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(54) **FUEL COMPOSITIONS AND METHODS THEREOF**

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(57) **ABSTRACT**

Anti-knock gasoline fuel compositions are provided including anti-knock additives and mixtures thereof. The octane quality of fuel for an internal combustion engine improved with the anti-knock additives.

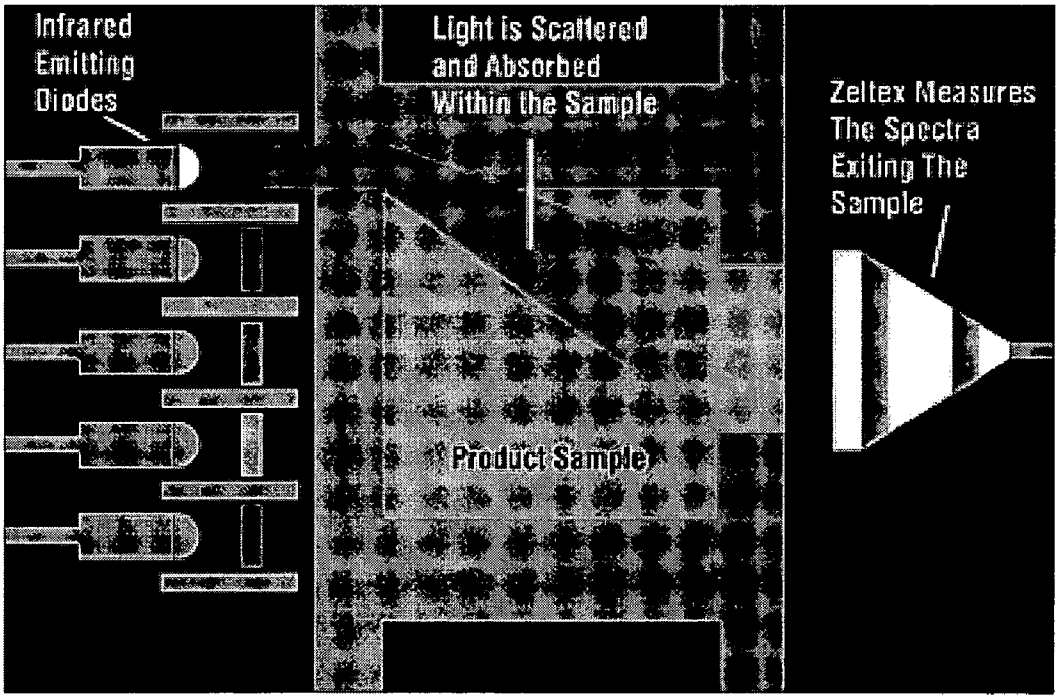

Infrared
Emitting
Diodes
Light is Scattered
and Absorbed
Within the Sample
Zeltex Measures
The Spectra
Exiting The
Sample
Product Sample

FIG. 1

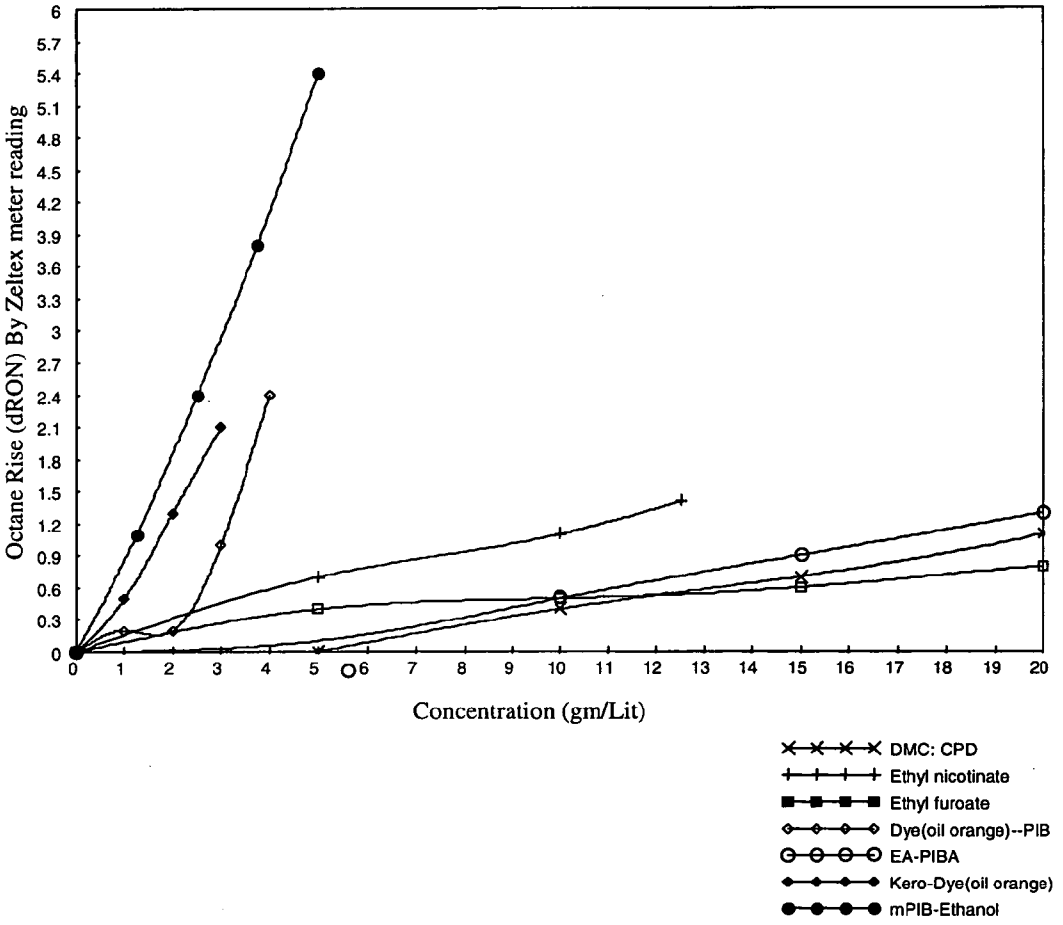

Octane Rise (dRON) By Zeltex meter reading
6
5.7
5.4
5.1
4.8
4.5
4.2
3.9
3.6
3.3
3
2.7
2.4
2.1
1.8
1.5
1.2
0.9
0.6
0.3
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
Concentration (gm/Lit)
DMC: CPD
Ethyl nicotinate
Ethyl furoate
Dye(oil orange)--PIB
EA-PIBA
Kero-Dye(oil orange)
mPIB-Ethanol

FIG. 2

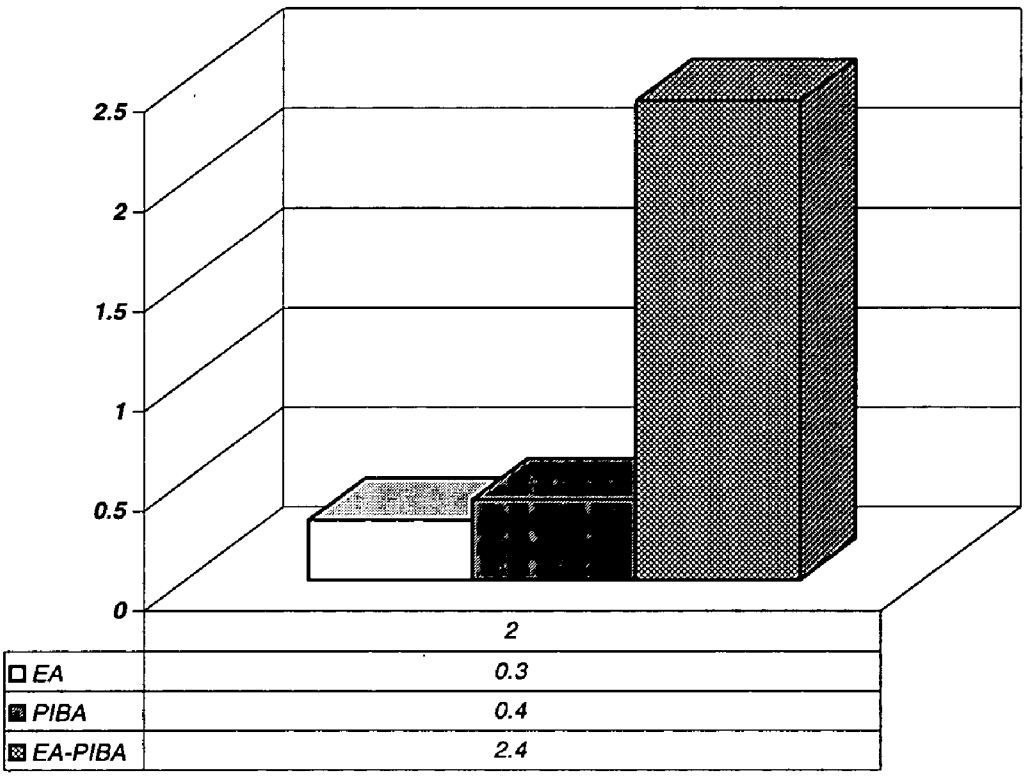


FIG. 3

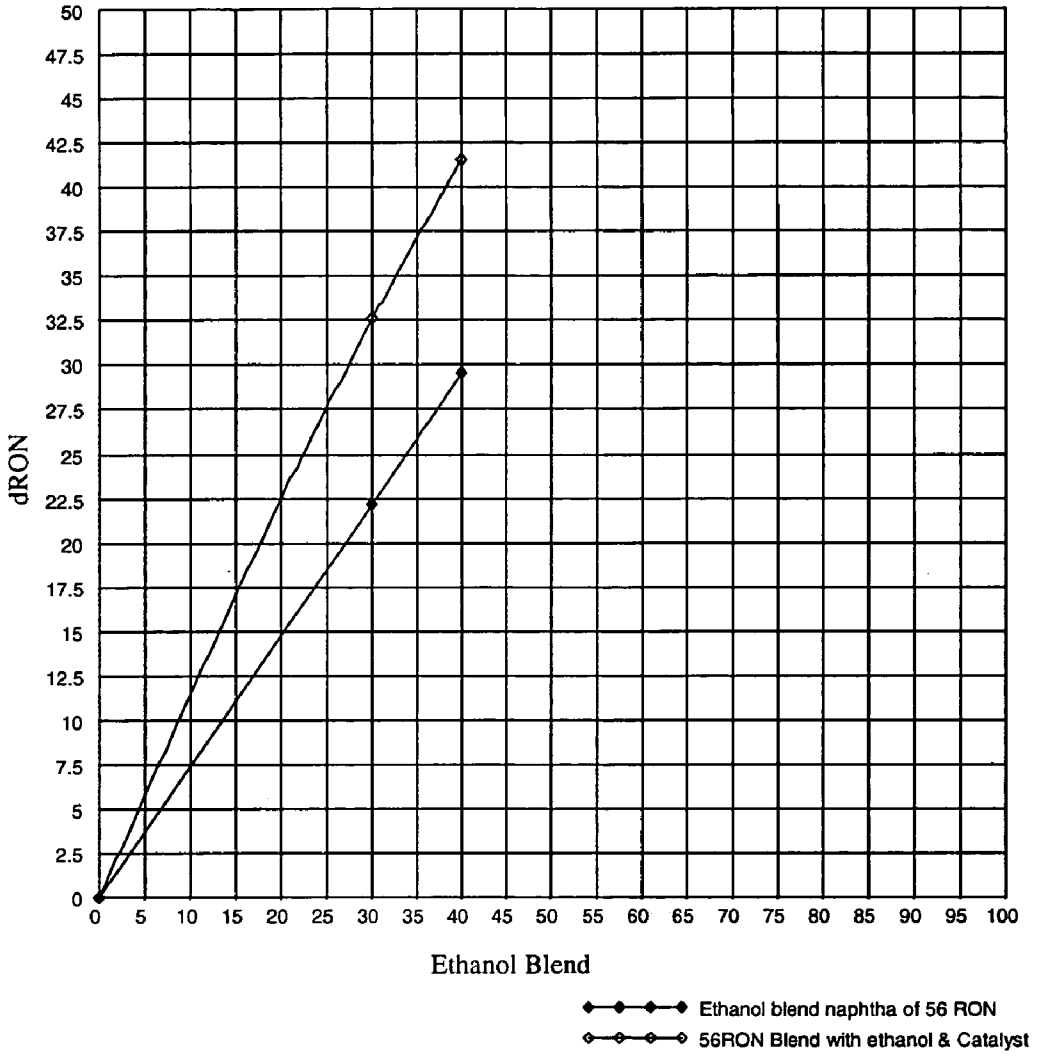

dRON
50
47.5
45
42.5
40
37.5
35
32.5
30
27.5
25
22.5
20
17.5
15
12.5
10
7.5
5
2.5
0
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100
Ethanol Blend
Ethanol blend naphtha of 56 RON
56RON Blend with ethanol & Catalyst

FIG. 4

FUEL COMPOSITIONS AND METHODS THEREOF

CLAIM OF PRIORITY

[0001] This application claims the benefit of filing date of U.S. Provisional Application Ser. Nos. 60/562,028 filed on Apr. 14, 2004 and 60/643,620 filed on Jan. 13, 2005, which are incorporated by reference in their entirety.

FIELD OF INVENTION

[0002] The present invention relates to anti-knock gasoline fuel compositions and methods of increasing octane index of the gasoline fuel. The invention also relates to methods of improving anti-knock of gasoline fuel by admixing the above-referenced compositions without significant environmental consequences.

BACKGROUND OF INVENTION

[0003] Fuels, particularly gasoline grade fuels have undergone many changes over the years in order to improve engine performance and reduce engine emissions. Many octane improving compounds used for improving engine performance and extending fuel supplies, such as tetraethyl lead, aromatic compounds, methylcyclopentadienyl manganese tricarbonyl, methyl tertiary butyl ether ("MTBE") and other such additives, have fallen into disfavor because of concerns about adverse environmental consequences arising from their use.

[0004] The octane requirement increase effect exhibited by internal combustion engines, e.g., spark ignition engines, is well known in the art. If the engine is operated with a gasoline fuel, which has a lower octane number than the minimum requirement for the engine, "knocking" can occur. Knocking occurs when a gasoline fuel spontaneously and prematurely ignites or detonates in the engine prior to spark plug initiated ignition. This effect is coincidental with the formation of deposits in the region of the combustion chamber of the engine.

[0005] During the initial operation of a new or clean engine there is a gradual increase in octane requirement, i.e., fuel octane number required for knock-free operation, which is observed with an increasing build up of combustion chamber deposits until a stable or equilibrium octane requirement level is reached. This level appears to correspond to a point in time when the quantity of deposit accumulation on the combustion chamber and valve surfaces no longer increases but remains relatively constant. This so-called "equilibrium value" is normally reached between 3,000 and 20,000 miles or corresponding hours of operation. Further accumulation of deposits on the intake valves of internal combustion engines, however presents problems. The accumulation of such deposits is characterized by overall poor drivability including hard starting, stalls, and stumbles during acceleration and rough engine idle.

[0006] Several additives when added to hydrocarbon fuels can prevent or reduce deposit formation, or remove or modify formed deposits, in the combustion chamber and on adjacent surfaces such as intake valves, ports, and spark plugs, which in turn causes a decrease in octane requirement. Organometallic compounds, which possess antiknock activity, have been proposed to replace tetraethyl lead. For example, methylcyclopentadienyl manganese tricarbonyl (MMT) is known to be an effective antiknock additive (See U.S. Pat. Nos. 2,818,417; 2,839,552; and 3,127,351), and is currently used in unleaded fuels in Canada and in leaded gasoline in the U.S.

[0007] Numerous non-metallic compounds have also been suggested as antiknock additives. Examples of such compounds include 1,4 and 1,3-diaminobutanes (See U.S. Pat. No. 4,445,909), 2-dimethylamino methyl-4-fluorophenol (See U.S. Pat. No. 4,378,231), norbornadiene (See U.S. Pat. No. 4,387,257), and alkyl carbonate (See U.S. Pat. No. 4,600,408). Particularly preferred antiknock compounds are aniline and certain of its alkyl derivatives such as 2,6-dimethylaniline, n-methylaniline, n-alkyl toluidines (See U.S. Pat. No. 4,294,587), and o-aminoazides (See U.S. Pat. No. 4,266,947).

[0008] Other anti-knock compounds have included fulvene derivatives. For example, U.S. Pat. No. 4,264,336 discloses use of halogenated fulvenes as antiknock compounds. However, the use of chloro or fluoro compounds, as antiknock agents may be environmentally undesirable due to their detrimental effect on the ozone layer. U.S. Pat. No. 3,706,541 discloses the use of certain aminofulvenes such as 6-dimethylamino fulvene as antiknock additives. More recently, 6-dimethylamino fulvene has been reported to be among the most active non-metallic antiknock additives (See S. Stournos et al. 199th National ACS Meeting, Boston, Mass., Apr. 22, 1990).

[0009] U.S. Pat. No. 5,607,486 describes engine fuel additives comprising terpenes, aliphatic hydrocarbons and lower alcohols. Hydrocarbon component containing one or more hydrocarbons such as five to eight carbon atoms straight-chained or branched alkanes have been described in U.S. Pat. No. 6,712,866.

[0010] WO8905339 relates to a gasoline mixture containing between 75 to 95% unleaded gasoline, 5 to 25% oxygenated hydrocarbons such as alcohols of less than 5 carbons, between about 0.05 g to 4 g Pb/gal. and between about 0.005 g to 0.15 g Mn/gal.

[0011] RU2161639 relates to a gasoline additive which contains by wt %: aromatic amine 6-20, crotonic aldehyde 0.1-1.5, acetic aldehyde 0.2-2.0, water 0.5-1.5, and organometallic additive 0.1-4.0. As an aromatic amine, N- methylaniline or toluidine mixture, or xylidine mixture is used and, as organometallic additive, methylcyclopentadienylmanganese tricarbonyl or dicyclopentadienyliron derivative is used. Such additive is contained in gasoline composition in concentrations 5 to 15 wt %. Enhanced octane number is obtained without worsening environmental properties and reducing CO and CH formation in internal combustion engines.

[0012] GB802181 relates to a fuel composition including an aliphatic oxygen compound which is not an aldehyde or an acid and a gasoline blend, the gasoline blend being such that when it contains 2.3 c.c. of tetraethyl lead per U.S. gallon it has a research octane rating of at least 6 octane numbers more than the research octave rating of a 75 per cent recovered distillate (clear) obtained from the gasoline blend. The blend may consist of a light virgin naphtha having a final boiling-point below 350 DEG F. and a research octave rating below 70, and a heavy catalytic reformate, which may be an ultraformate, platformate, or

fluid hydroformate, with a research octave rating above 85. The oxygen compound may be an alcohol, such as ethyl alcohol, isopropyl alcohol or an oxo alcohol, a ketone, an acetal, an ester, an ether, or a cyclic ether, such as furan and its derivatives. Compositions described contain ethanol, isopropyl alcohol, isopropyl ether, di-methyl furan, a mixture of alcohols obtained by oxidation of a virgin naphtha, and tetraethyl lead.

[0013] U.S. Pat. No. 5,288,393 to Unocal relates to a method of reducing NO_x, CO and/HC-hydrocarbons by controlling properties of a gasoline fuel. Preferred properties were Reid vapor pressure (RVP) no greater than 7.5 psi, essentially zero olefins and a 50% distillation point greater than 180 degree C. Action of other properties are increase in octane, decrease in 10% distillation point, increase in aromatics.

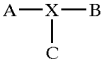
[0014] There are several limitations to the above described compounds as anti-knock fuel additives, for example, high cost, relatively low antiknock quality, hydrolytic, thermal or oxidative instability, low solubility in gasoline, environmental concern or high solubility in water. Accordingly, there is continuing interest in the development of antiknock fuel additives, which provide enhanced engine performance, reduced pollution and can be used to extend fuel supplies through the use of renewable fuels such as ethanol without adversely affecting the environment.

SUMMARY OF THE INVENTION

[0015] The present invention relates to anti-knock fuel compositions and methods of increasing the octane index of gasoline using compounds of Formula I and optionally other additives. The invention also relates to methods of making high-octane gasoline or super octane refinery stream by admixing naphtha or low octane gasoline with above-referenced compositions without significant environmental consequences. A gasoline mixture can include organic compounds, oxygenates, organometallics, and solvents. The actual percentages of in the gasoline mixture can be optimized as needed to produce the desired increase in octane, using empirical methods. Octanising technology of the present invention can be applicable in both up-stream and down-stream of a refinery by using naphtha as a base fuel for up-stream and a sub-grade gasoline is a base fuel for downstream.

[0016] In one aspect, an anti-knock gasoline fuel composition suitable for combustion in an automotive engine is described comprising:

[0017] i) a compound of Formula I:



Formula I

[0018] wherein each of A, B and C is independently selected from the group consisting of alkyls, alkenes, aryls, heterocyclyls, aryloxy, cycloalkyls, cycloalkenyl, heteroaryls, esters, amides, ethers, aldehydes, ketones, carbonates, diazenes, aldehydic acids, alcohols, oxides, ketonic acids, othroesters, diesters, phenols, glycol ethers, glycols, alkyl carbonates, dialkyl carbonates, di-carbonates, organic and inorganic peroxides, hydroperoxides, carboxylic acids, amines, nitrates, di-nitrates, oxalates, boric acids, orthoborates, hydroxyacids, orthoacids, anhydrides, acetates, acetyls, benzoic acids, nitrates, di-nitrates, and nitro-ethers; and X is a polyalkyl, polyalkoxy, polyether, or polycarbonate chain of from about 400 to 3600 g/mol; and

[0019] ii) optionally at least one or more additives.

[0020] In another aspect, an anti-knock gasoline fuel composition is described suitable for combustion in an automotive engine consisting of:

[0021] a) an organic compound selected from the group consisting of alkenes, aldehydes, esters, ketones, alkyl carbonates, aryl carbonates, aminoaryls, cycloalkyl, aromatics, dye-polymer conjugates, ester-polymer conjugates, and dye-paraffin conjugates;

[0022] b) optionally an organometallic compound selected from the group consisting of ferrocene, ruthenocene, chromocene, osmocene, methyl cyclopentadienyl manganese tricarbonyl, nickelcarbonyls, organosilicon metallocene, alkyltin, and derivatives thereof; and

[0023] c) optionally an oxygenate selected from the group consisting of alcohols, esters, ethers, and mixtures thereof.

[0024] In another aspect, a method for improving the antiknock property of a gasoline fuel is described, the method comprising admixing an effective amount of at least one composition of Claim **1** with the gasoline fuel.

[0025] Embodiments of the invention may have one or more of the following advantages. The composition advantageously provides improved anti-knock properties. The composition of the present invention can provide antiknock additives for fuels as a refinery stream additive or in gasoline fuels used for internal combustion engines. The compositions of this invention can potentially replace fossil fuel up to 49% with renewable ethanol while providing significant boost in octane number. The composition can address formulation of clean fuels, increase octane requirement, increase compliance to emission standards, and use renewable fuel in conventional gasoline formulations.

[0026] Other features and advantages of the invention will be apparent from the following detailed description.

DESCRIPTION OF DRAWINGS

[0027] **FIG. 1** is an illustration of the working principle of Zeltex meter.

[0028] **FIG. 2** is a graph of octane rise (dRON) vs. concentration (g/L).

[0029] **FIG. 3** is a graph illustrating synergistic interaction between compounds.

[0030] **FIG. 4** is a graph showing synergistic effect of ethanol with organic compound.

[0031] Like reference symbols in the various drawings indicate like elements.

DETAILED DESCRIPTION OF THE INVENTION

[0032] A gasoline fuel composition can be formulated to provide anti-knock property in an internal combustion

engine. The fuel composition can be blended in a refinery stream to increase octane performance or added as an additive to increase octane performance of a hydrocarbon fuel in an internal combustion engine.

[0033] Octane rating of hydrocarbons is determined by the structure of the molecule, with long, straight hydrocarbon chains producing large amounts of easily-autoignitable pre-flame decomposition species, while branched and aromatic hydrocarbons are more resistant. Unburnt "end gases" ahead of the flame front encounter temperatures up to about 700° C. due to compression and radiant and conductive heating, and commence a series of pre-flame reactions. These reactions occur at different thermal stages, with the initial stage (below 400° C.) commencing with the addition of molecular oxygen to alkyl radicals, followed by the internal transfer of hydrogen atoms within the new radical to form an unsaturated, oxygen-containing species. These new species are susceptible to chain branching involving the HO_2 radical during the intermediate temperature stage (400-600° C.), mainly through the production of OH radicals. Above 600° C., the most important reaction that produces chain branching is the reaction of one hydrogen atom radical with molecular oxygen to form O and OH radicals.

[0034] The addition of compositions of Claim **1** and oxygenates can significantly affect the pre-flame reaction pathways. Antiknock additives work by interfering at different points in the pre-flame reactions, with the oxygenates retarding undesirable low temperature reactions, and the compositions of Claim **1** react in the intermediate temperature region to deactivate the major undesirable chain branching sequence. The antiknock ability is related to the "autoignition temperature" of the hydrocarbons. The combination of vehicle and engine can result in specific requirements for octane that depend on the fuel. If the octane is distributed differently throughout the boiling range of a fuel, then engines can knock on one brand of 87 (RON+MON)/2, but not on another brand. This "octane distribution" is especially important when sudden changes in load occur, such as high load, full throttle, acceleration. The fuel can segregate in the manifold, with the very volatile fraction reaching the combustion chamber first and, if that fraction is deficient in octane, then knock will occur until the less volatile, higher octane fractions arrive.

[0035] Anti knocks delay the pre-ignition of fuel. The ignition delay of pre-ignition occurs when accumulated energy needed for detonation has not the reached the minimum energy needed for detonation. The delay of accumulation of energy may be because of reactions involving initiation, propagation of free radicals such as HO2., OH. involved in the oxidation of fuel hydrocarbons. Interventions in the chains of the hundreds of oxidation reactions can be caused by regulating the initiation and propagation steps in the chain. Following interventions have been found to be influencing positively and in occasional circumstances negatively: these interventions are Base RON, oxygenates such as ethyl alcohol, impurities in fuel processing and anti knocks agents. Since all of these are important and also dependant on the components in fuel and fuel additives (even smaller amount of impurities especially metallic impurities) could in occasional cases have intervention.

[0036] Unless indicated otherwise, the following definitions apply throughout the present specification and claims. These definitions apply regardless of whether a term is used by itself or in combination with other terms. For example, the definition of "alkyl" also applies to the "alkyl" portion of "alkoxy". It should also be noted that any of the moieties can be further substituted by substituents well known to one skilled in the art, for example, alkyl further substituted, with for example, alcohol or halide.

[0037] The term "polyalkyl" or "paraffin" means a group having a carbon atom directly attached to the remainder of the molecule and having a hydrocarbon or predominantly hydrocarbon character within the context of this invention. Such groups include the following:

[0038] (1) Purely hydrocarbon groups; That is, aliphatic, (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl or cycloalkenyl), aromatic, aliphatic- and alicyclic-substituted aromatic, aromatic-substituted aliphatic and alicyclic groups, and the like, as well as cyclic groups wherein the ring is completed through another portion of the molecule (that is, any two indicated substituents may together form an alicyclic group). Non-limiting examples include methyl, ethyl, octyl, decyl, octadecyl, cyclohexyl, and phenyl;

[0039] (2) Substituted hydrocarbon groups; that is, groups containing non-hydrocarbon substituents which do not alter the predominantly hydrocarbon character of the group. Non-limiting examples include include hydroxy, nitro, cyano, alkoxy, acyl, etc.; and

[0040] (3) Hetero groups; that is, groups which, while predominantly hydrocarbon in character, contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Non-limiting examples include nitrogen, oxygen and sulfur.

[0041] "An effective amount" means to describe an amount of compound of the present invention or another agent effective to reduce knock and thus producing the desired effect.

[0042] "Alkyl" means an aliphatic hydrocarbon group, which may be straight or branched and comprising about 1 to about 20 carbon atoms in the chain. Alkyl groups can contain about 1 to about 12 carbon atoms in the chain. More specifically, alkyl groups can contain about 1 to about 6 carbon atoms in the chain. Branched means that one or more lower alkyl groups such as methyl, ethyl, or propyl, are attached to a linear alkyl chain. Non-limiting examples of suitable alkyl groups include methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl, n-pentyl, heptyl, nonyl, and decyl.

[0043] "Alkylaryl" means an alkyl-aryl- group in which the alkyl and aryl are as described herein. Preferred alkylaryls comprise a lower alkyl group. Non-limiting examples of suitable alkylaryl groups include o-tolyl, p-tolyl and xylyl. The bond to the parent moiety is through the aryl.

[0044] "Aryl" means an aromatic monocyclic or multicyclic ring system, wherein at least one ring is aromatic, comprising about 6 to about 14 carbon atoms, or from about 6 to about 10 carbon atoms. Non-limiting examples of suitable aryl groups include: phenyl, naphthyl, indenyl, tetrahydronaphthyl, indanyl, anthracenyl, and fluorenyl.

[0045] "Aryloxy" means an aryl-O- group in which the aryl group is as previously described. Non-limiting examples of suitable aryloxy groups include phenoxy and naphthoxy. The bond to the parent moiety is through the ether oxygen.

[0046] "Cycloalkyl" means a non-aromatic mono- or multicyclic ring system comprising about 3 to about 10 carbon atoms, or from about 5 to about 10 carbon atoms. Cycloalkyl rings can contain about 5 to about 7 ring atoms. Non-limiting examples of suitable monocyclic cycloalkyls include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and the like. Non-limiting examples of suitable multicyclic cycloalkyls include 1-decalin, norbornyl, adamantly and the like.

[0047] "Cycloalkenyl" means a non-aromatic mono or multicyclic ring system comprising about 3 to about 10 carbon atoms, preferably about 5 to about 10 carbon atoms which contains at least one carbon-carbon double bond. Preferred cycloalkenyl rings contain about 5 to about 7 ring atoms. The cycloalkenyl can be optionally substituted with one or more "substituents" which may be the same or different, and are as defined above. Non-limiting examples of suitable monocyclic cycloalkenyls include cyclopentenyl, cyclohexenyl, cycloheptenyl, and the like. Non-limiting example of a suitable multicyclic cycloalkenyl is norbornylenyl.

[0048] "Heterocyclyl" means a non-aromatic saturated monocyclic or multicyclic ring system (i.e., a saturated carbocyclic ring or ring system) comprising 3 to 10 ring atoms (e.g., 3 to 7 ring atoms), or 5 to 10 ring atoms, in which one or more of the atoms in the ring system is an element other than carbon, for example nitrogen, oxygen or sulfur, alone or in combination. There are no adjacent oxygen and/or sulfur atoms present in the ring system. Heterocyclyls can have 5 to 6 ring atoms. The prefix aza, oxa or thia before the heterocyclyl root name means that at least a nitrogen, oxygen or sulfur atom, respectively, is present as a ring atom. The nitrogen or sulfur atom of the heterocyclyl can be optionally oxidized to the corresponding N-oxide, S-oxide or S,S-dioxide. Non-limiting examples of monocyclic heterocyclyl rings include: piperidyl, pyrrolidinyl, piperazinyl, morpholinyl, thiomorpholinyl, thiazolidinyl, 1,3-dioxolanyl, 1,4-dioxanyl, tetrahydrofuranyl, tetrahydrothiophen-yl, and tetrahydrothiopyranyl.

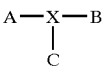
[0049] "Heteroaryl" means an aromatic monocyclic or multicyclic ring system comprising 5 to 14 ring atoms, or 5 to 10 ring atoms, in which one or more of the ring atoms is an element other than carbon, for example nitrogen, oxygen or sulfur, alone or in combination. Heteroaryl can contain 5 to 6 ring atoms. The prefix aza, oxa or thia before the heteroaryl root name means that at least a nitrogen, oxygen or sulfur atom respectively, is present as a ring atom. A nitrogen atom of a heteroaryl can be optionally oxidized to the corresponding N-oxide. Non-limiting examples of heteroaryls include: pyridyl, pyrazinyl, furanyl, thienyl, pyrimidinyl, isoxazolyl, isothiazolyl, oxazolyl, thiazolyl, pyrazolyl, furazanyl, pyrrolyl, pyrazolyl, triazolyl, 1,2,4-thiadiazolyl, pyrazinyl, pyridazinyl, quinoxalinyl, phthalazinyl, imidazo[1,2-a]pyridinyl, imidazo[2,1-b]thiazolyl, benzofurazanyl, indolyl, azaindolyl, benzimidazolyl, benzothienyl, quinolinyl, imidazolyl, thienopyridyl, quinazolinyl, thienopyrimidyl, pyrrolopyridyl, imidazopyridyl, isoquinolinyl, benzoazaindolyl, 1,2,4-triazinyl, and benzothiazolyl.

[0050] The fuel composition, as described above, provides a synergistic increase in octane number of the additive composition and fuel over what would be expected based on the octane number of the components. For the purposes of this invention, the octane number is defined as (R+M)/2 wherein R is the research octane number and M is the motor octane number. The designation dRON is the difference between the RON of the base fuel and RON of the same base fuel with the antiknock additive. It is noted that the compounds of the present invention were used with or without further purification.

[0051] The inventive compositions, in one embodiment, are also useful in reducing intake valve deposits as anti-knocks, thus improving quality of combustion in the engine. In one embodiment, the compositions provide fuel economy by controlling octane of gasoline fuels. An anti-knock gasoline fuel composition suitable for combustion in an automotive engine includes:

[0052] A. Compounds of Formula I:

[0053] i) a compound of Formula I:



Formula I

[0054] wherein each of A, B and C is independently selected from the group consisting of alkyls, alkenes, aryls, heterocyclyls, aryloxy, cycloalkyls, cycloalkenyl, heteroaryls, esters, amides, ethers, aldehydes, ketones, carbonates, diazenes, aldehydic acids, alcohols, oxides, ketonic acids, othroesters, diesters, phenols, glycol ethers, glycols, alkyl carbonates, dialkyl carbonates, di-carbonates, organic and inorganic peroxides, hydroperoxides, carboxylic acids, amines, nitrates, di-nitrates, oxalates, boric acids, orthoborates, hydroxyacids, orthoacids, anhydrides, acetates, acetyls, benzoic acids, nitrates, di-nitrates, and nitro-ethers; and

[0055] X is a polyalkyl, polyalkoxy, polyether, polyterphthalate or polycarbonate chain of from about 400 to 3600 g/mol; and

[0056] ii) optionally at least one or more additives.

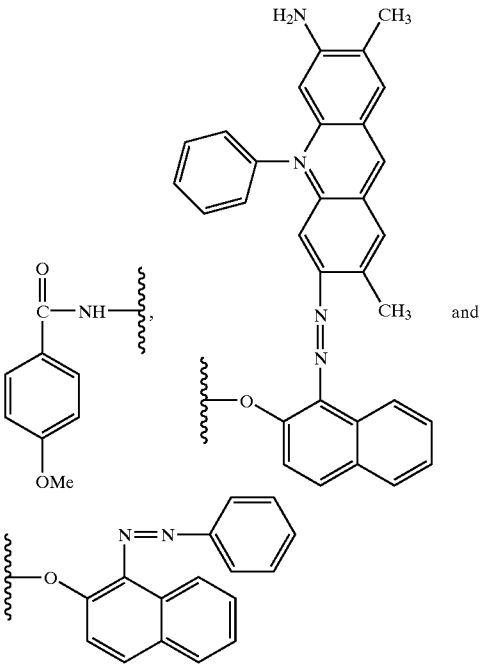
[0057] Each of A, B or C can be an aryloxy moiety which can be a dye. The dye can be, for example, a reactive dye, direct dye, pigment powder, napthols, and basic dye. For example, the dye can be a substituted diazene, for example, a oil yellow, oil orange, oil orange R, oil red, oil green, oil cynanine green, oil violet, oil brilliant blue, and oil pink. Suitable dyes include group consisting of oil orange R, oil brilliant blue, and indoineblue.

[0058] Each of A, B, or C can be an acid. Non limiting examples of acids, include but not limited to benzoic acid derivatives e.g. 2,4-dimethyl benzoic acid, methyl red, p-tert-butylbenzoic acid, 2-(1-methylethyl)benzoic acid, benzoic acid anhydride, 4-benzoyl benzoic acid, 2,4-dih-

droxy benzoic acid, 2,4-dimethyl-benzoic acid, 3-ethoxy benzoic acid, 2-hydroxy-4-methyl benzoic acid, 2-hydroxy benzontrile, 4-methoxy benzotrile, acetic acid derivatives, e.g. anhydride acetic acid, chloroacetic acid, decyl ester acetic acid, dibromoacetic acid, and the like, may be employed. Non-limiting examples of salts include binary, ternary and higher metallic acid salts, hydroxy acids, etc. Other non-limiting compounds acids are set forth below and include for example, oxamic acid, lithium acetate acid, lithium salt acetic acid, propanoic acid lithium salt, cyclohexanebutyric acid lithium salt, aminobenzole acid lithium salt, borate ester, dimethyl borate, di-n-butyl borate, dicyclohexyl borate, didodecylborate, di-p-cresyl borates, boric acids, orthoborates, henylboronic acid, diphenylboronic acid, o-tolylboronic acid, p-tolylboronic acid, m-tolylboronic acid, cylohexylboronic acid, cylohexenylboronic acid, cyclopentylboronic acid, methylphenylboronic acid, methylcylohexyl-boronic acid, methylcyclopentylboronic acid, methylbenzylboronic acid, dimethylphenylboronic acid, dimethylcylohexylboronic acid, dimethylcyclopentylboronic acid, dimethylbenzylboronic acid, diphenylboronic acid, dibenzylboronic acid, dicylohexylboronic acid, dicylohexenylboronic acid, dicyclopentylboronic acid, mgethyldiphenylboronic acid, bis[(methyl)cylohexyl]boronic acid, bis[(methyl)cyclopentyl]boronic acid, bis[(methyl)benzyl] boronic acid, bis[(dimethyl)phenyl]boronic acid, bis[(dimethyl)cylohexyl]boronic acid, bis[(dimethyl)cyclopentyl] boronic acid, or bis[(dimethyl)benzyl]boronic acid.

[0059] In the alternative, A, B or C can be an alcohol moiety. Non-limiting examples of alcohols include ethanetriols, propanetriols, butanetriols, 1,2,3 butanetriol, pentanetriols, 1,2,3 pentanetriol, 2,3,4 pentanetriol, hexanetriols, septanetriols, octanetriols, or tertraethylene glycol, triethylene glycol, 1-octene, high flash point ketone, naphthalenes, triethylene glycol, trimethylene glycol, isopropyl acetone, diisopropyl acetone, diisopropyl diacetone, diethylene acetate, diethylene diacetate, ethylene acetate compound, phenol, or other flash point temperature reducing co-solvent set forth in aforementioned PCT Applications. Co-solvents should not be corrosive or hazardous to fuel systems.

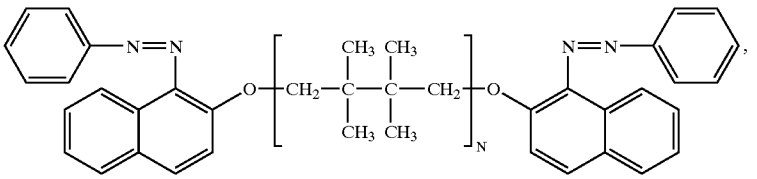
[0060] In the alternative, each of A, B or C can be an aldehyde. Non-limiting examples of amides include any aliphatic or aromatic amide. For example, A, B or C can be substituted or unsubstituted benzaldehyde or anisaldehyde. Alternatively each of A, B or C can be



[0061] Examples of X group include butyl, isobutyl, pentyl, hexyls, octyl, nonyl, dodecyl, docosyl, polyethylene, polypropylene, polyisobutylene, ethylene-propylene copolymer, chlorinated olefin polymer, polyether, paraffin and oxidized ethylene-propylene copolymer. The X moiety can be polyisobutylene. The polyisobutylene can have a number average molecular weight of 400 to 3600 g/mol. The polyisobutylene can be substituted, the substituent can be, for example, alkoxy, hydroxyl, halo, alkyl, substituted alkyl, and nitro. Alternatively, X can be a paraffin.

[0062] A fuel composition can be formulated to include a mixture of a major amount of liquid hydrocarbon diluents and minor amount of a composition of Claim 1.

[0063] The composition can include, for example, compounds



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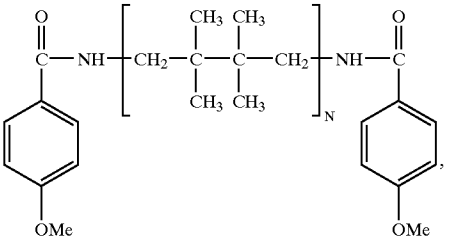
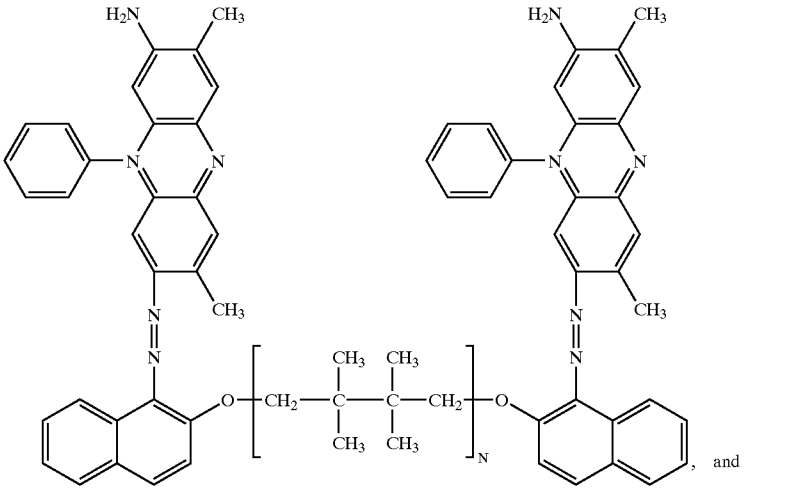
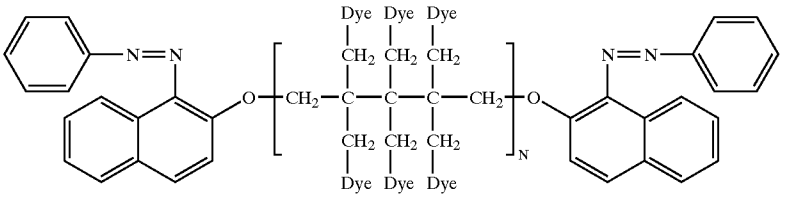
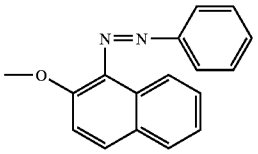




, and

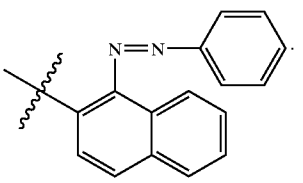


where Dye = 

[0064] or mixtures thereof.

[0065] Alternatively, fuel compositions can include

[0066] (a) a compound represented by Formula II:



Formula II

D=Y=E

[0067] wherein each of D and E is selected from the group consisting of aryl, aryloxy, heteroaryl, or diazene;

[0068] Y is —CH—, —C(═O)O—, —C(═O); and

[0069] (b) a hydrocarbon diluent. For example, each of D and E can be cyclopentadiene, substituted phenyl, and

[0070] B. Additives:

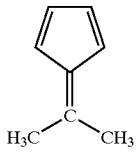
[0071] The composition can include optionally at least one or more additives, for example, a dye or mixture of two or more additives. The additive can be a dye, for example, oil orange R dye or brilliant blue dye. The dye can be present in an amount from about 1 ppm by weight to about 500 ppm by weight based on the total weight of the composition.

Liquid hydrocarbon diluents and/or fuels can be a gasoline fuel or diesel fuel. Suitable hydrocarbon diluents are mixtures of hydrocarbons with a boiling range of from about 25° C. to about 232° C. and include saturated hydrocarbons, olefinic hydrocarbons, and aromatic hydrocarbons. For example, the diluent can have a saturated hydrocarbon content of from about 40 to about 80 percent, an olefinic hydrocarbon content from about 0 to about 30 percent volume and an aromatic hydrocarbon content from about 10 to about 60 percent volume.

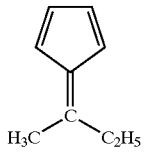
[0072] The additives can include fulvenes, aldehydes, esters, ketones, alkyl carbonates, phenyl carbonates, dyes, aromatics, dye-polymer conjugates, ester-polymer conjugates, and dye-paraffin conjugates, organometallics and oxygenates.

[0073] The additives include fulvenes, for example, dimethyl carbonate fulvene, anisaldehyde fulvene, ethyl anisate fulvene; dyes, for example, oil orange R dye, oil brilliant blue MBA; esters and carbonates, for example, ethyl anisate, 2-ethyl furoate, tert-butyl acetate, ethyl nicotinate, dimethyl carbonate; dye-attached to polymer to form conjugates, for example, oil orange R-PIB conjugate ["dye-PIBA"], oil orange R-multibrominated PIB conjugate; esters attached to polymer to form ester-polymer conjugate, for example, ethyl anisate-PIBA ("EA-PIBA"]; ester attached to dye, for example, ethyl anisate-oil orange R dye conjugate, dye attached to paraffin, for example, kerosene-oil orange R dye conjugate; oxygenate attached to paraffin, for example, kerosene-ethanol conjugate. Representative examples of additives include:

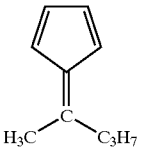
i) Fulvenes



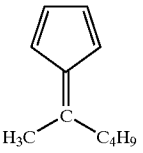
6,6-Dimethyl fulvene



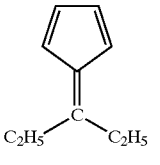
6-Methyl-6-ethyl fulvene



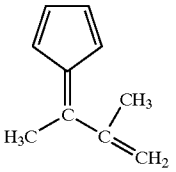
6-Methyl-6-isopropyl fulvene



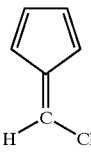
6-Methyl-6-butyl fulvene



6,6-Diethyl fulvene



6-Methyl-6-propenyl fulvene



5-(1-Methyl Methylidene)-1,3-Cyclopentadiene

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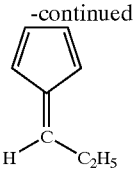
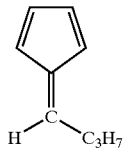
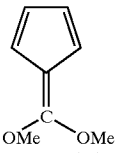


5-(1-Ethyl Methylidene)-1,3-Cyclopentadiene



5-(1-Propyl Methylidene)-1,3-Cyclopentadiene

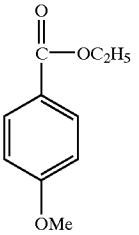
Eg: 6,6 Dimethoxy fulvene



eg: 6-Methyl aminofulvenes.
eg: 6,6-Pentamethylene fulvene
eg: 6,6-Tetramethylene fulvene.
eg: 6-cyclohexyl fulvene.
eg: 6-Phenyl fulvene.

[0074] ii) Aldehyde, Esters & Ketone:

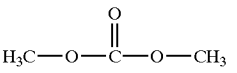
[0075] Aldehydes can include, for example, anisaldehyde and benzaldehyde. Esters can include, for example, ethyl Anisate.



[0076] Ketones can include, for example, benzophenone.

[0077] iii) Alkyl &/or phenyl carbonate:

[0078] Akyl carbonates can include, for example, dimethyl carbonate



[0079] or phenyl carbonate. Suitable example of phenyl carbonate is diphenyl carbonate

[0080] iv) Dyes: Any dye can be used as an additive. Examples of dyes are listed in Table 1.

TABLE 1

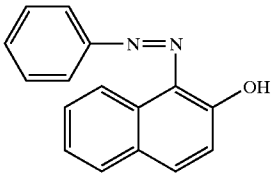
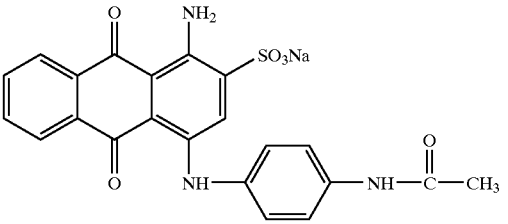
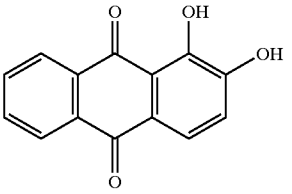
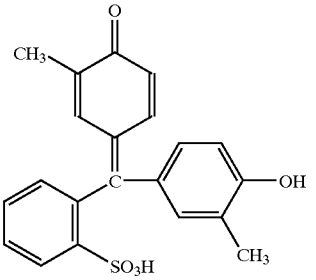
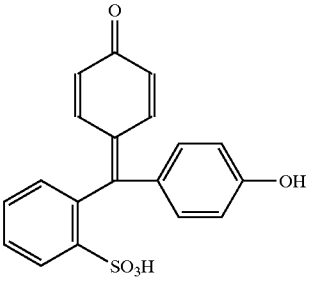
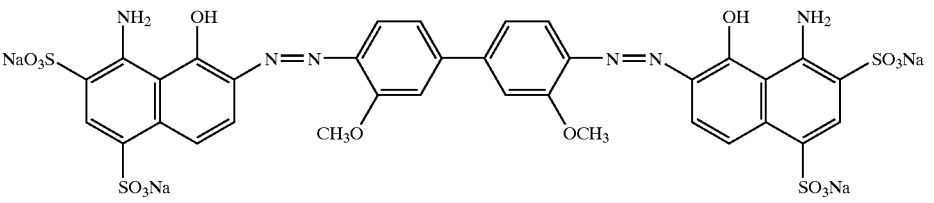
Name	Structure
Oil orange R	
Acid Blue 40 Alizarin Direct Blue A2G	
Alizarin Mordant Red 11	
Cresol Red o- Cresolsulfonephthalein	
Phenol Red Phenolsulfonephthalein	
Chicago Sky Blue 6B Direct Blue 1	

TABLE 1-continued

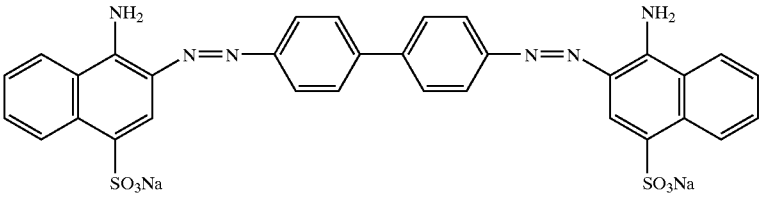
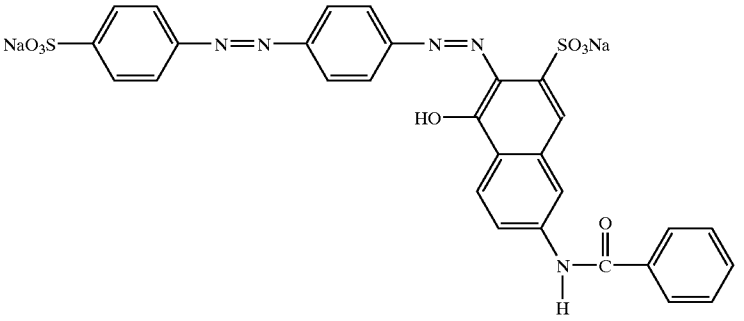
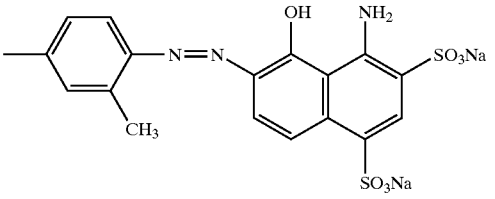
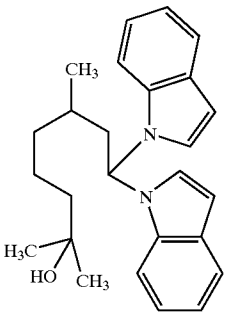
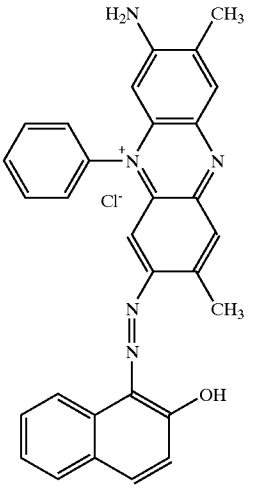
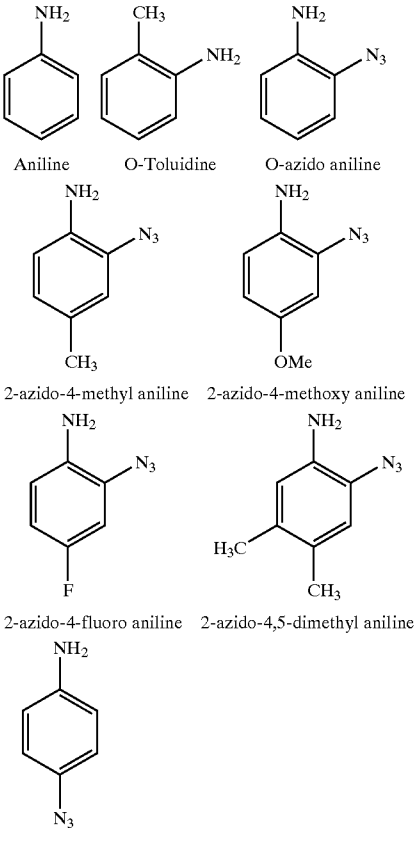
Name	Structure
CongoRed Direct Red 28	
Direct Red 81 Sirius Red 4B	
Evan's Blue Direct Blue 53	
Indolene-50	

TABLE 1-continued

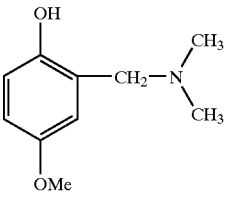
Name	Structure
Indoine Blue Basic Blue 16	

[0081] v) Aromatics, for example,



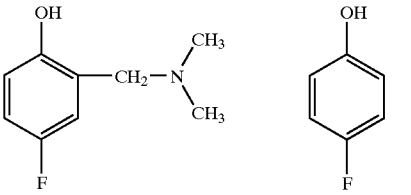
[0082] Additives can include alkyl toluidene, for example, 4-methyl benzamine. Additives can include, fluorophenol, or 2-dimethylaminomethyl-4-methoxyphenol

[0083]

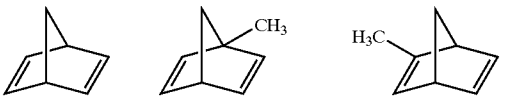


2-dimethylaminomethyl-4-fluoroxyphenol

[0084]



[0085] vi) Norbornadiene:



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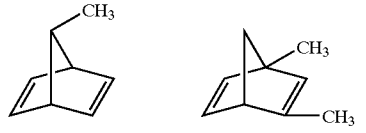
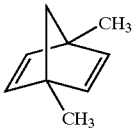


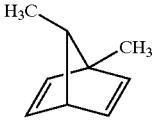
7-methyl Norbornadiene

1,5-dimethyl Norbornadiene

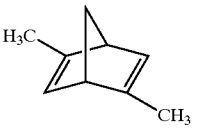
1,2-dimethyl Norbornadiene



1,4-dimethyl Norbornadiene



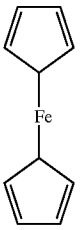
1,7-dimethyl Norbornadiene



2,5-dimethyl Norbornadiene

[0086] vii) Organometallics: Alternatively, additives can include, organometallic compounds, for example, ferrocene, ruthenocene, chromocene, osmocene, methyl cyclopentadienyl manganese tricarbonyl and derivatives thereof.

[0087] a. Ferrocene

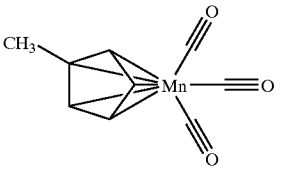


[0088] eg: Iron tetracarbonyl, $Fe_3(CO)_{12}$

[0089] eg: Iron pentacarbonyl, $Fe(CO)_5$

[0090] eg: Novel carboxylic ferrocene

[0091] b. Methyl cyclopentadienyl manganese tricarbonyl (MMT)



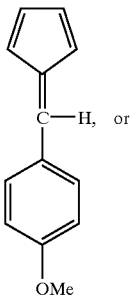
[0092] c) Nickel for example, nickel pentacarbonyl, eg: $Ni(CO)_5$

[0093] d) Silicon eg., organosilicon metallocene compound

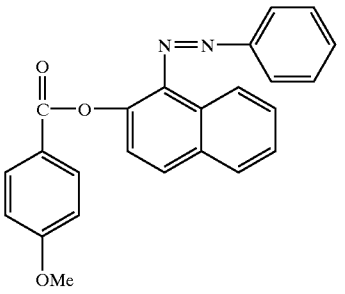
[0094] e) Tin eg., tetraethyl tin.

[0095] f) Ruthenocene, napthacenes, methylferrocene, cobaltocene, nickelocene, titanocene dichloride, zirconocene dichloride, uranocene, decamethylferrocene, decamethylsilicocene, decamethylgermaniumocene, decamethylstannocene, decamethylphosocene, decamethylosmocene, decamethylruthenocene, decamethylzirconocene, silicocene, and decamethylsilicocene.

[0096] viii) The composition can include an additive, or mixture of two or more additives, for example, the additive can be a dye. The compounds can include ethyl anisate-cyclopentadiene conjugate (EA—CPD) and ethyl anisate-dye conjugate (EA-Dye).



EA-CPD



EA-Dye (Oil Orange Dye)

[0097] xi) Oxygenates: In the alternative, oxygenates can be additives. Oxygenates can be selected from the group consisting of alcohols, esters, ethers, acetates and mixtures thereof.

[0098] a. Alcohols: Methanol, ethanol, butanol etc

[0099] b. Ethers: methyl tert-butyl ether, ethyl tert-butyl ether

[0100] c. Ester: Ethyl acetate, Methyl acetate, polyvinyl acetate etc

[0101] d. Carboxylic acid: Formic acid, Acetic acid etc

[0102] The oxygenates can include, for example, ethanol, methanol, t-butyl alcohol, methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ether(TAME), tetrahydrofuran or mixtures thereof. The concentration of oxygenate can be at least hundred times that of organic compound of Formula I. The additives can further include dyes, detergents, dispersants, demulsifiers, antioxidants, corrosion inhibitors, or stabilizers and other antiknock

additives. Concentration of each of the compounds of Formula I in compositions of Claim **1** can be minute, for example, less than 1500 ppm. The concentration of the additive in compositions of Claim **1** can be less that, for example, 49% by weight of gasoline fuel. Some of the components in composition of Claim **1** can be chemically bound and gives greater rise to the octane number than the individual components. For example, oxygenates when mixed with compounds of Formula I and organometallic compounds, an unexpected rise in greater octane number is observed.

[0103] The fuel compositions of the present invention may additionally include additives such as dyes, detergents, dispersants, demulsifiers, antioxidants, corrosion inhibitors, or stabilizers. Furthermore, the fuel composition may additionally include other anti-knock additives. The compositions of Claim **1** can be present in less than about 10% of fuel. Suitable concentration from about 1 ppm by weight to about 1500 ppm, or less than 300 ppm by weight based on the total weight of the composition. The compounds of Formula I can be used in a gasoline fuel, or alternatively, for example, in a diesel fuel, naphtha or residual oil. Surprisingly, there is a synergy between the compounds of Formula I and selected additives. Thus, the compositions give a synergistic rise in octane number, wherein the octane rise is greater than the sum of octane rise by individual components of compounds of Formula I and additives.

[0104] In the compositions according Claim **1**, there exists a synergy within the molecules of compounds of Formula I, as shown below Table 2. [See also **FIG. 3**]

TABLE 2

Sr No	Compound	Wt of O in gm	RON	dRON
1	SF[1]	0	88.2	**
2	SF + EA	2	88.6	0.3
3	SF	0	88.4	**
4	SF + PIBA	2	88.4	0.4
5	SF	0	88.2	**
6	SF + EA-PIBA	2	90.6	2.4

[1]SF = Synthetic fuel; EA is ethyl anisate; and EA-PIBA is ethyl anisate-polyisobutylene conjugate

[0105] The results of the above table show that research octane number of ethyl anisate-polyisobutylelene amine conjugate which is more than the sum of individual research octane numbers of ethyl anisate and polyisobutylene. Here, the research octane number for SF and EA-PIBA conjugate blend is 2.4 instead of the additive sum of 0.7 based on SF and PIBA blend (dRON 0.4) and SF and EA blend (dRON 0.3), leading to an increase of unexpected synergistic increase of 1.7.

[0106] The fuel compositions described above can improve antiknock property of a hydrocarbon base fuel. The efficiency of the antiknock compounds for improving antiknock properties of liquid hydrocarbons was tested as shown in Table 3. The octane enhancing property of the above referenced compositions can be measured by Waukesha Engine [ASTM D2699(RON), D2700(MON), D4815(Oxygen)]. In the following table, the composition was blended with a synthetic reference fuel (SF) in a blend of 1% by volume reference fuel and 100% by volume product. Compounds Dye-polyisobutylene (Dye-PIB) and ethyl anisate-polyisobutylene conjugate (EA-PIBA) were tested against dimethyl fulvene in variety of fuels. Significant increases in dRON were observed for Dye-PIB and EA-PIBA.

TABLE 3

Compound	Quantity (gm)	% EtOH	Fuel Type	Base RON	Final RON	tti-dRON
Dimethyl fulvene	1.5	0	SF	82.8	86.4	3.6
Dimethyl fulvene	1.5	0	SF	84.7	87.6	2.9
Dimethyl fulvene	1	0	SF	84.7	87.1	2.4
Dimethyl fulvene	0.75	0	SF	84.7	86.6	1.9
Dye-Pib	1.5	0	SF	82.7	85.5	2.8
Dye-Pib	1.5	0%	Regular	92.6	94	1.4
0	0	0	SF	82.7	83.1	0.4
Dimethyl fulvene	1.5	10%	SF	84.7	93.8	9.1
Dimethyl fulvene	1.25	10%	SF	84.7	92.8	8.1
Dimethyl fulvene	1	10%	SF	84.7	92	7.3
Dye-Pib	1.5		SF	82.8	95.7	12.9
Dye-Pib	1.5		SF	82.8	84.3	9.8
Dye-Pib	1.5	10%	SF	82.8	92.6	9.8
Dye-Pib	1.5	10%	SF	82.7	92.1	9.4
Dye-Pib	1.5	10%	randum	96.2	99.9	3.7
Dye-Pib	1.5	10%	regular	92.6	97.2	4.6
Dye-Pib	1.5	10%	naphtha	86.4	91.5	5.1

TABLE 3-continued

Compound	Quantity (gm)	% EtOH	Fuel Type	Base RON	Final RON	tti-dRON
Dye-Pib	1.5	MTBE-10%	regular	91.1	94.5	3.4
Dye-Pib	1.5	1%	regular	92.6	94.1	1.5
0	0	1%	regular	91.1	91.2	0.1
0	0	10%	SF	84.5	89.1	4.6
Dye-Pib	0.5	10%	SF	84.5	90.4	5.9
0	0	20%	SF	70.4	82.3	11.9
Dye-Pib	1.5	20%	SF	70.4	92	21.6
0	0	30%	naphtha	56	78.2	
Dye-Pib	1.5	30%	naphtha	56	91.6	35.6
0	0	1%	SF	91.8	93.1	1.3
Dye-Pib	0.5	1%	SF	91.8	93.2	1.4
0	0	10%	SF	84.5	89.1	
0	0	30%	naphtha	56	78.2	
EA-PIBA	0.4	30%	naphtha	56	88.8	32.8
EA-PIBA	..25	30%--acetone	naphtha	56	74.6	18.6
EA-PIBA	0.4	30%--acetone	naphtha	56	77.9	21.9
EA-PIBA	0.25	30%--MTBE	naphtha	56	74	18
EA-PIBA	0.4	30%--MTBE	naphtha	56	83.6	27.6
EA-PIBA	..25	40%	naphtha	56	85.6	
EA-PIBA	0.4	40%	naphtha	56	97.6	41.6
EA-PIBA	..25	40%-MTBE	naphtha	56	80	24
EA-PIBA	0.4	40%-MTBE	naphtha	56	87.9	31.9
EA-PIBA	0.4	1%	regular	91.8	93.3	1.5
EA-PIBA	0.4	1%	regular	91.8	93.1	1.3
EA-PIBA	0.4	10%	naphtha	56	68.4	12.4
EA-PIBA	0.4	25%	naphtha	56	82.1	26.1
EA-PIBA	0.4	50%	naphtha	56	88.9	32.9
EA-PIBA	0.4	75%	naphtha	56	102.7	46.7
EA-PIBA	0.4	85%	naphtha	56	112.1	56.1
0	0	5.11%	Arco-reg	91.8	na	na
0	0	5.11%	Arco-reg	91.7	na	na
EA-PIBA	0.4	5.11%	Arco-reg	91.8	95.6	3.8
EA-PIBA	0.4	5.11%	Arco-reg	91.7	95.5	3.8
		5.65%	2.2 blended regular gasoline	92	na	na
EA-PIBA	0.1	5.65%	2.2 blended regular gasoline	92	92.4	0.4
		5.65%	RBOB gasoline W/2.2% oxygen	89.3	na	na
EA-PIBA	0.4	5.65%	RBOB gasoline W/2.2% oxygen	89.3	93.4	4.1
EA-PIBA	0.4	11.8(3.5)%	Arco regular gasoline	93 cal	97.4	4.4

[0107] Without being bound to a particular theory, Applicant believes that physical features of chemical molecules, for example, polarity, ionization, electron density, size, shape and physico-chemical properties such as electron delocalization, influence the anti-knock activity of the composition.

[0108] The above results in Table 3 show that the fuel additive compositions of the invention have a substantially higher octane number as compared to the synthetic fuel alone. Any increase in RON as indicated by the ΔRON is advantageous to fuel economy, engine operability and the reduction of pollutants.

[0109] The octane enhancing property of the above referenced compositions can also measured by a Zeltex meter as shown in Table 4. Zeltex meter is a portable octane analyzer of all grade of unleaded gasoline, which works on the principle of near IR. It shows the results of analysis in 20 second only directly in printed form or on screen along with optical data of absorption of applied infrared light. The Zeltex meter measures the research octane number (RON), motor octane number (MON) and pump octane number (RON+MON)/2. The Zeltex reading is accurate and provides repeatability equivalent to ASTM-approved CFR engines. The working principle of the Zeltex meter is that near IR light is applied to the sample kept in sample holder, the light energy that enters the sample is scattered and absorbed within the sample. The Zeltex meter measures the spectra of existing sample and directly display the results. [See **FIG. 1**] Here on the basis of data, accuracy of Zeltex meter readings and their equivalency to ASTM-test method for octane, we have used the Zeltex meter for octane testing of some of the compounds. For testing purpose and initial screening of potential high performance antiknocks, we have used ZX-101C model of Zeltex meter provided by Zeltex INC. [See also **FIG. 2**].

TABLE 4

		TEST ON SYNTHETIC FUEL By Zeltex Meter				
Sr No.	Compounds	Gm/liter	RON	MON	R + M/2	dRON
I	Reference compounds:					
A	Fulvene					
1	Dimethyl fulvene	SF	88.4	83.2	85.8	
		5	88.8	82.3	85.5	0.8
		10	89.5	82.1	85.8	1.5
2	SF + methyl ethyl fulvene	SF	88.1	82.9	85.9	
		5	88.6	83.2	86.1	0.5
		10	88.8	83.4	86.1	0.7
		15	89	83.2	86	0.9
		20	89	83.2	86	0.9
		30	89.2	83.1	86.1	1.1
B	Alkylaldehyde & ester					
3	SF + TBA	SF	88.3	82.5	85.4	
		5	88.4	83	85.7	0.1
		10	88.9	83.2	86	0.6
		15	89.1	83.3	86.2	0.8
		20	89.6	83.6	86.6	1.3
		50	90	84	87	1.7
4	SF + EA	SF	88.1	82.9	85.9	
		5	88.3	82.8	85.6	0
		10	88.6	82.7	85.7	0.3
		15	88.7	82.9	85.8	0.4
		20	88.9	82.9	85.9	0.6
		25	89.2	82.8	86	0.9
		30	89.2	83	86.1	0.9
		35	89.5	83.2	86.3	1.2
C	Alkyl phenyl Carbonate					
5	Dimethyl carbonate	SF	88	82.2	85.1	
		10	88.6	82.7	85.6	0.6
II	Present invention:					
A	Cyclopentadiene derivative					
1	SF + DMC: CPD	SF	88.3	82.5	85.4	
		5	88.3	82.8	85.5	0
		10	88.7	82.6	85.6	0.4
		15	89	82.8	85.9	0.7
		20	89.4	82.5	85.9	1.1
		25	90	82	86	1.7
2	Dimethyl carbonate Cyclopentadiene conjugate	Not miscible				
3	Anisaldehyde Cyclopentadiene conjugate	Not miscible				
B	Dyes					
4	OIL Brilliant blue	SF	88.4	83.2	85.8	
		100 mg	88.9	83	85.9	0.5
		250 mg	89.2	82.8	86	0.8
		500 mg	90.2	82.3	86.3	1.8
		750 mg	90.9	81.9	86.5	2.5
		1000 mg	91.7	81.8	86.7	3.3
5	Oil orange R dye	SF	88	82.2	85.1	
		100 mg	88.2	82.4	85.2	0.2
		250 mg	88.5	82.5	85.5	0.5
		500 mg	88.5	82.3	85.4	0.5
		750 mg	88.7	82.2	85.4	0.7
		1000 mg	89	82.1	85.6	1
6	Polysol yellow	100 mg	88.1	88.2	85.1	0.1
		250 mg	88.1	88.2	85.1	0.1
		500 mg	INSOLUBLE			
C	Esters					
7	SF + ethyl nicotinate	SF	88.1	82.9	85.4	
		5	88.8	83.1	86	0.7
		10	89.2	83	86.1	1.1
		12.5	89.5	83.1	86.3	1.4
8	SF + ethyl furoate	SF	88.1	82.9	85.4	
		5	88.5	82.9	85.8	0.4
		10	88.6	82.9	85.8	0.5
		20	88.9	82.9	85.9	0.8
		25	89	83.2	86	0.9
		30	89	83.2	86	0.9
		40	89.1	83.1	86.1	1
D	Dye-polymer conjugation					
9	SF + dye-PIB	SF	88.3	82.5	85.4	

TABLE 4-continued

Sr No.	Compounds	TEST ON SYNTHETIC FUEL By Zeltex Meter Gm/liter	RON	MON	R + M/2	dRON
		1	88.5	82.5	85.5	0.2
		2	88.5	82.5	85.5	0.2
		3	89.3	82.6	85.9	1
		4	90.7	82.1	86.4	2.4
E	Ester-poly isobutyl amine conjugation					
10	SF + EA-PIBA	SF	88.3	82.5	85.4	
		5	88.4	82.9	85.6	0.1
		10	88.8	82.9	85.8	0.5
		15	89.3	82.7	86	0.9
		20	89.7	82.9	86.3	1.3
F	Ester-dye conjugate					
11	EA-Dye (oil orange R)	Not miscible				
G	Dye attached to paraffin					
12	SF + kerosene-dye	SF	88.3	82.5	85.4	
	(oil orange R)	1	88.8	82.6	85.7	0.5
		2	89.6	82.3	86	1.3
		3	90.4	82.2	86.3	2.1
H	Oxygenate-polymer					
13	SF + mPIB-ethanol	SF	88.2	86.3	87.2	
		1.25	89.3	85.9	87.6	1.1
		2.5	90.6	85.3	88	2.4
		3.75	92	84.7	88.4	3.8
		5	93.6	84.3	88.9	5.4

[0110] In yet another embodiment, an anti-knock gasoline fuel composition suitable for combustion in an automotive engine includes:

[0111] a) an organic compound selected from the group consisting of alkenes, aldehydes, esters, ketones, alkyl carbonates, aryl carbonates, aminoaryls, cycloalkyl, aromatics, dye-polymer conjugates, ester-polymer conjugates, and dye-paraffin conjugates;

[0112] b) optionally an organometallic compound selected from the group consisting of ferrocene, ruthenocene, chromocene, osmocene, methyl cyclopentadienyl manganese tricarbonyl, nickelcarbonyls, organosilicon metallocene, alkyltin, and derivatives thereof; and

[0113] c) optionally an oxygenate selected from the group consisting of alcohols, esters, ethers, and mixtures thereof.

[0114] Yet another embodiment is a method of improving the antiknock property of a hydrocarbon base fuel, the method comprising adding an effective amount of at least one composition of Claim **1**.

[0115] Yet another embodiment is a method of improving the antiknock property of a hydrocarbon base fuel, the method comprising adding an effective amount of at least one composition of Claim **20**.

[0116] A method for controlling octane requirement increase is contemplated, comprising admixing at least composition of Claim **1**. Some of the polymers of formula I, such as poly ether amines, polyisobutylene amines have an amine attached to the molecule. Amination of polymers can also be carried out for the antiknocks that do not have the amine moiety. Hence, the polymers will become multifunctional. In addition to the molecule being primarily an antiknock, other functional groups attached to the molecule will enhance the molecule's function as a detergent for cleaning intake valve deposits and the combustion chamber deposits. Reapited use of the enhanced molecule will remove the combustion chamber deposits and lower the ORI.

[0117] A method comprising a fuel composition admixing in the refinery stream, the composition of Claim **1**. When compositions of the present invention are used on base fuels, the lower the octane of the base fuel, higher is the synergetic increase in octane. Hence, it is advantageous to use compounds of Claim **1** upstream in the refinery.

[0118] A method for decreasing intake valve deposits in an internal combustion engine is described, the method comprising burning in the engine the composition of Claim **1**.

[0119] A method for decreasing volatility of refinery blends is described comprising: blending a downstream refinery blend with an effective amount of compound of Claim **1**.

[0120] A method of decreasing volatility of a refinery blend is described comprising: blending an upstream refinery blend with an effective amount of compound of Claim **1**. The upstream refinery hydrocarbon blends can be naphtha, residual oil. Ethanol can be admixed to the blend.

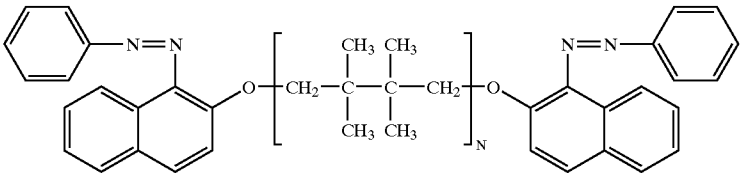
[0121] A method for monitoring the octane number of a fuel is described comprising: measuring a parameter associated with engine knock by rapid compression machine (RCM); continuously outputting a signal indicative of the parameter; and mathematically converting the signal to an output signal indicative of the octane number.

[0122] The invention disclosed herein is exemplified by the following preparations and examples, which should not be construed to limit the scope of the disclosure. Alternative preparations and analogous structures may be apparent to those skilled in the art.

EXAMPLE 1

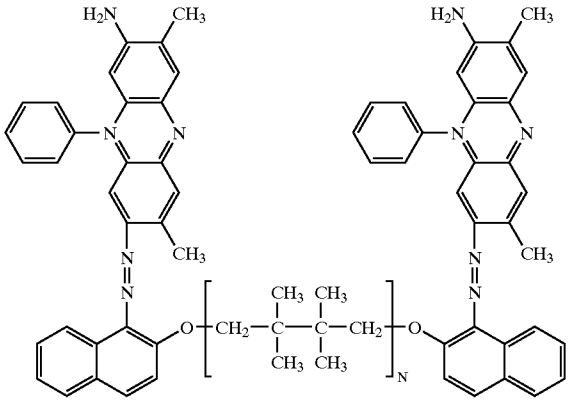
[0123] A mixture of 15 gm of oil orange dye, 24.15 gm of polyisobutelene bromide and 100 ml diphenyl ether was refluxed for 8-10 hrs under stirring with elimination of HBr. The reaction monitored by TLC. After completion, reaction

mixture was dumped in 200 ml water to remove acidity. Solvent was removed azeotropically and residue is distilled at reduced pressure. The yield of oil orange dye-polyisobutelene-oil orange dye conjugate reaction product was 52%.



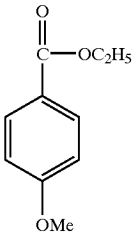
EXAMPLE 2

[0124] A mixture of 15 gm of free base of dye (indoine blue), 18.3 gm of Polyisobutelene bromide and 50 ml of diphenyl ether was refluxed for 4 hrs under stirring with elimination of HBr. The reaction monitored by TLC. After completion, the reaction mixture was dumped in water, solvent was removed azeotropically and residue was distilled at reduced pressure. The yield of indoine blue dye-polyisobutelene-indoine blue dye conjugate reaction product was 96%.



EXAMPLE 3

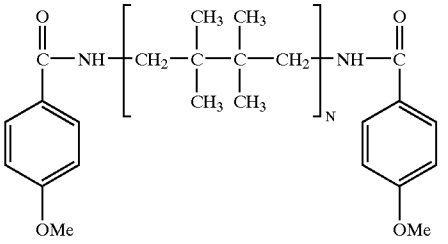
[0125] A mixture of anisic acid (5 gm), 2 ml of concentrated sulphuric acid and 55 ml of absolute ethanol was refluxed at 80° C. for 8 hrs under stirring. The reaction monitored by TLC. After completion, reaction mixture was dumped in cold water and oily layer was separated. The aqueous layer was extracted with dichloromethane. This extracted layer and oily layer were combined and washed with 5% sodium bicarbonate solution to remove unreacted anisic acid. The dichloromethane was removed and residue was distilled at reduced pressure. The yield of ethyl anisate was 86%.



Ethyl Anisate

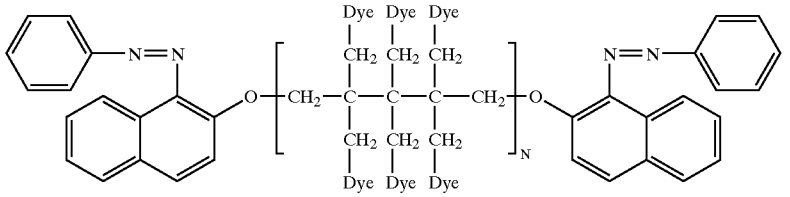
EXAMPLE 4

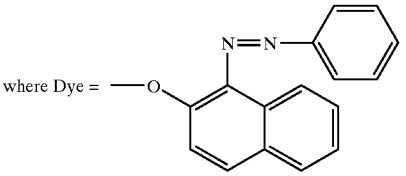
[0126] A mixture of ethyl anisate (5.81 gm), 34.56 gm of Polyisobutelene amine, 2 gm of ammonium chloride as catalyst and 75 ml of toluene was refluxed for 8-10 hrs under stirring. The reaction was monitored by TLC. After completion solvent and ethanol were removed from the product. The yield of ethyl anisate-PIB conjugate reaction product was 90%.



EXAMPLE 5

[0127] A mixture of oil orange R dye (30 gm), 26.06 gm of multibrominated polyisobutelene bromide and 120 ml diphenyl ether was refluxed for 10-12 hrs under stirring with elimination of HBr. Reaction was monitored by TLC. After completion, reaction mixture was dumped in 200 ml water to remove acidity. Solvent removed azeotropically and residue was distilled at reduced pressure. The yield of oil orange R dye-polyisobutelene-oil orange R dye conjugate reaction product was 25%.



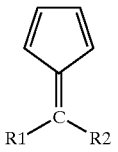


EXAMPLE 6

[0128] A mixture of appropriate aldehyde or ketone and 20 gm of freshly distilled cyclopentadiene is added to a solution of 6.9 gm of sodium in 75 ml of distilled methanol. After 3 hrs of stirring under nitrogen completion of reaction is monitored by TLC, then reaction mass is poured into 250 ml of water. The organic phase is extracted in dichloromethane and washed with water until the pH of aqueous washes is neutral. It is then dried over anhydrous sodium sulphate and filtered. The dichloromethane is removed and residue is distilled at reduced pressure. The yield of respective fulvene is indicated in the Table 5.

[0129] The general formula of fulvene is

TABLE 5



Ex. No	FULVENE	R1	R2	Aldehyde/ Ketone	YIELD (%)
6-13	6-(4-methoxy-phenyl) fulvene	—H	—C_6H_4.OMe	Anisaldehyde (40.8 gm)	89
6-2	6,6-Dimethoxy fulvene	—OMe	—OMe	Dimethyl carbonate	

EXAMPLE 7

[0130] This example describes the preparation and evaluation of the blends in gasoline fuel. See Tables 6 and 7. Blends were prepared by mixing the measured components as specified in the blends below, at room temperature and pressure. The RON values were measured by ASTM D2699.

TABLE 6

Blend No.	Compound	Quantity	RON
Blend 1	Naphtha	0.25 L	99
	Commercial Grade Ethanol	0.25 L	
	Ethylanisate-PIB conjugate[1]	0.20 mg	
	t-butylalcohol	0.086 mg	
Blend A	n-heptane (lab. Grade)	0.33 L	
	Iso-octane	0.42 L	
Blend B	Ethanol (Lab grade)	0.25 L	
	Blend A	0.25 L	
Blend 4	Blend B reference		101.3
Blend 5	Blend B	0.5 L	101.3
	Ethylanisate-PIB conjugate[1]	0.20 mg	
	t-butylalcohol	0.086 mg	
Blend 6	Commercial grade Ethanol	0.25 L	101.6
	n-heptane (lab. grade)	0.11 L	
	Iso-octane (lab. Grade)	0.14 L	
Blend 7	Commercial grade ethanol	0.25 L	99.0
	Naphtha	0.25 L	
	Ethylanisate-PIB conjugate[1]	0.20 mg	
	t-butylalcohol	0.086 mg	

[1](containing 0.02 mg impurities?)Additional 0.02 mg impurities

[0131]

TABLE 7

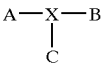
Blend No.	Compound	Quantity	Base RON	Final RON	dRON
1	Ethylanisate-Polyisobuttylene conjugate	0.4 gram[1]	56	97.6	41.6
	t-butyl alcohol	0.167 gram			
	Ethanol	0.4 L			
	n-heptane	0.264 L			
	Iso-octane	0.336 L			
2	Ethylanisate-Polyisobuttylene conjugate	0.4 gram[1]	56	68.4	12.4
	t-butyl alcohol	0.167 gram			
	Ethanol	0.1 L			
	n-heptane	0.396 L			
	Iso-octane	0.504 L			
3	Orange Dye-Polyisobutylene	0.4 gram[1]	84.7	92.6	7.9
3	Orange Dye-Polyisobutylene conjugate	0.4 gram[1]	84.7	92.6	7.9
	Ethanol	.1 L			
	Synthetic Fuel	.9 L			

[0132] Several scenarios have changed in the fuel sourcing, prices, policies for renewables, upcoming tighter emission standards. The present invention incorporates use of renewable ethanol and an organic antiknock that raises the octane far beyond the compositions and the method of uses known to one skilled in the art. Use of ethanol can raise the RVP. Methods of use suggested in this invention screen the organic anti-knocks for suitability with the fuel mixture of heavy straight chain (hence low RVP), naphtha and ethanol using IR, followed by ASTM tests. Blends of heavy naphtha or single component liquids derived from coal liquefaction (will be cheaper under the present scenario of high price of crude) will enhance the ability of present invention to reduce RVP, aromatic content and T90, increase the content of paraffins and simultaneously to reduce pollution (mixture of many hydrocarbons is replaced by single component.). Use of single component hydrocarbon and ethanol will automatically reduce olefins, T50, sulfur, T10 and also T90.

[0133] It is contemplated, and will be apparent to those skilled in the art from the foregoing specification, and examples, that modifications and/or changes may be made in the embodiments of the invention. Accordingly it is expressly intended that the foregoing are only illustrative of the preferred embodiments and modes of operation, not limiting thereto, and that the true spirit and scope of the present invention be determined by reference to the appended claims.

1) An anti-knock gasoline fuel composition suitable for combustion in an automotive engine comprising:

a) a compound of Formula I:



Formula I

wherein each of A, B and C is independently selected from the group consisting of alkyls, alkenes, aryls, heterocyclyls, aryloxy, cycloalkyls, cycloalkenyl, heteroaryls, esters, amides, ethers, aldehydes, ketones, carbonates, diazenes, aldehydic acids, alcohols, oxides, ketonic acids, othroesters, diesters, phenols, glycol ethers, glycols, alkyl carbonates, dialkyl carbonates, di-carbonates, organic and inorganic peroxides, hydroperoxides, carboxylic acids, amines, nitrates, di-nitrates, oxalates, boric acids, orthoborates, hydroxyacids, orthoacids, anhydrides, acetates, acetyls, benzoic acids, nitrates, di-nitrates, and nitro-ethers;

and X is polyalkyl, polyalkoxy, polyether, polyterphthalate or polycarbonate chain of from about 400 to 3600 g/mol; and

b) optionally at least one or more additives.

2) The composition according to claim 1, wherein X is selected from the group consisting of butyl, isobutyl, pentyl, hexyls, octyl, nonyl, dodecyl, docosyl, polyethylene, polypropylene, polyisobutylene, ethylene-propylene copolymer, chlorinated olefin polymer, polyether, paraffin and oxidized ethylene-propylene copolymer.

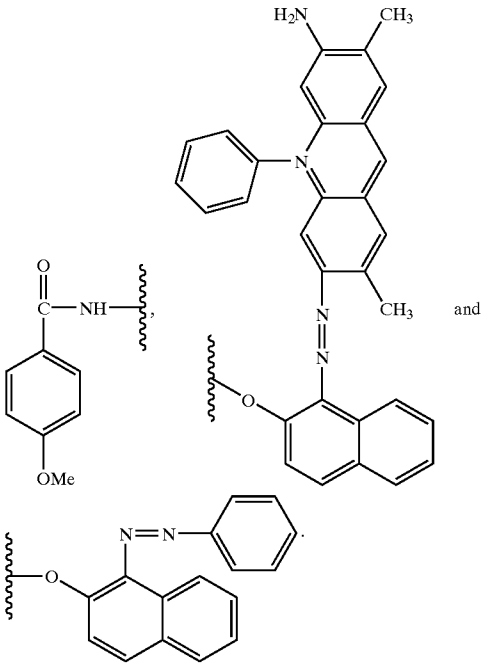
3) The composition according to claim 1, wherein X is polyisobutylene.

4) The composition according to claim 3, wherein the polyisobutylene has a number average molecular weight of from about 400 to about 3600 g/mol.

5) The composition according to claim 3, wherein the polyisobutylene is substituted, the substituents selected from the group consisting of alkoxy, hydroxyl, halo, alkyl, substituted alkyl, and nitro.

6) The composition according to claim 1, wherein X is paraffin.

7) The composition according to claim 1, wherein each of A, B or C are independently selected from the group consisting of:



8) The composition according to claim 1, wherein the substituted aryloxy is a dye moeity.

9) The composition according to claim 7, wherein the dye moiety is selected from the group consisting of reactive dye, direct dye, pigment powder, napthols, and basic dye.

10) The compound according to claim 7, wherein the dye moeity is selected from the group consisting of oil yellow, oil orange, oil orange R, oil red, oil green, oil cyanine green, oil violet, oil brilliant blue, and oil pink.

11) The composition according to claim 10, wherein the dye is selected from the group consisting of oil orange R, oil brilliant blue, and indoineblue.

12) The composition according to claim 1, wherein the additive is selected from the group consisting of fulvenes, alkyl carbonates, phenyl carbonates, dyes, aromatics, dye-polymer conjugates, ester-polymer conjugates, dye-paraffin conjugate, norbornadienes, organometallics and oxygenates.

13) The composition according to claim 1, wherein the additive is selected from the group consisting of ferrocene, ruthenocene, chromocene, osmocene, methyl cyclopentadienyl manganese tricarbonyl, napthacenes, methylferrocene, cobaltocene, nickelocene, titanocene dichloride, zirconocene dichloride, uranocene, decamethylferrocene, decamethylsilicocene, decamethylgermaniumocene, decamethylstannocene, decamethylphosocene, decamethylosmocene, decamethylruthenocene, decamethylzirconocene, silicocene, and decamethylsilicocene.

14) The composition according to claim 1, wherein the additive is selected from the group consisting of alcohols, esters, ethers, carboxylic acids and mixtures thereof.

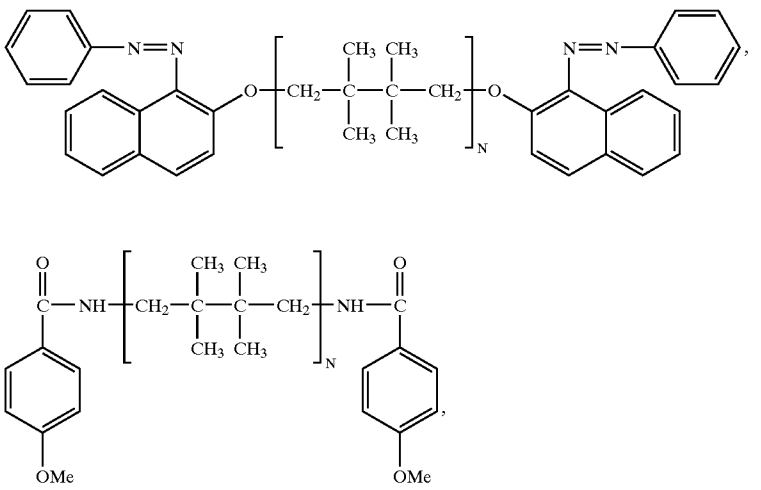
15) The composition according to claim 14, wherein the additive is ethanol, methanol, t-butyl alcohol, methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether(ETBE), tertiary amyl methyl ether(TAME), tetrahydrofuran or mixtures thereof.

16) The composition according to claim 1, wherein the concentration of compound of Formula I is less than 1500 ppm.

17) The composition according to claim 1, wherein the concentration of additive is less than 500 ppm.

18) The composition according to claim 1 wherein the concentration of additive is less than 49%.

19) A compound of claim 1 selected from the group consisting of compounds of the following formulae:



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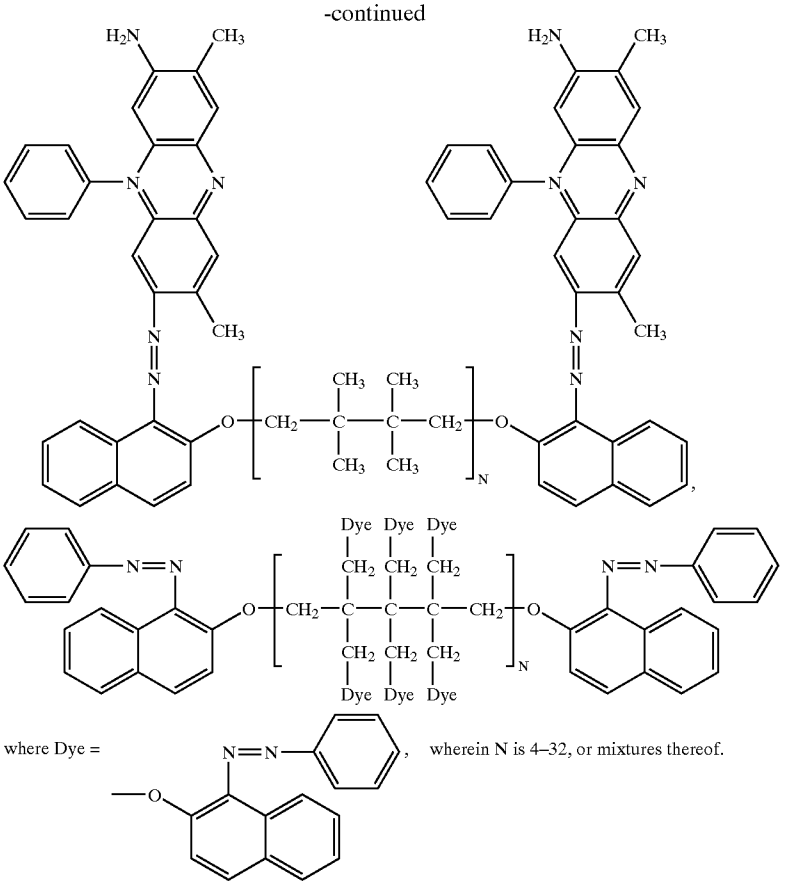

20) An anti-knock gasoline fuel composition suitable for combustion in an automotive engine consisting of:

a) an organic compound selected from the group consisting of alkenes, aldehydes, esters, ketones, alkyl carbonates, aryl carbonates, aminoaryls, cycloalkyl, aromatics, dye-polymer conjugates, ester-polymer conjugates, and dye-paraffin conjugates;

b) optionally an organometallic compound selected from the group consisting of ferrocene, ruthenocene, chromocene, osmocene, methyl cyclopentadienyl manganese tricarbonyl, nickelcarbonyls, organosilicon metallocene, alkyltin, and derivatives thereof; and

c) optionally an oxygenate selected from the group consisting of alcohols, esters, ethers, furans and mixtures thereof.

21) The composition according to claim 20 wherein the organic compound is selected from the group consisting of fulvenes, alkyl carbonates, phenyl carbonates, dyes, dye-polymer conjugates, ester-polymer conjugates, and dye-paraffin conjugate.

22) The composition according to claim 20 wherein the organometallic compound is selected from the group consisting of ferrocene, chromocene, and cyclopentadienyl manganese tricarbonyl.

23) The composition according to claim 20 wherein the oxygenate compound is selected from the group consisting of ethanol and tetrahydrofuran.

24) The composition according to claim 20 wherein the concentration of organic compound less than 1500 ppm.

25) The composition according to claim 20 wherein the concentration of organometallic is less than 500 ppm.

26) The composition according to claim 20 wherein the concentration of oxygenate is less than 49%.

27) The composition according to claim 20, wherein the composition further comprises a second additive, or mixture of two or more additives.

28) The composition of claim 20, wherein the organic compound is present in an amount from about 1 ppm by weight to about 1500 ppm by weight based on the total weight of the composition.

29) A method for improving the antiknock property of a gasoline fuel, the method comprising admixing an effective amount of at least one composition of claim 1 with the gasoline fuel.

30) The composition as claimed in claim 29, wherein the composition further comprises dyes, detergents, dispersants, demulsifiers, antioxidants, corrosion inhibitors, or stabilizers and other antiknock additives.

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