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(54) **MANNICH CONDENSATION PRODUCTS AS
SEQUESTERING AGENTS FOR FUELS AND
LUBRICATING OILS**

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(57)

ABSTRACT

Sequestering agents for use in fuels and lubricating oils derived from Mannich condensation reaction utilizing a poly-isobutyl-substituted hydroxyaromatic compound, an aldehyde, an alkali metal base, and glycine or aspartic acid, or an ester thereof.

MANNICH CONDENSATION PRODUCTS AS SEQUESTERING AGENTS FOR FUELS AND LUBRICATING OILS

FIELD

[0001] Provided herein are sequestering agents for use in fuels and lubricating oils derived from Mannich condensation reaction utilizing a polyisobutyl-substituted hydroxyaromatic compound, an aldehyde, an alkali metal base, and aspartic acid or an ester thereof.

BACKGROUND

[0002] Lubricating oils contain additives that perform many functions. Ashless dispersants are added to lubricating oils to disperse varnish, lacquer, and sludge that may be formed in the oil and prevent the formation of deposits. Ashless dispersants also disperse soot and prevent viscosity buildup caused by the agglomeration of soot in the oil. Over-based detergents are added to lubricating oils to neutralize acids. These acids can cause wear and corrosion, and can cause acid catalyzed reactions and rearrangements to occur in the oil. Anti-oxidants are added to lubricating oils to control oxidation of the oil by scavenging radicals or by decomposing hydroperoxides that are formed from the oxidation of the oil. Wear inhibitors are added to lubricating oils to prevent wear of the metal parts caused by friction. Other additives such as corrosion inhibitors, friction modifiers, viscosity index improvers, pour point depressants, seal, swell agents, etc., can also be added to lubricating oils to provide important properties to the finished lubricant.

[0003] Metal ions can play a role in the deterioration of lubricating oils. Transition metals such as Fe^{+3} , Cu^{+2} , Pb^{+2} , and other metals, can catalyze the oxidation of the oil resulting in the formation of the primary oxidation products such as hydroperoxides, carboxylic acids, carbonyl compounds, hydroxyl carbonyl compounds, and the like. In addition, metal ions such as Fe^{+3} , Cu^{+2} , Pb^{+2} , and other metals, can catalyze the polymerization of the primary oxidation products resulting in the formation of sludge, lacquer, and varnish.

[0004] Non-volatile constituents of fuel, such as additives, can form deposits or varnish on inlet valves and on heating elements. In addition, fuels are susceptible to chemical reactions, such as oxidation, on aging. Oxidation produces soluble and insoluble materials that form deposits that interfere with the proper functioning of internal combustion engines.

[0005] Thus, there is a need for agents that complex or sequester the metal ions and prevent the metal ions from acting as oxidation and polymerization catalysts in hydrocarbon mediums.

SUMMARY

[0006] Provided herein are compounds prepared by Mannich condensation of:

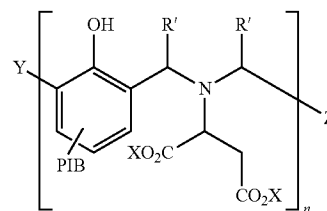
[0007] (a) a polyisobutyl-substituted hydroxyaromatic compound having a number average molecular weight of about 1600 to about 3000;

[0008] (b) an aldehyde;

[0009] (c) aspartic acid, or an ester thereof; and

[0010] (d) an alkali metal base.

[0011] Provided herein are also compounds of Formula I:

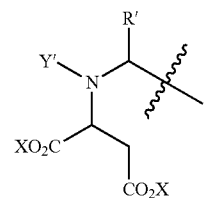


[0012] wherein PIB is a polyisobutyl group having a number average molecular weight of about 1600 to about 3000;

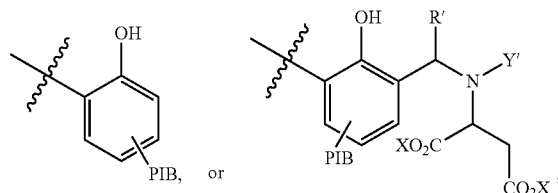
[0013] X is, independently, hydrogen, an alkali metal ion, an ammonium ion, or alkyl having one to ten carbon atoms;

[0014] R' is, independently, hydrogen or alkyl having one to 10 carbon atoms, cycloalkyl having from 3 to 10 carbon atoms, aryl having 6 to 10 carbon atoms, alkaryl having 7 to 20 carbon atoms, or aralkyl having 7 to 20 carbon atoms;

[0015] Y is hydrogen, alkyl having 1 to 10 carbon atoms, or $\text{CHR}'\text{OH}$, or

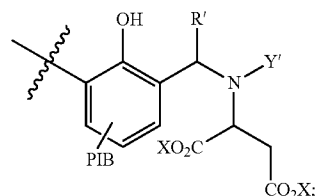


[0016] Z is hydrogen, hydroxyl,



[0017] n is an integer from 0 to 20;

[0018] wherein if n is 0, then Z is



[0019] and Y' is H or $\text{—CHR}'\text{OH}$.

DETAILED DESCRIPTION

Definitions

[0020] As used herein, the term “alkali metal” refers to Group 1A metals of the periodic table. In some embodiments, the alkali metal is lithium, sodium, or potassium.

[0021] As used herein, the term “alkali metal base” refers to alkali metal hydroxides and alkali metal alkoxides.

[0022] As used herein, the term “Mannich condensation” refers to reactions suitable to effect a condensation reaction of the components (a)-(d) recited herein. Exemplary conditions are provided herein.

[0023] As used herein, the term “oil of lubricating viscosity” refers to lubricating oils which may be mineral oil or synthetic oils of lubricating viscosity and, in some embodiments, useful in the crankcase of an internal combustion engine. Exemplary crankcase lubricating oils include those having a viscosity of about 1300 centistokes at -17.8°C . to 22.7 centistokes at 98.9°C . The lubricating oils may be derived from synthetic or natural sources. Mineral oil for use as the base oil include, e.g., paraffinic, naphthenic and other oils that are ordinarily used in lubricating oil compositions. Synthetic oils include, e.g., hydrocarbon synthetic oils, synthetic esters and Fischer-Tropsch derived base oil. Synthetic hydrocarbon oils include, e.g., liquid polymers of α -olefins having the proper viscosity. In some embodiments, the oil is a hydrogenated liquid oligomer of C_6 to C_{12} α -olefins, including, e.g., 1-decene trimer. In some embodiments, the oil is an alkyl benzene of proper viscosity, including but not limited to didodecyl benzene. Exemplary synthetic esters include, but are not limited to the esters of both mono-carboxylic acids and polycarboxylic acids as well as mono-hydroxy alkanols and polyols. Examples include, but are not limited to, didodecyl adipate, pentaerythritol tetracapoate, di-2-ethylhexyl adipate, di-laurylsebacate and the like. Esters also include, but are not limited to, complex esters prepared from mixtures of mono- and di-carboxylic acid and mono- and di-hydroxy alkanols. In some embodiments, blends of hydrocarbon oils and synthetic oils are utilized. Exemplary blends include, but are not limited to, blends of 10 weight percent to 25 weight percent hydrogenated 1-decene trimer with 75 weight percent to 90 weight percent 683 centistokes at 37.8°C . mineral oil.

[0024] As used herein, “polyisobutyl-substituted phenol” refers to a polyisobutyl-substituted phenol ring.

[0025] As used herein, “VW TDI-2 Engine Test” refers to engine procedure CEC L-78-T-99 published by the Coordinating European Council for the Development of Performance Tests for Transportation Fuels, Lubricants and Other Fluids.

Compounds

[0026] Provided herein are compounds prepared by Mannich condensation of:

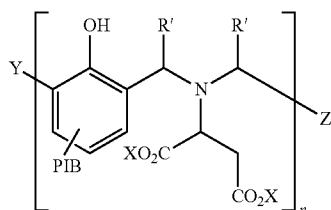
[0027] (a) a polyisobutyl-substituted hydroxyaromatic compound having a number average molecular weight of about 1600 to about 3000;

[0028] (b) an aldehyde;

[0029] (c) aspartic acid, or an ester thereof; and

[0030] (d) an alkali metal base.

[0031] The compounds, in certain embodiments, have the structure of the Formula I:

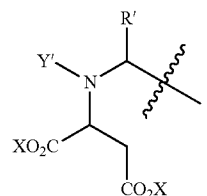


[0032] wherein PIB is a polyisobutyl group having a number average molecular weight of about 1600 to about 3000;

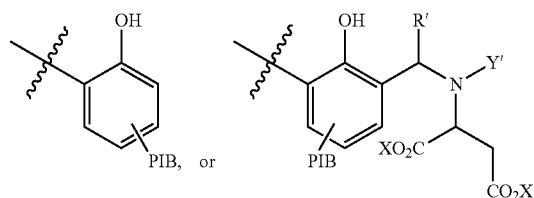
[0033] X is, independently, hydrogen, an alkali metal ion, or alkyl having one to ten carbon atoms;

[0034] R' is, independently, hydrogen or alkyl having one to 10 carbon atoms, cycloalkyl having from 3 to 10 carbon atoms, aryl having 6 to 10 carbon atoms, alkaryl having 7 to 20 carbon atoms, or aralkyl having 7 to 20 carbon atoms;

[0035] Y is hydrogen, alkyl having 1 to 10 carbon atoms, or $\text{CHR}'\text{OH}$, or

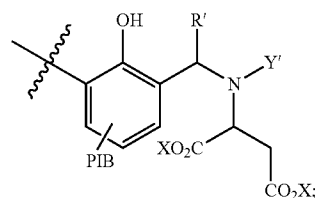


[0036] Z is hydrogen, hydroxyl,



[0037] n is an integer from 0 to 20;

[0038] wherein if n is 0, then Z is

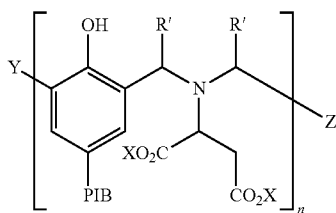


[0039] and Y' is H or $\text{—CHR}'\text{OH}$.

[0040] In some embodiments, the polyisobutyl group has a number average molecular weight of about 1700 to about 2900. In some embodiments, the polyisobutyl group has a number average molecular weight of about 1800 to about 2800. In some embodiments, the polyisobutyl group has a number average molecular weight of about 1900 to about 2700. In some embodiments, the polyisobutyl group has a number average molecular weight of about 2000 to about 2600. In some embodiments, the polyisobutyl group has a number average molecular weight of about 2100 to about 2500. In some embodiments, the polyisobutyl group has a number average molecular weight of about 2200 to about 2400. In some embodiments, the polyisobutyl group has a number average molecular weight of about 2300.

[0041] In some embodiments, the polyisobutyl group has at least 50 weight percent methylvinylidene isomer. In some embodiments, the polyisobutyl group has at least 70 weight percent methylvinylidene isomer. In some embodiments, the polyisobutyl group has at least 90 weight percent methylvinylidene isomer.

[0042] In some embodiments, the compound of Formula I has the following structure:

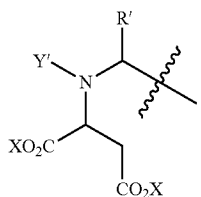


wherein PIB, X, Y, Z, R', and n are as defined herein.

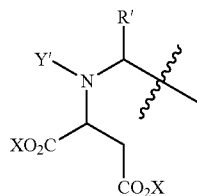
[0043] In some embodiments, X is hydrogen. In some embodiment, X is an alkyl having one to six carbon atoms. In some embodiments, X is an alkali metal ion. In some embodiments, X is lithium sodium, or potassium. In some embodiments, X is sodium. In some embodiments, X is an ammonium ion.

[0044] In some embodiments, R' is hydrogen or alkyl having one to 10 carbon atoms. In some embodiments, R' is hydrogen.

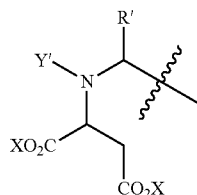
[0045] In some embodiments, Y is hydrogen. In some embodiments, Y is $-\text{CHR}'\text{OH}$. In some embodiments, Y is $-\text{CH}_2\text{OH}$. In some embodiments, Y is



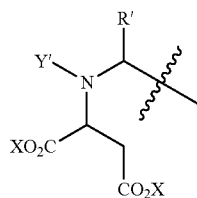
In some embodiments, Y is



wherein Y' is H. In some embodiments, Y is

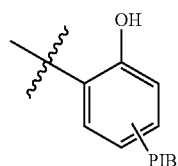


wherein Y' is $-\text{CHR}'\text{OH}$. In some embodiments, Y is

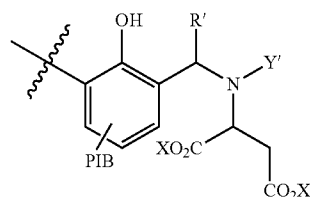


wherein Y' is $-\text{CH}_2\text{OH}$.

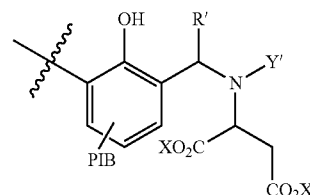
[0046] In some embodiments, Z is hydroxyl. In some embodiments, Z is hydrogen. In some embodiments, Z is



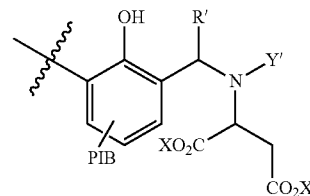
In some embodiments, Z is



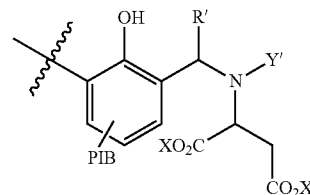
In some embodiments, Z is



wherein Y' is H. In some embodiments, Z is



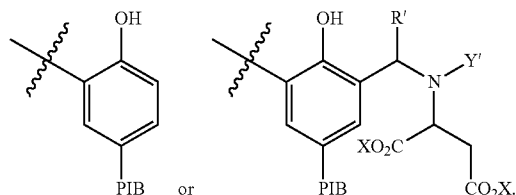
wherein Y' is $-\text{CHR}'\text{OH}$. In some embodiments, Z is



wherein Y' is

$-\text{CH}_2\text{OH}$.

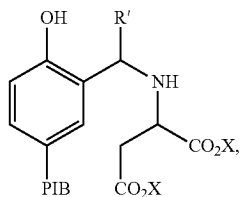
[0047] In some embodiments, Z is



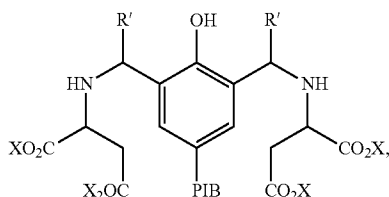
[0048] In some embodiments, n is an integer from 1-20. In some embodiments, n is an integer from 3-18. In some embodiments, n is an integer from 10-15. In some embodi-

ments, n is an integer from 11-13. In some embodiments, n is 10. In some embodiments, n is 11. In some embodiments, n is 12. In some embodiments, n is 13. In some embodiments, n is 14. In some embodiments, n is 15. In some embodiments, n is an integer from 0-5. In some embodiments, n is an integer from 6-10. In some embodiments, n is an integer from 11-15. In some embodiments, n is an integer from 16-20.

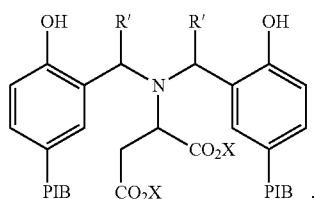
[0049] In some embodiments, the compound is a compound of Formula II, III, IV, V, VI, or VII:



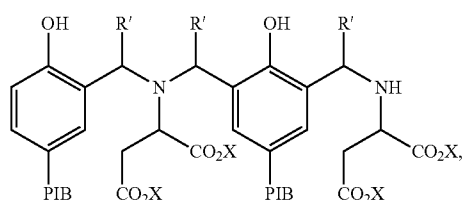
II



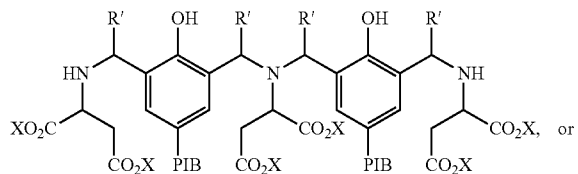
III



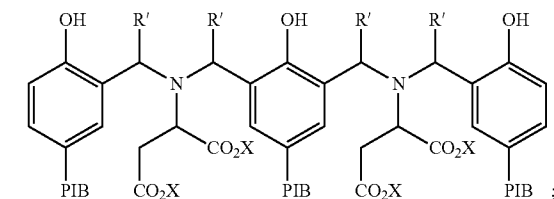
IV



V



VI

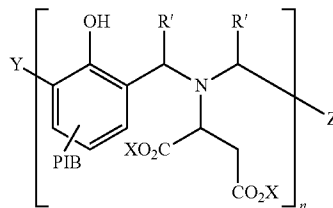


VII

wherein X and R' are as defined elsewhere herein.

[0050] In some embodiments, the compound is the product of a Mannich condensation of the compounds of Formula II, III, IV, V, VI, or VIII, an aldehyde described herein, and aspartic acid or ester thereof

[0051] In some embodiments, the compound of Formula I has the following structure:



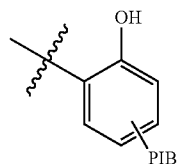
[0052] wherein PIB is a polyisobutyl group having a number average molecular weight of about 1600 to about 3000;

[0053] X is, independently, hydrogen, an alkali metal ion, an ammonium ion, or alkyl having one to six carbon atoms;

[0054] R' is, independently, hydrogen or alkyl having one to six carbon atoms;

[0055] Y is hydrogen, alkyl having 1 to 6;

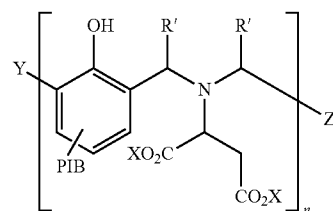
[0056] Z is hydrogen, hydroxyl, or



[0057] n is an integer from 0 to 20;

[0058] and Y' is H or $—CHR'OH$.

[0059] In some embodiments, the compound of Formula I has the following structure:



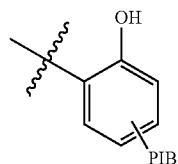
[0060] wherein PIB is a polyisobutyl group having a number average molecular weight of about 1600 to about 3000;

[0061] X is, independently, hydrogen, an alkali metal ion, an ammonium ion, or alkyl having one to six carbon atoms;

[0062] R' is, independently, hydrogen or alkyl having one to six carbon atoms;

[0063] Y is hydrogen, alkyl having 1 to 6;

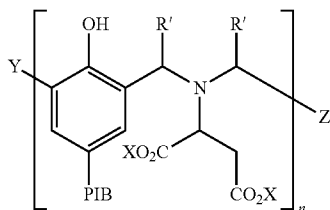
[0064] Z is hydrogen, hydroxyl, or



[0065] n is an integer from 10 to 15;

[0066] and Y' is H or $—CHR'OH$.

[0067] In some embodiments, the compound of Formula I has the following structure,



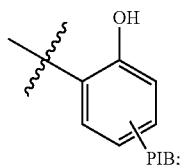
[0068] wherein PIB is a polyisobutyl group having a number average molecular weight of about 2100 to about 2500;

[0069] X is, independently, hydrogen or sodium;

[0070] R' is, independently, hydrogen or methyl;

[0071] Y is hydrogen;

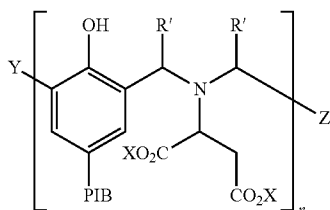
[0072] Z is hydrogen, hydroxyl, or



[0073] n is an integer from 10 to 15;

[0074] and Y' is H or $\text{—CH(CH}_3\text{)OH}$.

[0075] In some embodiments, the compound of Formula I has the following structure,



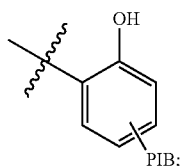
[0076] wherein PIB is a polyisobutyl group having a number average molecular weight of about 2200 to about 2400;

[0077] X is, independently, hydrogen or sodium;

[0078] R' is, independently, hydrogen or methyl;

[0079] Y is hydrogen;

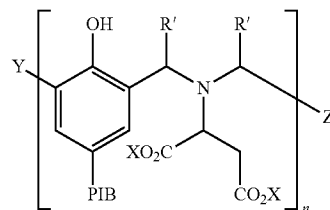
[0080] Z is hydrogen, hydroxyl, or



[0081] n is an integer from 10 to 15;

[0082] and Y' is H or $\text{—CH(CH}_3\text{)OH}$.

[0083] In some embodiments, the compound of Formula I has the following structure,



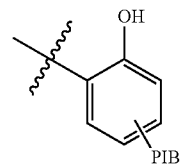
[0084] wherein PIB is a polyisobutyl group having a number average molecular weight of about 2100 to about 2500;

[0085] X is, independently, hydrogen or sodium;

[0086] R' is, independently, hydrogen or methyl;

[0087] Y is hydrogen;

[0088] Z is hydrogen, hydroxyl, or



[0089] n is 12;

[0090] and Y' is H or $\text{—CH(CH}_3\text{)OH}$.

Polyisobutyl-Substituted Aromatic Compound

[0091] Exemplary polyisobutyl-substituted aromatic compounds include those where the polyisobutyl group is derived from polyisobutene containing at least 50 weight percent methylvinylidene isomer. In some embodiments, the polyisobutyl group is derived from polyisobutene containing at least 70 weight percent methylvinylidene isomer. In some embodiments, the polyisobutyl group is derived from polyisobutene containing at least 90 weight percent methylvinylidene isomer.

[0092] The polyisobutyl group of the these compounds have a number average molecular weight of about 1600 to about 3000. In some embodiments, the polyisobutyl group has a number average molecular weight of about 1700 to about 2900. In some embodiments, the polyisobutyl group has a number average molecular weight of about 1800 to about 2800. In some embodiments, the polyisobutyl group has a number average molecular weight of about 1900 to about 2700. In some embodiments, the polyisobutyl group has a number average molecular weight of about 2000 to about 2600. In some embodiments, the polyisobutyl group has a number average molecular weight of about 2100 to about 2500. In some embodiments, the polyisobutyl group has a number average molecular weight of about 2200 to about 2400. In some embodiments, the polyisobutyl group has a number average molecular weight of about 2300.

[0093] In some embodiments, the polyisobutyl-substituted aromatic compound is a polyisobutyl-substituted hydroxyaromatic compound. In some embodiments, the attachment of the polyisobutyl substituent to the hydroxyaromatic ring is para to the hydroxyl moiety in at least 60 percent of the total polyisobutyl-substituted phenol molecules. In

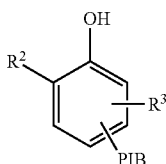
some embodiments, the attachment of the polyisobutyl substituent to the hydroxyaromatic ring is para to the hydroxyl moiety in at least 80 percent of the total polyisobutyl-substituted phenol molecules. In some embodiments, the attachment of the polyisobutyl substituent to the hydroxyaromatic ring is para to the hydroxyl moiety on the phenol ring in at least 90 percent of the total polyisobutyl-substituted phenol molecules.

[0094] In some embodiments, the polyisobutyl-substituted hydroxyaromatic compound is polyisobutyl-substituted phenol. In some embodiments, the polyisobutyl-substituted phenol is derived from polyisobutene containing at least 50 weight percent methylvinylidene isomer. In some embodiments, the polyisobutyl-substituted phenol is derived from polyisobutene containing at least about 70 weight percent methylvinylidene isomer. In some embodiments, the polyisobutyl-substituted phenol is derived from polyisobutene containing at least about 90 weight percent methylvinylidene isomer.

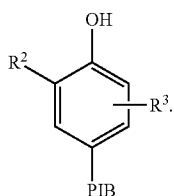
[0095] In some embodiments, the phenol has a position ortho to the hydroxyl group on the aromatic ring.

[0096] In some embodiments, the aromatic compound is a di-substituted phenol having an unsubstituted position ortho to the hydroxyl on the phenol ring. Examples of di-substituted phenols include, e.g., o-cresol derivatives substituted in the para position.

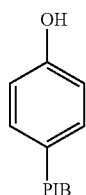
[0097] In some embodiments, the polyisobutyl-substituted aromatic compound has the following formula:



wherein PIB is a polyisobutyl group derived from polyisobutene containing at least 50 weight percent methylvinylidene isomer and having a number average molecular weight in the range of about 1600 to about 3000; R² is hydrogen or alkyl having 1 to about 10 carbon atoms; and R³ is hydrogen or hydroxyl. In some embodiments, the polyisobutyl-substituted aromatic compound has the following formula:



[0098] In some embodiments, the polyisobutyl-substituted aromatic compound is:



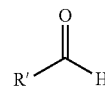
[0099] In some embodiments, the polyisobutenes may be prepared using boron trifluoride (BF₃) alkylation catalyst as

described in U.S. Pat. Nos. 4,152,499 and 4,605,808, the entireties of which are incorporated herein by reference. Commercially available polyisobutenes having a high alkylvinylidene content include Glissopal® 2300, available from BASF.

[0100] In some embodiments, the polyisobutyl-substituted phenol is a mono-substituted phenol, wherein the polyisobutyl substituent is attached at the para-position to the phenol ring.

Aldehyde

[0101] As used herein, the term “aldehyde” refers compound having the following formula:



wherein R' is hydrogen, alkyl, cycloalkyl, aryl, alkaryl, or aralkyl.

[0102] In some embodiments, the alkyl has one to 20 carbon atoms. In some embodiments, the alkyl has one to 10 carbon atoms. In some embodiments, the alkyl has one to 6 carbon atoms. In some embodiments, the alkyl has one to 3 carbon atoms. In some embodiments, the alkyl is branched. In some embodiments, the alkyl is linear.

[0103] In some embodiments, the cycloalkyl has 3 to 6 carbon atoms.

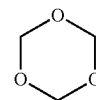
[0104] In some embodiments, the aryl has 6 to 10 carbon atoms.

[0105] In some embodiments, the alkaryl has 7 to 20 carbon atoms. In some embodiments, the alkaryl has 7 to 15 carbon atoms. In some embodiments, the alkaryl has 7 to 10 carbon atoms.

[0106] In some embodiments, the aralkyl has 7 to 20 carbon atoms. In some embodiments, the aralkyl has 7 to 15 carbon atoms. In some embodiments, that aralkyl has 7 to 10 carbon atoms.

[0107] Exemplary aldehydes include, but are not limited to aliphatic aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, caproaldehyde and heptaldehyde. Further exemplary aldehydes include, but are not limited to aromatic aldehydes such as benzaldehyde and alkylbenzaldehyde, e.g., para-tolualdehyde. Exemplary aldehydes also include, but are not limited to formaldehyde producing reagents, such as paraformaldehyde and aqueous formaldehyde solutions such as formalin. In some embodiments, the aldehyde is paraformaldehyde and formalin.

[0108] In some embodiments, the aldehyde is formaldehyde. In some embodiments, the aldehyde in a gaseous, liquid, or solid form. Exemplary gaseous formaldehyde forms include the monomer CH₂O and the trimer, (CH₂O)₃ (trioxane) having the formula given below:



Exemplary liquid formaldehyde forms include:

[0109] 1. monomer CH₂O in ethyl ether;

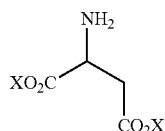
[0110] 2. monomer CH₂O in water which has the formulas CH₂(H₂O)₂ (methylene glycol) and HO(—CH₂O)_n—H; and

[0111] 3. monomer CH₂O in methanol which has the formulas OHCH₂OCH₃ and CH₃O(—CH₂O)_n—H.

[0112] Formaldehyde solutions are commercially available in water and various alcohols. In water it is available as a 37%-50% solution. Formalin is a 37% solution in water. Formaldehyde is also commercially available as linear and cyclic (trioxane) polymers. Linear polymers may be low molecular weight or high molecular weight polymers.

Aspartic Acid or Ester Thereof

[0113] The compounds provided herein are prepared by Mannich condensation utilizing aspartic acid or an ester thereof. In some embodiments, aspartic acid is utilized. In some embodiments, an ester of aspartic acid is utilized. In some embodiments, the ester has the following formula:



wherein X is alkyl. In some embodiments, X is alkyl of one to ten carbon atoms. In some embodiments, X is alkyl of one to six carbon atoms. In some embodiments, X is methyl, ethyl, n-propyl, isopropyl, tert-butyl, sec-butyl, isobutyl, or n-butyl. In some embodiments, X is methyl or ethyl.

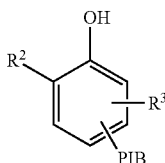
Alkali Metal Base

[0114] In some embodiments, the alkali metal base an alkali metal hydroxide selected from the group consisting of sodium hydroxide, lithium hydroxide and potassium hydroxide. In some embodiments, the alkali metal hydroxide is sodium hydroxide or potassium hydroxide. In some embodiments, the base is sodium hydroxide.

[0115] In some embodiments the alkali metal may also be replaced with Group II metals of the Periodic Table. In some embodiments when the Mannich condensation product sequestering agent is to be used as a fuel additive, the alkali metal ion is replaced with an ammonium ion.

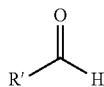
[0116] In some embodiments, the compounds provided herein are prepared by Mannich condensation of:

[0117] (a) a compound having the following formula:



[0118] wherein PIB is a polyisobutyl group derived from polyisobutene containing at least 50 weight percent methylvinylidene isomer and having a number average molecular weight in the range of about 1600 to about 3000, R² is hydrogen or alkyl having 1 to about 10 carbons; and R³ is hydrogen or hydroxyl;

[0119] (b) a compound having the following formula:



[0120] wherein R' is hydrogen, alkyl having one to three carbon atoms;

[0121] (c) aspartic acid, or an ester thereof; and

[0122] (d) sodium hydroxide, lithium hydroxide or potassium hydroxide.

Compositions and Methods of Use

[0123] The present disclosure is also directed to a method for preventing metal ion catalyzed oxidation and polymerization reactions in a hydrocarbon medium comprising sequestering the metal ion by the addition of an effective amount of the compounds described herein. In some embodiments, the compounds described herein are added to engine oil. "Sequestering" refers to holding, associating with, or bonding with a metal atom, e.g., holding a metal atom between two or more atoms of a single molecule of the compound, thereby neutralizing or controlling harmful metal ions, e.g., Fe⁺³, in a lubricating oil or fuel.

[0124] A further embodiment of the present disclosure is directed to a lubricating oil composition comprising a major amount of an oil of lubricating viscosity and a minor effective amount of one or more of the compounds described herein.

[0125] A further embodiment of the present disclosure is directed to a lubricating oil concentrate comprising about 20 percent to 80 percent of a diluent oil of lubricating viscosity and an effective amount of one or more of the compounds described herein. In some embodiments, the lubricating oil composition or lubricating oil concentrate comprise other additives, e.g., those designed to improve the properties of the lubricating oil.

[0126] A further embodiment of the present disclosure is directed to a fuel compositions comprising a major amount of hydrocarbons boiling in the gasoline or diesel range and a minor effective amount of one or more of the above described compounds, wherein the compounds have been further reacted to remove/replace any alkali metal. In some embodiments, the compounds described herein are reacted or treated in such a way that any alkali metal salt present is converted to an ammonium or other appropriate salt giving an ashless product.

[0127] A further embodiment of the present disclosure is directed to a fuel concentrate comprising an inert stable oleophilic organic solvent boiling in the range of from about 65° C. to about 204° C. and from about 10 weight percent to about 90 weight percent of one or more of the compounds described herein, wherein the one or more compounds has been further reacted to remove/replace any alkali metal present.

[0128] The compounds of the present disclosure may also be employed as dispersants in lubricating oil. For use as dispersants in fuels the alkali metal ions are replaced with ammonium ions.

[0129] The present disclosure is also directed to methods of sequestering metals and preventing metal ion catalyzed oxidation and polymerization reactions, while maintaining sufficient oil solubility for use in lubricating oils and fuels. In some embodiments, the sequestered metal is Fe⁺³.

[0130] The present disclosure is also directed to a lubricating oil additive composition comprising a major amount of an oil of lubricating viscosity and a minor amount of the compound described herein. A mixture of one or more of the compounds described herein are also contemplated in the lubricating oil additive composition. In some embodiments, the compounds described herein are present in the lubricating oil composition in the range of from about 0.01 weight percent to about 10 weight percent. In some embodiments, the compound is present in the range of from about 0.1 weight percent to about 5 weight percent. In some embodiments, the compound is present in the range of from about 0.3 weight percent to about 2 weight percent. In some embodiments, the lubricating oil additive composition contain other additives

including, e.g., detergents (overbased and non-overbased), dispersants, extreme pressure agents, wear inhibitors, rust inhibitors, foam inhibitors, corrosion inhibitors, pour point depressants, antioxidants, zinc dithiophosphates.

[0131] The present disclosure is also directed to a lubricating oil concentrate. Lubricating oil additive concentrates, in some embodiments, include from 90 weight percent to 10 weight percent of an organic liquid diluent and from 10 weight percent to 90 weight percent (on a dry polymer basis) of the compound described herein. In some embodiments, the concentrates contain sufficient diluent to make them easy to handle during shipping and storage. In some embodiments, the compounds described herein are present in the lubricating oil concentrate in the range of from about 10 weight percent to about 90 weight percent dry polymer Mannich condensation product described herein. In some embodiments, the compound is present in the range of from about 30 weight percent to about 70 weight percent dry polymer Mannich condensation product. In some embodiments, the compound is present in the range of about 50 weight percent dry polymer Mannich condensation product.

[0132] The present disclosure is also directed to a fuel additive composition comprising a major amount of hydrocarbons boiling in the gasoline or diesel range and a minor effective amount of the compound described herein. A mixture of one or more of the compounds described herein are also contemplated in the fuel composition. In some embodiments, the fuel composition will contain the compound described herein in the range of from about 25 parts per million to about 2,500 parts per million. In some embodiments, the composition contains the compound in the range of from about 50 parts per million to about 1,500 parts per million. In some embodiments, the composition contains the compound in the range of from about 70 parts per million to about 1,000 parts per million. The gasoline fuel additive composition provided herein may include other fuel additives, including, e.g., oxygenates, anti-knock agents, dispersants, detergents, lead scavengers, anti-oxidants, pour point depressants, corrosion inhibitors and demulsifiers. The gasoline fuels may also contain amounts of other fuels, for example, methanol. The diesel fuel additive composition described herein may also contain other additives, including, e.g., pour point depressants, flow improvers and cetane improvers. The diesel fuels may also contain amounts of other fuels, for example, methanol.

[0133] A further embodiment of the present disclosure is also directed to a fuel concentrate comprising an inert stable oleophilic organic solvent boiling in the range of from about 65° C. to about 204° C. and from about 10 weight percent to about 90 weight percent of one or more compounds described herein. In some embodiments, the fuel concentrate will contain the compounds described herein in the range of from about 10 weight percent to about 70 weight percent. In some embodiments, the fuel concentrate contains the compounds described herein in the range of from about 10 weight percent to about 50 weight percent. In some embodiments, the fuel concentrate contains the compounds described herein in the range of from about 20 weight percent to about 40 weight percent.

[0134] A fuel-soluble, non-volatile carrier fluid or oil may also be used with the fuel additive composition described herein. The carrier fluid is a chemically inert hydrocarbon-soluble liquid vehicle which substantially increases the non-volatile residue, or the solvent-free liquid fraction of the fuel

additive composition while not overwhelmingly contributing to octane requirement increase. The carrier fluid may be a natural or a synthetic oil, such as mineral oil or refined petroleum oils.

[0135] In some embodiments, an engine lubricating oil composition may contain the following components:

- (a) a major amount of oil of lubricating viscosity;
- (b) 0.01 weight percent to 10.0 weight percent of at least one of the compounds described herein, e.g., compounds of Formula I;
- (c) 1.0 weight percent to 10.0 weight percent of at least one borated or non-borated succinimide ashless detergent;
- (d) 0.05 weight percent to 0.5 weight percent, as calcium, of at least one calcium sulfonate, phenate or salicylate detergent;
- (e) 0.02 weight percent to 0.2 weight percent, as phosphorus, of at least one secondary or mixture of primary and secondary alkyl zinc dithiophosphate;
- (f) 0.0 weight percent to 5.0 weight percent of at least one diphenyl amine oxidation inhibitor;
- (g) 0.0 weight percent to 0.5 weight percent of, as molybdenum, of at least one molybdenum succinimide oxidation inhibitor;
- (h) 0.0 weight percent to 5.0 weight percent of at least one partial; carboxylic ester or borated ester friction modifier;
- (i) 0.0 weight percent to 0.05 weight percent of at least one supplemental anti-wear/extreme pressure agent, such as molybdenum dithiocarbamate;
- (j) 0.0 weight percent to 0.1 weight percent of at least one foam inhibitor; and
- (k) 0.0 weight percent to 2.0 weight percent of at least one olefin copolymer viscosity index improver.

[0136] The compounds described herein may also be employed as dispersants in lubricating oil. For use as dispersants in fuels, in some embodiments, the alkali metal ions of the compounds described herein are replaced with ammonium ions.

Preparation of Compounds

[0137] Another embodiment of the present disclosure is directed to a process for preparing a compound comprising reacting a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl moiety is derived from polyisobutene containing at least 50 weight percent methylvinylidene isomer and a number average molecular weight in the range of about 1600 to about 3000, an aldehyde, aspartic acid or ester thereof, and optionally a diluent, in the presence of a base.

[0138] In some embodiments, the diluents is an alkanol having one to 10 carbon atoms. In some embodiments, the alkanol is methanol.

[0139] The aspartic acid may be added in the form of the acid or its alkali metal ion salt. In some embodiments, the alkali metal ion is a sodium ion or a potassium ion. In some embodiments, the alkali metal is sodium.

[0140] The compounds provided herein may be prepared via Mannich condensation reactions. General procedures for such reaction are provided in U.S. Pat. Nos. 7,964,543 and 7,351,864, the entireties of which are incorporated by reference. In some embodiments, the compounds are prepared by combining under reaction conditions a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group has a number average molecular weight in the range of from about 1600 to about 3,000, an aldehyde, aspartic acid or ester thereof, and an alkali metal base. In some embodiments,

the reaction is carried out batch wise. In some embodiments, the reaction is carried in continuous or semi-continuous mode.

[0141] In some embodiments, the reaction is carried under atmospheric pressure. In some embodiments, the reaction is carried out under sub atmospheric or super atmospheric.

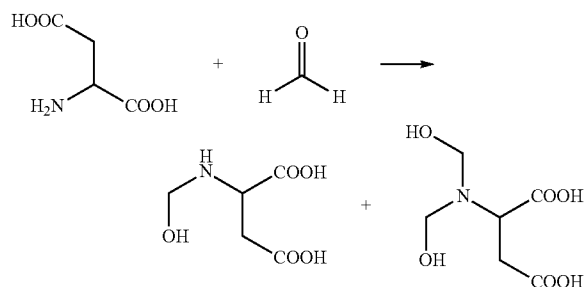
[0142] The temperature for this reaction may vary widely. In some embodiments, the temperature range is from about 10° C. to about 200° C. In some embodiments, the temperature range is from about 50° C. to about 150° C. In some embodiments, the temperature range is from about 70° C. to about 130° C.

[0143] The reaction may be carried out in the presence of a diluent or a mixture of diluents capable of dissolving the starting materials of this reaction and allowing the reacting materials to come in contact with each other. Mixtures of diluents can be used for this reaction. Useful diluents for this reaction include but are not limited to water, alcohols, (including methanol, ethanol, isopropanol, 1-propanol, 1-butanol, isobutanol, sec-butanol, butanediol, 2-ethylhexanol, 1-pentanol, 1-hexanol, ethylene glycol, and the like), DMSO, NMP, HMPA, cellosolve, diglyme, various ethers (including diethyl ether, THF, diphenylether, dioxane, and the like), aromatic diluents (including toluene, benzene, o-xylene, m-xylene, p-xylene, mesitylene and the like), esters, alkanes (including pentane, hexane, heptane, octane, and the like), and various natural and synthetic diluent oils (including 100 neutral oils, 150 neutral oils, polyalphaolefins, Fischer-Tropsch derived base oil and the like, and mixtures of these diluents. Mixtures of diluents that form two phases such as methanol and heptane are suitable diluents for this reaction. Diluents also include, but are not limited to chlorobenzene, neutral oils of lubricating viscosity, paraffins, naphthenes, Chevron® Aromatic 100N or Exxon® 150 N.

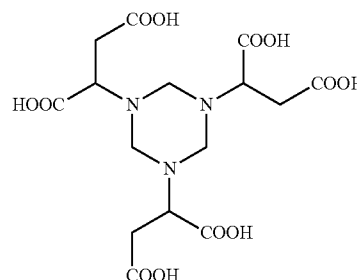
[0144] In some embodiments when the compounds described herein are to be used as an additive in lubricating oil, the polyisobutyl-substituted phenol is first dissolved in an alkyl-substituted aromatic solvent. The certain embodiments, the alkyl substituent on the aromatic solvent has from 3 carbon atoms to 15 carbon atoms. In some embodiments, the alkyl substituent on the aromatic solvent has from 6 carbon atoms to 12 carbon atoms.

[0145] In some embodiments, the reaction is carried out by first reacting the hydroxyaromatic compound with the alkali metal base, followed by the addition of aspartic acid or ester thereof and the aldehyde. In some embodiments, the aspartic acid or ester thereof is reacted with the aldehyde followed by the addition of the hydroxyaromatic compound and the alkali metal base.

[0146] Without being limited to any theory, it is believed that the reaction of the aspartic acid or ester thereof, plus the aldehyde, such as formaldehyde, may produce the intermediate formula

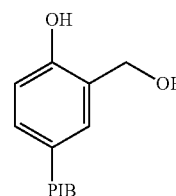


which may ultimately form the cyclic formula



[0147] Without being limited to any theory, it is believed that these intermediates may react with the hydroxyaromatic compound and the base to form the compounds described herein.

[0148] Without being limited to any theory, in the alternative, it is believed that the reaction of the hydroxyaromatic compound with the aldehyde may produce the intermediate formula



[0149] Without being to any theory, it is also believed that this intermediate may react with the amino acid or ester derivative thereof and the base to form the compounds described herein.

[0150] The time of the reaction can vary widely depending on the temperature. In some embodiments, the reaction is between about 0.1 hour to about 20 hours. In some embodiments, the reaction time is from about 2 hours to about 10 hours. In some embodiments, the reaction time is from about 3 hours to about 7 hours.

[0151] The charge mole ratio (CMR) of the reagents can also vary over a wide range. In some embodiments, the compounds contain at least one polyisobutyl-substituted phenol ring and one aspartic acid group connected by one aldehyde group and one alkali metal. In such an instance, the polyisobutyl-substituted phenol/aldehyde/aspartic acid/base charge mole ratio is 1.0/1.0/1.0/1.0. In some embodiments, the polyisobutyl-substituted phenol/aldehyde/aspartic acid/base charge mole ratio is 1.0 to 20.0:1.0 to 39.0:1.0 to 20.0:1.0 to 4.0. In some embodiments, the polyisobutyl-substituted phenol/aldehyde/aspartic acid/base charge mole ratio is 1.0 to 5.0:1.0 to 10.0:1.0 to 6.0:1.0 to 3.0. In some embodiments, the polyisobutyl-substituted phenol/aldehyde/aspartic acid/base charge mole ratio is 1.0 to 3.0:1.0 to 5.0:1.0 to 3.0:1.0 to 2.0. In some embodiments, the polyisobutyl-substituted phenol/aldehyde/aspartic acid/base charge mole ratio is 1:1:2:1.

EXAMPLES

Compound Preparation

Example 1

Mannich Condensation Product Derived from 2300 MW PIB-Phenol

[0152] To a 1 L 4-neck glass round bottom flask equipped with a mechanical stirrer, thermocouple and temperature con-

troller, nitrogen line, and reflux condenser was added 153.17 g (0.0632 moles) of a polyisobutyl phenol prepared from highly reactive polyisobutene with >70% methylvinylidene content and number average molecular weight of 2300 Daltons; the polyisobutyl phenol had a hydroxyl number of 23.2 mg KOH/g. It was stirred and warmed to about 80° C. 0.358 g (0.07 mole equivalents) of 50% aqueous NaOH were added, and the mixture was stirred for about 3 minutes then 3.999 g (2 mole equivalents) of paraformaldehyde was added. Stirring was continued at about 80° C. for about 90 minutes. 16.718 g of a hot (about 75° C.) aqueous solution containing 14% NaOH (0.93 mole equivalents) and 50% aspartic acid (1 mole equivalent). Stirring continued at about 80° C. for an additional 90 minutes. The reaction mixture was a pale yellow. A Dean-Stark trap was added to the reaction vessel, and the temperature was ramped to 160° C. and water was removed. Stirring continued at 160° C. for 1.5 hours. The heat was removed and at about 110° C. 128.63 g of Chevron 100N diluent oil was added. The product was a yellow oil. 150.3 g of toluene was added to the product and the solution was vacuum filtered through Celite 535 in a warmed Buchner funnel using a Whatman #1 filter. The toluene was removed en vacuo to yield a turbid yellow oil. The product had the following analysis:

[0153] TBN: 18.76 mg KOH/g

[0154] % Na: 4129.6 ppm

[0155] % N: 0.29%

Example 2

Mannich Condensation Product Derived from 2300 MW PIB-Phenol

[0156] A second sample was prepared in the same manner as example 1, except that 208.95 g (0.0820 moles) of 2300 MW polyisobutyl phenol having a hydroxyl number of 22.025 mg KOH/g was used, and the hold time at 160° C. was 1 hour. All other reagents were adjusted to the polyisobutyl phenol charge, and 172.28 g of diluent oil was used. The product was a turbid yellow oil; it was combined with the product from example 1.

The combined products had the following analysis:

[0157] TBN: 17.87 mg KOH/g

[0158] % Na: 4082.7 ppm

[0159] % N: 0.29%

Comparative Example 1

Mannich Condensation Product Derived from 1000 MW PIB-Phenol

[0160] A product was prepared in the same manner as example 1 except that 150.20 g (0.151 moles) of a 1000 MW polyisobutyl phenol prepared from highly reactive polyisobutene with >70% methylvinylidene content and number average molecular weight of 1000 Daltons, and 2 mole equivalents of NaOH were used; the polyisobutyl phenol had a hydroxyl number of 56.42 mg KOH/g. All other reagents were adjusted to the polyisobutyl phenol charge, and 138.45 g of diluent oil was used. The product was a turbid yellow oil with the following analysis:

[0161] TBN: 77.26 mg KOH/g

[0162] % Na: 2.05%

[0163] % N: 0.66%

Compound Evaluation

[0164] The VW TDI-2 Engine Test was utilized to evaluate the performance of a sample of 2300 molecular weight PIB-derived Mannich product (prepared as per the Examples above) and Comparative Example. Specifically, fully formulated SAE 5W-30 grade passenger car motor oil containing approximately 3.45 weight percent of the 2300 MW product was compared against fully formulated SAE 5W-30 grade passenger car motor oil containing approximately 1.5 weight percent of the comparative example. The difference in weight percent of the samples tested accounts for the difference in molecular weight of the PIB. The results of the experiments described above are summarized in the table below.

TABLE 1

Piston	Baseline	PIB number average molecular weight: 1000 (Comparative)	PIB number average molecular weight: 2300
Piston 1	65.9	64.5	72.2
Piston 2	58.3	57.7	65.1
Piston 3	53.3	62	60.3
Piston 4	64.8	62.6	65.4
Average	61	62	66

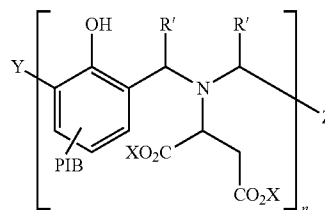
[0165] As shown in Table 1 above, the compounds of the present disclosure were found to be superior to both the baseline oil (without chelating agent) and the comparative example, achieving a “pass” result of >65 in the stringent TDi test.

[0166] The embodiments of the invention described above are intended to be merely exemplary, and those skilled in the art will recognize, or will be able to ascertain using no more than routine experimentation, numerous equivalents of specific compounds, materials, and procedures. All such equivalents are considered to be within the scope of the invention and are encompassed by the appended claims.

[0167] All of the patents, patent applications and publications referred to herein are incorporated herein in their entireties. Citation or identification of any reference in this application is not an admission that such reference is available as prior art to this invention. The full scope of the invention is better understood with reference to the appended claims.

What is claimed is:

1. A compound of Formula I:

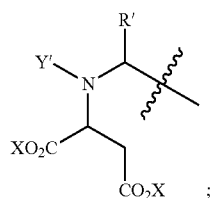


wherein PIB is a polyisobutyl group having a number average molecular weight of about 1600 to about 3000;

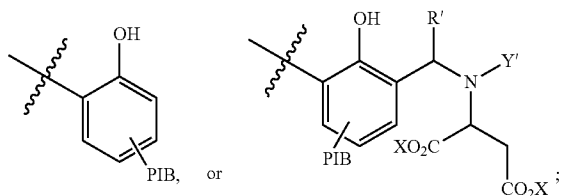
X is, independently, hydrogen, an alkali metal ion, an ammonium ion, or alkyl having one to ten carbon atoms;

R' is, independently, hydrogen or alkyl having one to 10 carbon atoms, cycloalkyl having from 3 to 10 carbon atoms, aryl having 6 to 10 carbon atoms, alkaryl having 7 to 20 carbon atoms, or aralkyl having 7 to 20 carbon atoms;

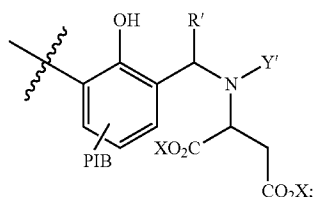
Y is hydrogen, alkyl having 1 to 10 carbon atoms, or CHR'OH, or



Z is hydrogen, hydroxyl,

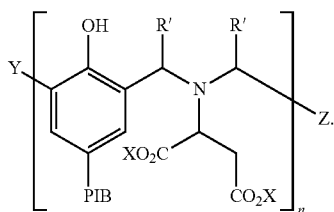


n is an integer from 0 to 20;
wherein if n is 0, then Z is



and Y' is H or —CHR'OH.

2. The compound of claim 1, wherein the compound has the following formula:

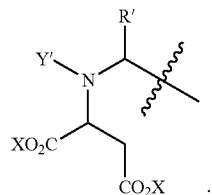


3. The compound of claim 1, wherein the polyisobutyl group has a number average molecular weight of about 2100 to about 2500.

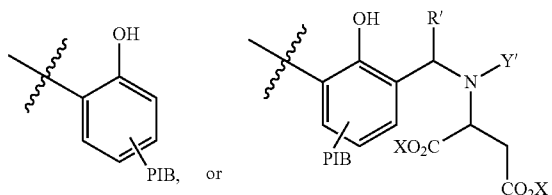
4. The compound of claim 1, wherein X is ammonium, lithium, sodium, or potassium.

5. The compound of claim 1, wherein R' is hydrogen.

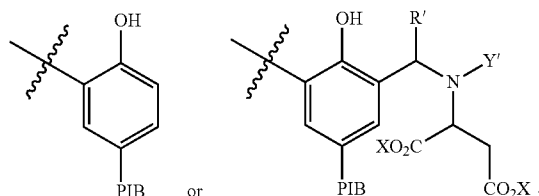
6. The compound of claim 1, wherein Y is hydrogen or



7. The compound of claim 1, wherein Z is



8. The compound of claim 1, wherein Z is



9. The compound of claim 1, wherein Y' is H.

10. The compound of claim 1, wherein n is an integer from 0 to 5.

11. The compound of claim 1, wherein the polyisobutyl group contains at least 50 weight percent of methylvinylidene isomer.

12. The compound of claim 1, wherein the polyisobutyl group contains at least 90 weight percent of methylvinylidene isomer.

13. A compound prepared by the Mannich condensation of:
(a) a polyisobutyl-substituted hydroxyaromatic compound having a number average molecular weight of about 1600 to about 3000;

(b) an aldehyde;

(c) aspartic acid, or an ester thereof; and

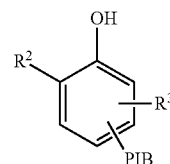
(d) an alkali metal base.

14. The compound of claim 13, wherein the polyisobutyl-substituted hydroxyaromatic compound has a number average molecular weight of about 2100 to about 2500.

15. The compound of claim 13, wherein the polyisobutyl-substituted hydroxyaromatic compound is derived from polyisobutene containing at least 50 weight percent methylvinylidene isomer.

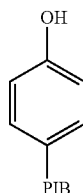
16. The compound of claim 13, wherein the polyisobutyl-substituted hydroxyaromatic compound is derived from polyisobutene containing at least 90 weight percent methylvinylidene isomer.

17. The compound of claim 13, wherein the polyisobutyl-substituted hydroxyaromatic compound has the following formula:



wherein PIB is a polyisobutyl group derived from polyisobutene containing at least 50 weight percent methylvinylidene isomer and having a number average molecular weight in the range of about 1600 to about 3000; R² is hydrogen or alkyl having 1 to about 10 carbon atoms; and R³ is hydrogen or hydroxyl.

18. The compound of claim **17**, wherein the polyisobutyl-substituted hydroxyaromatic compound has the following formula:



19. The compound of claim **13**, wherein the aldehyde is formaldehyde.

20. The compound of claim **13**, wherein the alkali metal base is sodium hydroxide, lithium hydroxide or potassium hydroxide.

21. A method for preventing or controlling metal ion catalyzed oxidation and polymerization reactions in a hydrocarbon medium comprising sequestering the metal ion by the addition of an effective amount of the compound of claim **1**.

22. A fuel composition comprising a major amount of hydrocarbons boiling in the gasoline or diesel range and a minor effective amount of one or more of the compounds of claim **1**.

23. A lubricating oil composition comprising a major amount of an oil of lubricating viscosity and a minor effective amount of one or more of the compounds of claim **1**.

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