqueous hydrocarbon fuel emulsion comprising incorporating therein a combustion improving amount of a nitrogen containing combustion improver selected from the group comprising:

- (a) a nitro compound;
- (b) a hydroxylamine or a salt thereof wherein each hydroxylamino group of the hydroxylamine or salt thereof contains no more than one tertiary substituent;
- (c) a compound having at least one strained ring group containing from 3 to 5 ring atoms;

(d) organic nitrites;

(e) nitramines; and

(f) mixtures thereof.

19. The method of claim 18 wherein the improved combustion characteristics comprise at least one of reduced particulate emissions, reduced NO_x emissions, reduce carbon monoxide emissions reduced hydrocarbon emissions or combinations thereof.

20. A method for operating an internal combustion engine comprising providing to the combustion chamber of said engine during operation thereof, the fuel composition of claim 1.

21. An aqueous hydrocarbon fuel emulsion comprising, a liquid hydrocarbon fuel, water, at least one emulsifier and a non-nitrogen containing combustion modifier containing at least one strained ring compound.

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