

1 MANNICH CONDENSATION PRODUCTS USEFUL
2 AS SEQUESTERING AGENTS

3
4 FIELD OF THE INVENTION

5 The present invention is directed to Mannich condensation product
6 sequestering agents or mixtures of Mannich condensation product
7 sequestering agents for use in fuels and lubricating oils. The present
8 invention is also directed to a process for preparing the Mannich condensation
9 product sequestering agents. The present invention is also directed to a
10 product formed by combining, under reaction conditions, a polyisobutyl-
11 substituted hydroxyaromatic compound, an aldehyde, an amino acid or ester
12 thereof, and an alkali metal base to form the Mannich condensation product
13 sequestering agent. The present invention is also directed to a lubricating oil
14 composition, a lubricating oil concentrate, a fuel composition, and a fuel
15 concentrate having the Mannich condensation product sequestering agents of
16 the present invention.

17 BACKGROUND OF THE INVENTION

18 Lubricating oils contain additives that perform many important functions.
19 Ashless dispersants are added to lubricating oils to disperse varnish, lacquer,
20 and sludge that may be formed in the oil and prevent the formation of
21 deposits. Ashless dispersants also disperse soot and prevent viscosity
22 buildup caused by the agglomeration of soot in the oil. Overbased detergents
23 are added to lubricating oils to neutralize acids. These acids can cause wear
24 and corrosion, and can cause acid catalyzed reactions and rearrangements to
25 occur in the oil. Anti-oxidants are added to lubricating oils to control oxidation
26 of the oil by scavenging radicals or by decomposing hydroperoxides that are
27 formed from the oxidation of the oil. Wear inhibitors are added to lubricating
28 oils to prevent wear of the metal parts caused by friction. Other additives
29 such as corrosion inhibitors, friction modifiers, viscosity index improvers, pour

1 point depressants, seal, swell agents, etc., can also be added to lubricating
2 oils to provide important properties to the finished lubricant.

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

10 In order to prevent the metal catalyzed oxidation and polymerization of
11 lubricating oils, it would be desirable to find a way to complex or sequester the
12 metal ions and prevent the metal ions from acting as oxidation and
13 polymerization catalysts.

14 Sequestering agents have many uses, in living plants for supplying necessary
15 trace elements, in metal plating baths, removing rust stains, removing
16 impurities and in fuels and lubricating oils. Most well known sequestering
17 agents are useful only in aqueous media. There is a great need for good
18 sequestering agents that are oil-soluble. Oil-soluble sequestering agents are
19 also useful for the introduction of metals into non-aqueous systems, for
20 providing oil-borne micro-nutrients to plants and many other uses known to
21 persons skilled in the art. Oils useful for lubricating internal combustion
22 engines are generally either mineral oils or synthetic oils of lubricating
23 viscosity. Thus, sequestering agents for use in lubricating oils or hydrocarbon
24 fuels must be oil-soluble.

25 The conventional oil-soluble Mannich condensation products are useful in
26 internal combustion engine fuels. Non-volatile constituents of fuel, such as
27 additives, sometimes form deposits or varnish on inlet valves and on heating
28 elements. Such deposits and varnish impair the efficiency of these elements.
29 In addition, fuels are susceptible to chemical reactions, such as, oxidation, on

1 aging. One effect of oxidation is to produce soluble and insoluble materials
2 that form deposits which interfere with the proper functioning of the internal
3 combustion engines. The conventional oil-soluble Mannich condensation
4 products help to reduce deposits.

5 Oil-soluble Mannich condensation products are also useful in internal
6 combustion engine lubricating oils. These products generally act as
7 dispersants to disperse sludge, varnish, and lacquer, and prevent the
8 formation of deposits. In general, conventional oil-soluble Mannich
9 condensation products are formed from the reaction of polyisobutyl-
10 substituted phenols with formaldehyde and an amine or a polyamine. These
11 products have limited ability to sequester Fe^{+3} and have limited ability to
12 prevent the Fe^{+3} catalyzed oxidation and polymerization that often occur.

13 Water soluble Mannich condensation products are well known as
14 sequestering agents. However, such products cannot be used as
15 sequestering agents in fuels and lubricating oils.

16 The preparation of Mannich condensation products is well known in the art. A
17 number of patents disclose Mannich condensation products of alkylphenols,
18 aldehydes and amines. However, none of the known Mannich condensation
19 products contain both the needed oil solubility and the ability to sequester
20 Fe^{+3} to prevent Fe^{+3} catalyzed oxidation and polymerization reaction in
21 lubricating oil.

22 U. S. Patent No. 4,032,304 discloses an improved fuel composition containing
23 a normally liquid fuel, a carboxylic acid ester of lubricating viscosity and an oil-
24 soluble nitrogen-containing dispersant. The dispersant is characterized by the
25 presence therein of a substantially saturated hydrocarbon-based radical
26 having at least 50 carbon atoms. The dispersant is preferably a carboxylic
27 dispersant or a Mannich-type dispersant. The Mannich-type dispersant is for
28 example the reaction product of an alkylphenol with formaldehyde and a
29 polyethylene polyamine.

1 U. S. Patent No. 4,069,249 discloses a novel Mannich condensation product
2 chelating agent for iron (III) or iron (II). The chelating agent is a Mannich
3 condensation product made from phenol or substituted-phenol, formaldehyde,
4 a di-amino di-acid and a di-amine. The process for making these Mannich
5 condensation products is disclosed in U.S. Patent No. 4,338,460.

6 U. S. Patent No. 4,166,726 discloses a fuel additive and fuel composition. The
7 additive compound is a mixture of a polyisobutylene amine and the reaction
8 product of an alkylphenol, an aldehyde and an amine. The additive provides
9 surprising stability in preventing thermal degradation of fuels, particularly fuels
10 for compression ignition engines.

11 U. S. Patent No. 4,116,991 discloses an aromatic chelating agent having a
12 hydroxyl group at the center of the molecule. Such chelating agents have
13 better stability in an alkaline environment.

14 U. S. Patent No. 4,130,582 discloses a process for the preparation of phenolic
15 ethylenediamine polycarboxylic acids in predominantly the ortho isomeric form
16 which comprises reacting a phenol compound, ethylenediamine, glyoxylic acid
17 and a base, said phenol compound functioning both as a reactant and as a
18 solvent for the reaction system.

19 U. S. Patent No. 4,197,091 discloses a composition for inhibiting the corrosion
20 of ferrous metal pipelines used to transport petroleum hydrocarbons
21 comprising a major portion of a mixture of C₃₆ di-carboxylic dimer acid and a
22 C₅₄ trimer acid, which mixture has an acid number of at least 110 and from 0,5
23 up to 5% of a composition from the group consisting of (a) an N,N'-di(ortho-
24 hydroxyarylidene)-1,2-alkyldiamine in which the arylidene radical contains 6-7
25 carbon atoms and the alkylene radical contains 2-3 carbon atoms; and (b) a
26 polymeric condensation product obtained by the reaction of a phenol having
27 two reactive ring positions, a lower aliphatic aldehyde and a polyamine.

1 U. S. Patent No. 4,225,502, a division of application Serial No. 630,792,
2 Patent No. 4,069,249 discussed above, discloses a novel Mannich
3 condensation product chelating agent for iron (III) or iron (II). The chelating
4 agent is a Mannich condensation product made from phenol or substituted-
5 phenol, formaldehyde, a di-amino di-acid and a di-amine. The single claim is
6 to a cyano-substituted compound.

7 U. S. Patent No. 4,200,545 discloses combinations of amino phenols, wherein
8 said phenols contain a substantially saturated hydrocarbon substituent of at
9 least 10 aliphatic carbon atoms, and one or more detergent/dispersants
10 selected from the group consisting of (I) neutral or basic metal salts of an
11 organic sulfur acid, phenol or carboxylic acid; (II) hydrocarbyl-substituted
12 amines wherein the hydrocarbyl substituent is substantially aliphatic and
13 contains at least 12 carbon atoms; (III) acylated nitrogen-containing compounds
14 having a substituent of at least 10 aliphatic carbon atoms; and (IV) nitrogen-
15 having condensates of a phenol, aldehyde and amino compound. Fuels and
16 lubricants having such combinations as additives are particularly useful in
17 two-cycle (two-stroke) engines.

18 U. S. Patent No. 4,387,244 discloses that alkyl-substituted hydroxybenzyl
19 amino acid oligomers are effective metal chelating agents in a broad range of
20 non-aqueous systems. The products claimed display surprisingly high
21 solubilities in a broad range of substituted and unsubstituted aliphatic and
22 aromatic solvents.

23 U. S. Patent No. 4,655,949 discloses a novel lubricating oil composition
24 comprising an organometallic additive, including a metal selected from
25 Groups I, Ib and VIII of the Periodic System of Elements, e.g. Na, K, Cu, Co,
26 Ni or Fe, chelated with the reaction product of formaldehyde, an amino acid
27 and a phenol, dissolved in a lubricating oil. Depending on the choice of metal,
28 the above organometallic additive imparts rust inhibition, sludge dispersant,
29 wear reduction and anti-oxidant properties to the said lubricating oil.

1 U. S. Patent No. 4,734,212 discloses Bis-Mannich base deposit inhibitors;
2 lubricating oil compositions having these inhibitors and a process for
3 preparing these inhibitors.

4 U. S. Patent No. 4,847,415 discloses certain Mannich reaction products (i.e.
5 alkylated phenol, polyoxyalkylenediamine, and an aldehyde) which are used
6 to deactivate iron species already present in hydrocarbon fluids. Left
7 untreated, such iron species lead to decomposition resulting in the formation
8 of gummy, polymer masses in the hydrocarbon liquid. The method for the
9 preparation of these Mannich condensation products are claimed in the
10 divisional U. S. Patent No. 4,883,580.

11 U. S. Patent No. 4,894,139 discloses certain Mannich reaction products
12 formed from the reaction of an alkyl-substituted catechol, a polyamine and an
13 aldehyde which are used to deactivate copper metal species contained in
14 hydrocarbon fluids. Left untreated, such species lead to decomposition
15 resulting in the formation of gummy, polymer masses in the hydrocarbon
16 liquid.

17 U. S. Patent No. 5,122,161 discloses a diesel fuel composition comprising (a)
18 a major portion of a diesel fuel, and (b) a minor amount, as a diesel fuel
19 injector detergent, of a glycolated Mannich coupled product of bis-
20 polyisobutylene succinimide of a polyamine, prepared by: (i) reacting an
21 alkylsuccinic acid anhydride with a polyamine to form a bis-succinimide; (ii)
22 reacting the bis-succinimide with a phenol in the presence of an aldehyde to
23 form a Mannich phenol coupled bis-succinimide product; (iii) glycolating the
24 Mannich phenol coupled bis-succinimide product with glycolic acid to form a
25 glycolated Mannich phenol coupled bis-succinimide product; and (iv)
26 recovering the glycolated Mannich phenol coupled bis-succinimide product.

27 U. S. Patent No. 5,641,394 discloses a composition for use in deactivating
28 iron species in hydrocarbon fluids, comprising the products resulting from the
29 reaction of (I) a substituted-catechol, (II) a mixture of polyamines, and (III) an

1 aldehyde. The composition also functions as an anti-oxidant in hydrocarbon
2 fluids. The anti-oxidant function is separate from, and in addition to the metal
3 deactivating properties of the invention. These functional properties of the
4 invention can act either singly, or in concert, for stabilization of hydrocarbon
5 fluids.

6 An article titled "Preparation of Amphiphilic Polyisobutylenes-b-
7 polyethylenamines by Mannich Reaction. III. Synthesis of Polyisobutylenes-b-
8 polyethylenamines," by J.D. Jamois, M. Tessier and E. Marechal, Journal of
9 Polymer Science: Part A: Polymer Chemistry, Vol. 31, 1959-1966 (1993)
10 discloses preparation of copolymers associating alpha-phenololigoisobutylene
11 and triethylenetetramine blocks in the same chain by reacting aqueous
12 formaldehyde with alpha-phenololigoisobutylene and triethylenetetramine.

13 SUMMARY OF THE INVENTION

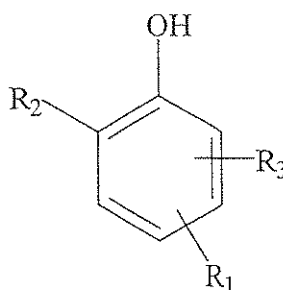
14 The present invention is directed to a Mannich condensation product
15 sequestering agent or mixtures of Mannich condensation product
16 sequestering agents for use in fuels and lubricating oils. The present
17 invention is also directed to a method for preparing the Mannich condensation
18 product sequestering agents. The present invention is also directed to a
19 product formed by combining, under reaction conditions, a polyisobutyl-
20 substituted hydroxyaromatic compound, an aldehyde, an amino acid or ester
21 thereof, and an alkali metal base to form the Mannich condensation product
22 sequestering agent. The present invention is also directed to a lubricating oil
23 composition, a lubricating oil concentrate, a fuel composition, and a fuel
24 concentrate having the Mannich condensation product sequestering agents of
25 the present invention.

26 Accordingly, the present invention is directed to a Mannich condensation
27 product prepared by the Mannich condensation of:

- 1 (a) a polyisobutyl-substituted hydroxyaromatic compound, wherein
2 the polyisobutyl group is derived from polyisobutene containing
3 at least about 50 weight percent methylvinylidene isomer and
4 has a number average molecular weight in the range of from
5 about 400 to about 5,000;
- 6 (b) an aldehyde;
- 7 (c) an amino acid or ester derivative thereof; and
- 8 (d) an alkali metal base.

9 In another embodiment the present invention is directed to a Mannich
10 condensation product prepared by the Mannich condensation of:

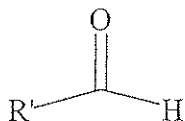
- 11 (a) a polyisobutyl-substituted hydroxyaromatic compound having
12 the formula:



13

14 wherein R₁ is a polyisobutyl group derived from polyisobutene
15 containing at least 50 weight percent methylvinylidene isomer
16 and having a number average molecular weight in the range of
17 about 400 to about 5,000, R₂ is hydrogen or lower alkyl having
18 one carbon atom to about 10 carbon atoms, and R₃ is hydrogen
19 or -OH;

- 20 (b) a formaldehyde or an aldehyde having the formula:



1

2

3

4

5

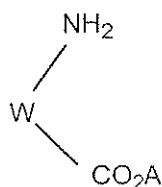
6

7

wherein R' is branched or linear alkyl having one carbon atom to about 10 carbon atoms, cycloalkyl having from about 3 carbon atoms to about 10 carbon atoms, aryl having from about 6 carbon atoms to about 10 carbon atoms, alkaryl having from about 7 carbon atoms to about 20 carbon atoms, or aralkyl having from about 7 carbon atoms to about 20 carbon atoms;

8

(c) an amino acid or ester derivative thereof having the formula:



9

10

11

12

13

14

15

16

17

wherein W is $-\text{[CHR'']}_m$ wherein each R'' is independently H, alkyl having one carbon atom to about 15 carbon atoms, or a substituted-alkyl having one carbon atom to about 10 carbon atoms and one or more substituents selected from the group consisting of amino, amido, benzyl, carboxyl, hydroxyl, hydroxyphenyl, imidazolyl, imino, phenyl, sulfide, or thiol; and m is an integer from one to 4, and A is hydrogen or alkyl having one carbon atom to about 6 carbon atoms; and

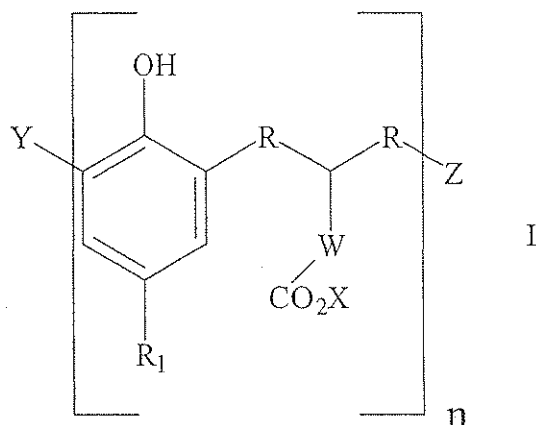
18

(d) an alkali metal base.

19

20

In general, the principal Mannich condensation product of the invention can be represented by the formula:



1

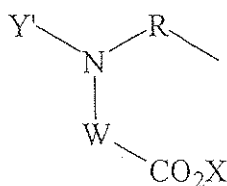
2 wherein each R is independently -CHR'-, wherein R' is as defined above, R₁
 3 is a polyisobutyl group derived from polyisobutene containing at least 50
 4 weight percent methylvinylidene isomer and having a number average
 5 molecular weight in the range of about 400 to about 5,000;

6 X is hydrogen, an alkali metal ion or alkyl having one to about 6 carbon
 7 atoms;

8 W is -[CHR'']-_m wherein each R'' is independently H, alkyl having one
 9 carbon atom to about 15 carbon atoms, or a substituted-alkyl having one
 10 carbon atom to about 10 carbon atoms and one or more substituents
 11 selected from the group consisting of amino, amido, benzyl, carboxyl,
 12 hydroxyl, hydroxyphenyl, imidazolyl, imino, phenyl, sulfide, or thiol; and m is
 13 an integer from one to 4;

14 Y is hydrogen, alkyl having one carbon atom to about 10 carbon atoms, -
 15 CHR'OH, wherein R' is as defined above,

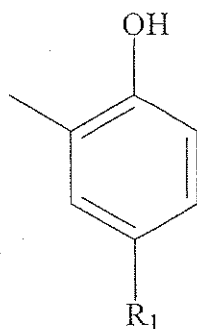
16 or



17

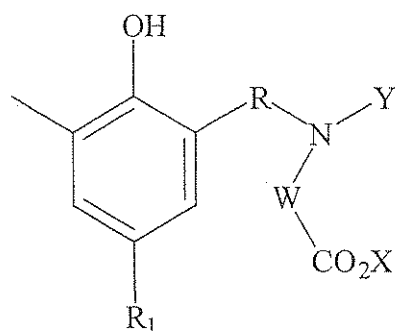
1 wherein Y' is -CHR'OH, wherein R' is as defined above; and R, X,
2 and W are as defined above;

3 Z is hydroxyl, a hydroxyphenyl group of the formula:



4

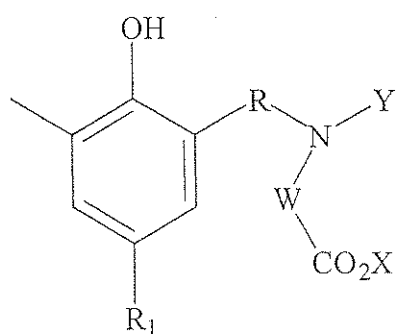
5 or



6

7 wherein R, R₁, Y', X, and W are as defined above,

8 and n is an integer from 0 to 20, with the proviso that when n = 0, Z must be:



9

1 wherein R, R₁, Y', X, and W are as defined above.

2 Preferably the R₁ polyisobutyl group has a number average molecular weight
3 of about 500 to about 2,500. More preferably the R₁ polyisobutyl group has a
4 number average molecular weight of about 700 to about 1,500. Most
5 preferably the R₁ polyisobutyl group has a number average molecular weight
6 of about 700 to about 1,100.

7 Preferably the R₁ polyisobutyl group is derived from polyisobutene containing
8 at least about 70 weight percent methylvinylidene isomer and more preferably
9 the R₁ polyisobutyl group is derived from polyisobutene containing at least 90
10 weight percent methylvinylidene isomer.

11 In the compound of formula I above, preferably X is hydrogen, more
12 preferably an alkali metal ion and most preferably a sodium ion.

13 In another embodiment of the invention, in the compound of formula I above,
14 X is alkyl selected from methyl or ethyl.

15 In a preferred embodiment of the Mannich condensation product of the
16 present invention R is CH₂, R₁ is derived from polyisobutene containing at
17 least 50 weight percent methylvinylidene isomer and a number average
18 molecular weight in the range of about 700 to about 1,100, W is CH₂, X is
19 sodium ion and n is 0 to 20.

20 Another embodiment of the present invention is directed to a method for
21 preventing metal ion catalyzed oxidation and polymerization reactions in a
22 hydrocarbon medium comprising sequestering the metal ion by the addition of
23 an effective amount of the Mannich condensation product of the present
24 invention, as described above. The method for preventing metal ion
25 catalyzed oxidation and polymerization reactions is particularly suitable for
26 sequestering the metal ion by the addition of an effective amount of the
27 Mannich condensation product of the present invention in engine oil.

1 The present invention is also directed to a product formed by combining,
2 under reaction conditions, a polyisobutyl-substituted hydroxyaromatic
3 compound, an aldehyde, an amino acid or amino acid ester, and an alkali
4 metal base to form the Mannich condensation product sequestering agent.

5 Another embodiment of the present invention is directed to a process for
6 preparing a Mannich condensation product comprising reacting a polyisobutyl-
7 substituted hydroxyaromatic compound, wherein the polyisobutyl moiety is
8 derived from polyisobutene containing at least 50 weight percent
9 methylvinylidene isomer and a number average molecular weight in the range
10 of about 400 to about 5,000, an aldehyde, an amino acid or amino acid ester
11 and optionally a diluent, in the presence of a base.

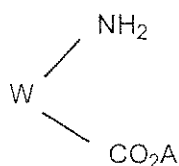
12 Preferably the polyisobutyl-substituted hydroxyaromatic compound is
13 polyisobutyl-substituted phenol wherein the polyisobutyl moiety is derived
14 from polyisobutene containing at least 70 weight percent methylvinylidene
15 isomer and more preferably the polyisobutyl moiety is derived from
16 polyisobutene containing at least 90 weight percent methylvinylidene isomer.

17 Preferably the aldehyde is formaldehyde or paraformaldehyde. More
18 preferably the aldehyde is paraformaldehyde.

19 Preferably the diluent is an alkanol having one carbon atom to about 10
20 carbon atoms. More preferably the alkanol is methanol.

21 Preferably the base is an alkali metal hydroxide. More preferably the alkali
22 metal hydroxide is sodium hydroxide.

23 The amino acid or ester derivative thereof has the formula



24

1 wherein W are as defined above and A is hydrogen or alkyl having one
2 carbon atom to about 6 carbon atoms.

3 Preferably the amino acid is glycine.

4 In the above process the amino acid may be added in the form of its alkali
5 metal ion salt. Preferably the alkali metal ion is a sodium ion or a potassium
6 ion, more preferably the alkali metal ion is a sodium ion.

7 A further embodiment of the present invention is directed to a lubricating oil
8 composition comprising a major amount of an oil of lubricating viscosity and a
9 minor effective amount of one or more of the above described Mannich
10 condensation products of the present invention.

11 A further embodiment of the present invention is directed to a lubricating oil
12 concentrate comprising about 20 percent to 80 percent of a diluent oil of
13 lubricating viscosity and an effective amount of one or more of the above
14 described Mannich condensation products of the present invention. Both the
15 lubricating oil composition and the lubricating oil concentrate may contain
16 other additives designed to improve the properties of the lubricating oil.

17 A further embodiment of the present invention is directed to a fuel composition
18 comprising a major amount of hydrocarbons boiling in the gasoline or diesel
19 range and a minor effective amount of one or more of the above described
20 Mannich condensation products of the present invention which has been
21 further reacted to remove/replace any alkali metal. In general it is not
22 desirable for a fuel additive composition to contain ash. Therefore, it is
23 desirable to react the above described Mannich condensation products of the
24 present invention in such a way that any alkali metal salt present is converted
25 to an ammonium or other appropriate salt giving an ashless Mannich
26 condensation product.

1 A further embodiment of the present invention is directed to a fuel concentrate
2 comprising an inert stable oleophilic organic solvent boiling in the range of
3 from about 65°C to about 204°C and from about 10 weight percent to about
4 90 weight percent of one or more of the above described Mannich
5 condensation product of the present invention which has been further reacted
6 to remove/replace any alkali metal present.

7 The Mannich condensation products of the present invention may also be
8 employed as dispersants in lubricating oil. For use as dispersants in fuels the
9 alkali metal ions in Mannich condensation products are replaced with
10 ammonium ions.

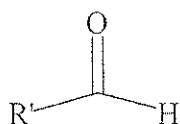
11 Among other factors, the present invention is based upon the discovery that
12 the Mannich condensation products of the present invention are effective in
13 sequestering metals, especially Fe^{+3} , and preventing metal ion catalyzed
14 oxidation and polymerization reactions, while maintaining sufficient oil
15 solubility for use in lubricating oils and fuels.

16 DETAILED DESCRIPTION OF THE INVENTION

17 DEFINITIONS

18 As used herein, the following terms have the following meanings unless
19 expressly stated to the contrary:

20 The term "aldehydes" as used herein refer to formaldehyde or aldehydes
21 having the formula



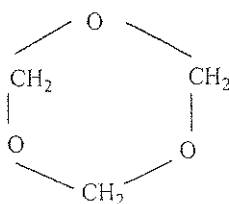
22

1 wherein R' is branched or linear alkyl having from one carbon atom to about
2 10 carbon atoms, cycloalkyl having from about 3 carbon atoms to about 10
3 carbon atoms, aryl having from about 6 carbon atoms to about 10 carbon
4 atoms, alkaryl having from about 7 carbon atoms to about 20 carbon atoms,
5 or aralkyl having from about 7 carbon atoms to about 20 carbon atoms.

6 Representative aldehydes for use in the preparation of the Mannich
7 condensation products of the present invention include, but are not limited to
8 aliphatic aldehydes such as formaldehyde, acetaldehyde, propionaldehyde,
9 butyraldehyde, valeraldehyde, caproaldehyde and heptaldehyde. Aromatic
10 aldehydes are also contemplated for use in the preparation of the Mannich
11 condensation products of the present invention, such as benzaldehyde and
12 alkylbenzaldehyde. Para-tolualdehyde is an example of an
13 alkylbenzaldehyde. Also useful are formaldehyde producing reagents, such
14 as paraformaldehyde and aqueous formaldehyde solutions such as formalin.
15 Aldehydes most preferred for use in the in the preparation of the Mannich
16 condensation products of the present invention are paraformaldehyde and
17 formalin.

18 Aldehydes most preferred for use in the in the preparation of the Mannich
19 condensation products of the present invention are paraformaldehyde and
20 formalin.

21 Preferably the aldehyde is formaldehyde. By formaldehyde is meant all its
22 forms, including gaseous, liquid and solid. Examples of gaseous
23 formaldehyde is the monomer CH_2O and the trimer, $(\text{CH}_2\text{O})_3$ (trioxane) having
24 the formula given below.



25

1 Examples of liquid formaldehyde are the following:

2 1. Monomer CH_2O in ethyl ether.

3 2. Monomer CH_2O in water which has the formulas $\text{CH}_2(\text{H}_2\text{O})_2$ (methylene
4 glycol) and $\text{HO}(-\text{CH}_2\text{O})_n\text{H}$.

5 3. Monomer CH_2O in methanol which has the formulas $\text{OHCH}_2\text{OCH}_3$ and
6 $\text{CH}_3\text{O}(-\text{CH}_2\text{O})_n\text{H}$.

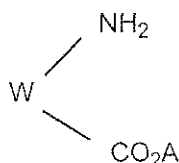
7

8 Formaldehyde solutions are commercially available in water and various
9 alcohols. In water it is available as a 37% - 50% solution. Formalin is a 37%
10 solution in water.

11 Formaldehyde is also commercially available as linear and cyclic (trioxane)
12 polymers. Linear polymers may be low molecular weight or high molecular
13 weight polymers.

14 The term "alkali metal" as used herein refers to Group I A metals of the
15 Periodic Table, such as lithium, sodium and potassium.

16 The term "amino acid or ester derivative thereof" as used herein refers to
17 amino acids having the formula

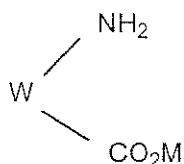


18

19 wherein W is $-\text{[CHR'']}-_m$ wherein each R'' is independently H, alkyl
20 having one carbon atom to about 15 carbon atoms, or a substituted-
21 alkyl having one carbon atom to about 10 carbon atoms and one or
22 more substituents selected from the group consisting of amino, amido,
23 benzyl, carboxyl, hydroxyl, hydroxyphenyl, imidazolyl, imino, phenyl,
24 sulfide, or thiol; and m is an integer from one to 4, and A is hydrogen or

1 alkyl having one carbon atom to about 6 carbon atoms. Preferably the
2 alkyl is methyl or ethyl.

3 The term "amino acid salt" as used herein refers to salts of amino acids
4 having the formula



5
6 wherein W is as defined above and M is an alkali metal ion. Preferably
7 M is a sodium ion or a potassium ion. More preferably X is a sodium
8 ion.

9 The term "base" as used herein refers to alkali metal hydroxides and alkali
10 metal alkoxides. Preferably the base is an alkali metal hydroxide selected
11 from the group consisting of sodium hydroxide, lithium hydroxide or potassium
12 hydroxide. More preferably the alkali metal hydroxide is sodium hydroxide or
13 potassium hydroxide.

14 The term "color test" as used herein refers to the color test used for
15 determination of the ability of the Mannich condensation products of the
16 present invention to sequester Fe^{+3} ions. The test is briefly described below:

17 Test for Iron Sequestering Ability

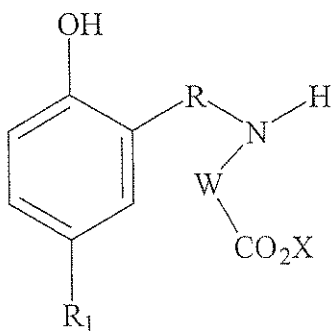
18 The test used for iron sequestering ability was as described in U.S. Patent No.
19 4,387,244. A 0.15 to 0.25 gram sample of the Mannich condensation product
20 is placed into an 8 dram vial to which is added 15 milliliters toluene and
21 shaken to homogeneity. Next 15 milliliters 0.05 molar solution of FeCl_3 in
22 water is added to the vial and the vial is mechanically shaken for one hour.
23 The contents of the vial are allowed to separate and the toluene layer
24 changes color from yellow to purple, as evidence of iron being chelated, in the

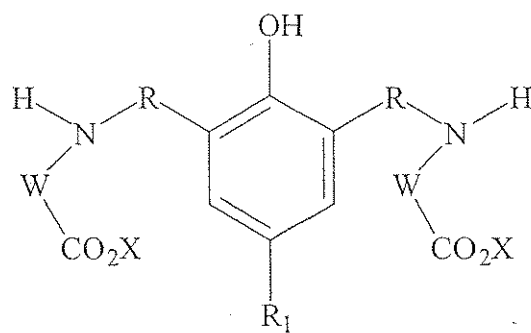
1 presence of the Mannich condensation product sequestering agents of the
2 present invention.

3 The term "hydroxyl number" as used herein refers to the amount of potassium
4 hydroxide required to neutralize the polyisobutyl-substituted phenol per gram
5 of sample (milligrams KOH per gram sample).

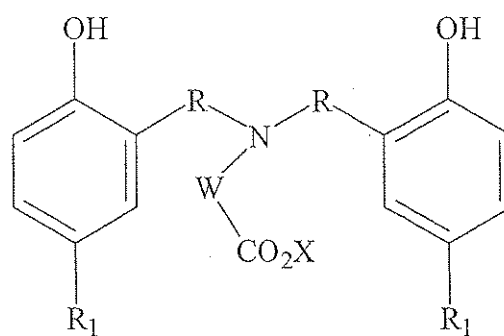
6 The term "inert stable oleophilic organic solvent" as used herein refers to
7 solvents that dissolve in gasoline or diesel fuel. Preferably the inert stable
8 oleophilic organic solvent is an aliphatic or an aromatic hydrocarbon solvent,
9 such as benzene, toluene, xylene or higher-boiling aromatics or aromatic
10 thinners. Aliphatic alcohols having from about 3 carbon atoms to about 8
11 carbon atoms may also be used in combination with the hydrocarbon
12 solvents. Aliphatic alcohols contemplated for use in the present invention are
13 isopropanol, isobutylcarbinol, n-butanol and the like.

14 The term "Mannich condensation product" as used herein refers to a mixture
15 of products obtained by the condensation of a polyisobutyl-substituted
16 hydroxyaromatic compound with an aldehyde and an amino acid, such as,
17 glycine, to form condensation products having the formulas given below. The
18 formulas given below are provided only as some examples of the Mannich
19 condensation products believed to be of the present invention and are not
20 intended to exclude other possible Mannich condensation products that may
21 be formed using the methods of the present invention.

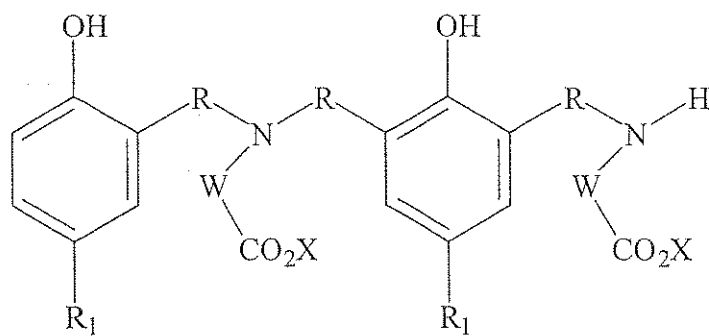




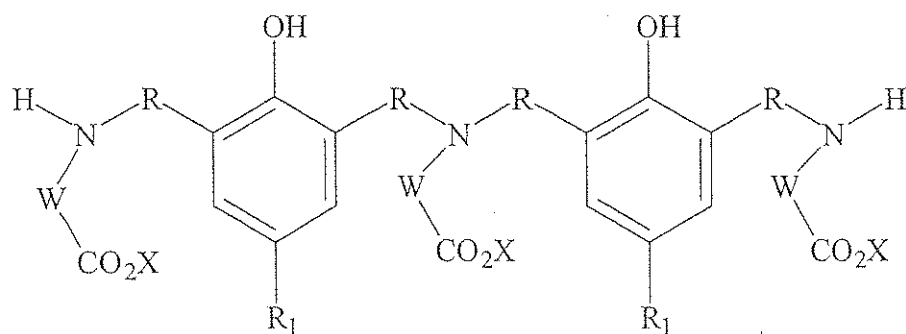
1



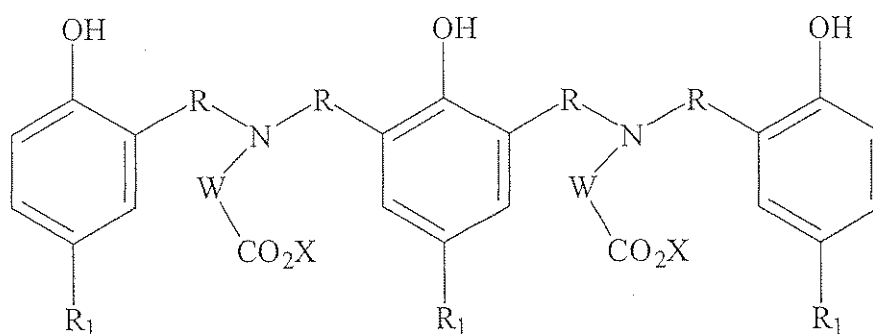
2



3



4
5



1

2

wherein R, R₁, X and W are as defined above.

3

The Mannich condensation products shown above may react further with an aldehyde and an amino acid to form larger oligomers.

4

5

Preferably the R₁ polyisobutyl group is derived from polyisobutene containing at least 70 weight percent methylvinylidene isomer and more preferably the R₁ polyisobutyl group is derived from polyisobutene containing at least 90 weight percent methylvinylidene isomer.

6

7

8

9

In a preferred embodiment of the Mannich condensation products R is CH₂,

10

R₁ is derived from polyisobutene containing at least 50 weight percent

11

methylvinylidene isomer and has a number average molecular weight of about

12

700 to about 1300, W is CH₂, and X is a sodium ion.

13

The term "oil of lubricating viscosity" as used herein refers to lubricating oils

14

which may be mineral oil or synthetic oils of lubricating viscosity and

15

preferably useful in the crankcase of an internal combustion engine.

16

Crankcase lubricating oils ordinarily have a viscosity of about 1300

17

centistokes at -17.8°C to 22.7 centistokes at 98.9°C. The lubricating oils may

18

be derived from synthetic or natural sources. Mineral oil for use as the base

19

oil in this invention includes paraffinic, naphthenic and other oils that are

20

ordinarily used in lubricating oil compositions. Synthetic oils include

21

hydrocarbon synthetic oils, synthetic esters and Fischer-Tropsch derived base

22

oil. Useful synthetic hydrocarbon oils include liquid polymers of alpha-olefins

1 having the proper viscosity. Especially useful are the hydrogenated liquid
2 oligomers of C₆ to C₁₂ alpha-olefins such as 1-decene trimer. Similarly, alkyl
3 benzenes of proper viscosity, such as didodecyl benzene, may be used.
4 Useful synthetic esters include the esters of both mono-carboxylic acids and
5 polycarboxylic acids as well as mono-hydroxy alkanols and polyols. Typical
6 examples are didodecyl adipate, pentaerthritol tetracapoate, di-2-ethylhexyl
7 adipate, di-laurylsebacate and the like. Complex esters prepared from
8 mixtures of mono- and di-carboxylic acid and mono- and di-hydroxy alkanols
9 can also be used. Blends of hydrocarbon oils and synthetic oils may also be
10 used. For example, blends of 10 weight percent to 25 weight percent
11 hydrogenated 1-decene trimer with 75 weight percent to 90 weight percent
12 683 centistokes at 37.8°C mineral oil gives an excellent oil base.

13 The term "polyisobutyl or polyisobutyl substituent" as used herein refers to the
14 polyisobutyl substituent on the hydroxyaromatic ring. The polyisobutyl
15 substituent has a number average molecular weight in the range of about 400
16 to about 5,000. Preferably the polyisobutyl moiety has a number average
17 molecular weight in the range of about 500 to about 2,500. More preferably
18 the polyisobutyl moiety has a number average molecular weight in the range
19 of about 700 to about 1,500, and most preferably the polyisobutyl moiety has
20 a number average molecular weight in the range of about 700 to about 1,100.

21 Preferably the attachment of the polyisobutyl substituent to the
22 hydroxyaromatic ring is para to the hydroxyl moiety in at least 60 percent of
23 the total polyisobutyl-substituted phenol molecules, more preferably the
24 attachment of the polyisobutyl substituent to the hydroxyaromatic ring is para
25 to the hydroxyl moiety in at least 80 percent of the total polyisobutyl-
26 substituted phenol molecules, and most preferably the attachment of the
27 polyisobutyl substituent to the hydroxyaromatic ring is para to the hydroxyl
28 moiety on the phenol ring in at least 90 percent of the total polyisobutyl-
29 substituted phenol molecules.

1 The term "polyisobutyl-substituted phenol" as used herein refers to a
2 polyisobutyl-substituted phenol ring. The polyisobutyl-substituted phenol is
3 derived from polyisobutene containing at least 50 weight percent
4 methylvinylidene isomer. Preferably the polyisobutyl-substituted phenol is
5 derived from polyisobutene containing at least about 70 weight percent
6 methylvinylidene isomer and more preferably the polyisobutyl-substituted
7 phenol is derived from polyisobutene containing at least about 90 weight
8 percent methylvinylidene isomer.

9 The term "sequestering agent(s)" as used herein refers to compounds that
10 hold a metal atom between two or more atoms of a single molecule of the
11 compound, thereby neutralizing or controlling harmful metal ions, such as
12 Fe^{+3} , in a lubricating oil or fuel.

13 The term "VW TDI-1 and VW TDI-2 engine tests" as used herein refers to the
14 engine test procedures CEC L-78-T-97 and CEC L-78-T-99 respectively,
15 published by the Coordinating European Council (CEC) for the Development
16 of Performance Tests for Transportation Fuels, Lubricants and Other Fluids.

17 Unless otherwise specified, all percentages are in weight percent and the
18 pressure is atmospheric pressure.

19 The Mannich Condensation Product

20 In its broadest aspects the present invention is directed to a Mannich
21 condensation product prepared by the Mannich condensation of a
22 polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl
23 group has number average molecular weight in the range of from about 400 to
24 about 5,000, an aldehyde, an amino acid or ester derivative thereof, and an
25 alkali metal base.

1 General Procedure for Preparation of Mannich Condensation Product

2 Sequestering agents

3
4 The Mannich condensation products of this invention are prepared by
5 combining under reaction conditions a polyisobutyl-substituted
6 hydroxyaromatic compound, wherein the polyisobutyl group has a number
7 average molecular weight in the range of from about 400 to about 5,000, an
8 aldehyde, an amino acid or ester derivative thereof, and an alkali metal base.
9 The reaction can be carried out batch wise, or in continuous or semi-
10 continuous mode.

11 Normally the pressure for this reaction is atmospheric, but the reaction may
12 be carried out under sub atmospheric or super atmospheric pressure if
13 desired.

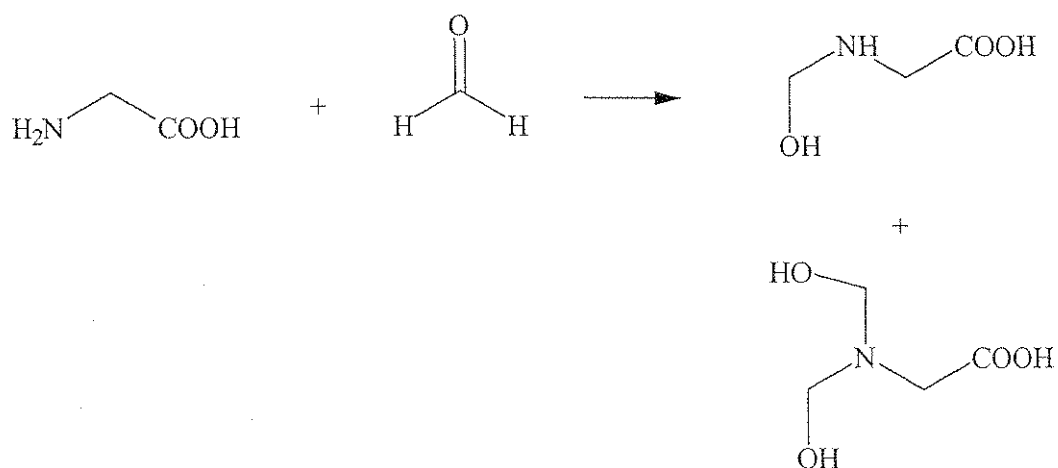
14 The temperature for this reaction may vary widely. The temperature range for
15 this reaction can vary from 10°C to about 200°C, preferably from about 50°C
16 to about 150°C, more preferably from about 70°C to about 130°C.

17 The reaction may be carried out in the presence of a diluent or a mixture of
18 diluents. It is important to ensure that the reactants come into intimate
19 contact with each other in order for them to react. This is an important
20 consideration because the starting materials for the Mannich condensation
21 products of the present invention include the relatively non polar polyisobutyl-
22 substituted hydroxyl aromatic compounds and the relatively polar amino acid
23 or ester derivative thereof. It is therefore necessary to find a suitable set of
24 reaction conditions or diluents that will dissolve all the starting materials.
25 diluents for this reaction must be capable of dissolving the starting materials
26 of this reaction and allowing the reacting materials to come in contact with
27 each other. Mixtures of diluents can be used for this reaction. Useful diluents
28 for this reaction include water, alcohols, (including methanol, ethanol,
29 isopropanol, 1-propanol, 1-butanol, isobutanol, sec-butanol, butanediol, 2-
30 ethylhexanol, 1-pentanol, 1-hexanol, ethylene glycol, and the like), DMSO,

1 NMP, HMPA, cellosolve, diglyme, various ethers (including diethyl ether, THF,
2 diphenylether, dioxane, and the like), aromatic diluents (including toluene,
3 benzene, o-xylene, m-xylene, p-xylene, mesitylene and the like), esters,
4 alkanes (including pentane, hexane, heptane, octane, and the like), and
5 various natural and synthetic diluent oils (including 100 neutral oils, 150
6 neutral oils, polyalphaolefins, Fischer-Tropsch derived base oil and the like,
7 and mixtures of these diluents. Mixtures of diluents that form two phases
8 such as methanol and heptane are suitable diluents for this reaction.

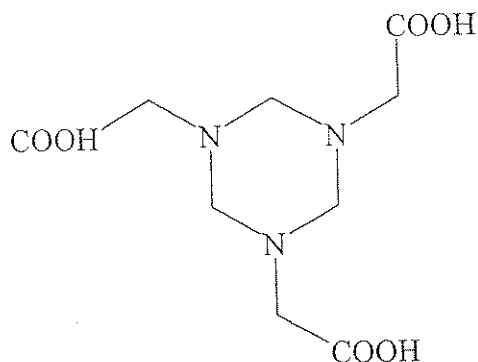
9 The reaction may be carried out by first reacting the hydroxyaromatic
10 compound with the alkali metal base, followed by the addition of the amino
11 acid or ester derivative thereof and the aldehyde, or the amino acid or ester
12 derivative thereof may be reacted with the aldehyde followed by the addition
13 of the hydroxyaromatic compound and the alkali metal base, etc.

14 It is believed that the reaction of the amino acid, such as glycine, or ester
15 derivative thereof, plus the aldehyde, such as formaldehyde, may produce the
16 intermediate formula



17

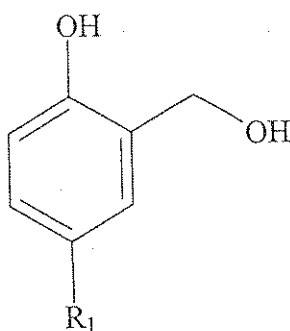
18 which may ultimately form the cyclic formula



1

2 It is believed that these intermediates may react with the hydroxyaromatic
3 compound and the base to form the Mannich condensation products of the
4 present invention.

5 Alternatively, it is believed that the reaction of the hydroxyaromatic compound
6 with the aldehyde may produce the intermediate formula



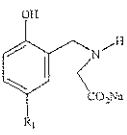
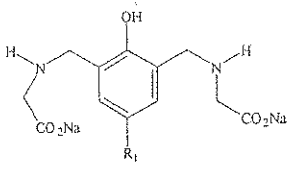
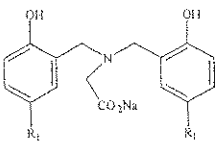
7

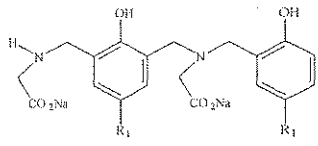
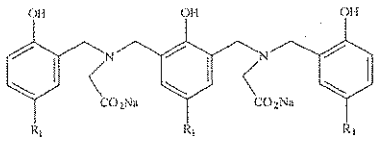
8 It is also believed that this intermediate may react with the amino acid or ester
9 derivative thereof and the base to form the Mannich condensation product of
10 the present invention.

11 The time of the reaction can vary widely depending on the temperature. The
12 reaction time can vary between 0.1 hour to about 20 hours, preferably from
13 about 2 hours to about 10 hours, more preferably from about 3 hours to about
14 7 hours.

1 The charge mole ratio (CMR) of the reagents can also vary over a wide range.
 2 Table I below gives a listing of the different formulae that can arise if different
 3 charge mole ratios are used. At a minimum the oil-soluble Mannich
 4 condensation products that sequester Fe^{+3} should preferable contain at least
 5 one polyisobutyl-substituted phenol ring and one amino acid group connected
 6 by one aldehyde group and one alkali metal. The polyisobutyl-substituted
 7 phenol/aldehyde/amino acid/base charge mole ratio for this molecule, also
 8 shown in Table I below, is 1.0 : 1.0 : 1.0 : 1.0. Other charge mole ratios are
 9 possible and the use of other charge mole ratios can lead to the production of
 10 different molecules of different formulas.

11 Table I

Product	Polyisobutyl-substituted phenol : aldehyde : amino acid : base (CMR)
	1.0 : 1.0 : 1.0 : 1.0
	1.0 : 2.0 : 2.0 : 2.0
	2.0 : 2.0 : 1.0 : 1.0

Product	Polyisobutyl-substituted phenol : aldehyde : amino acid : base (CMR)
	2.0 : 3.0 : 2.0 : 2.0
	3.0 : 4.0 : 2.0 : 2.0

1

2 All these products arising from other charge mole ratios may all be present
3 alone, as a single component, or as combinations of several components in a
4 complex mixture of products.

5 In the broadest sense the polyisobutyl-substituted phenol : aldehyde : amino
6 acid: base CMR can vary from 1.0 to 20.0 : 1.0 to 39.0 : 1.0 to 20.0 : 1.0 to
7 4.0. Preferably the polyisobutyl-substituted phenol : aldehyde : amino acid :
8 base CMR can vary from 1.0 to 5.0 : 1.0 to 10.0 : 1.0 to 6.0 : 1.0 to 3.0. More
9 preferably the polyisobutyl-substituted phenol : aldehyde : amino acid : base
10 CMR can vary from 1.0 to 3.0 : 1.0 to 5.0 : 1.0 to 3.0 : 1.0 to 2.0. Most
11 preferably the polyisobutyl-substituted phenol : amino acid : aldehyde : base
12 CMR is 1 : 1 : 2 : 1.

13 Compounds suitable for use in the preparation of the Mannich condensation
14 products of the present invention are given below:

15

16

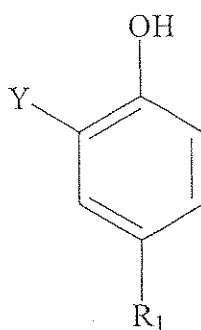
1 Polyisobutyl-substituted hydroxyaromatic compound

2 A variety of polyisobutyl-substituted hydroxyaromatic compounds can be
3 utilized in the preparation of the Mannich condensation products of this
4 invention. The critical feature is that the polyisobutyl substituent be large
5 enough to impart oil solubility to the finished Mannich condensation product.
6 In general the number of carbon atoms on the polyisobutyl substituent group
7 that are required to allow for oil solubility of the Mannich condensation product
8 is on the order of about C₂₀ and higher. This corresponds to a molecular
9 weight in the range of about 400 to about 5,000. It is desirable that the C₂₀ or
10 higher alkyl substituent on the phenol ring be located in the position para to
11 the OH group on the phenol.

12 In general, one unsubstituted carbon atom in the ortho position to the hydroxyl
13 group on the aromatic ring is required in order to prepare the Mannich
14 condensation products of this invention. For example, phenol substituted in
15 the para position with a polyisobutyl substituent that contains 20 or more
16 carbon atoms is a preferred polyisobutyl-substituted phenol raw material for
17 this invention.

18 Di-substituted phenols are also suitable starting materials for the Mannich
19 condensation products of this invention. Di-substituted phenols are suitable
20 provided that they are substituted in such a way that there is an unsubstituted
21 ortho position on the phenol ring. Examples of suitable di-substituted phenols
22 are o-cresol derivatives substituted in the para position with a C₂₀ or greater
23 polyisobutyl substituent and the like.

24 A preferred polyisobutyl-substituted phenol has the following formula:



1

2 wherein R₁ is polyisobutyl group derived from polyisobutene containing at
 3 least 50 weight percent methylvinylidene isomer and having a number
 4 average molecular weight in the range of about 400 to about 5,000, and Y is
 5 hydrogen.

6 In the above process the polyisobutyl substituent on the polyisobutyl-
 7 substituted phenol has a number average molecular weight in the range of
 8 about 400 to about 5,000. Preferably the polyisobutyl substituent on the
 9 polyisobutyl-substituted phenol has a number average molecular weight of
 10 about 500 to about 2,5000. More preferably the polyisobutyl substituent on
 11 the polyisobutyl-substituted phenol has a number average molecular weight of
 12 about 700 to about 1,500. Most preferably the polyisobutyl substituent on the
 13 polyisobutyl-substituted phenol has a number average molecular weight of
 14 about 700 to about 1,100.

15 The polyisobutyl-substituted phenol in the above process is preferably derived
 16 from polyisobutene containing at least about 50 weight percent
 17 methylvinylidene isomer. More preferably the polyisobutyl-substituted phenol
 18 is derived from polyisobutene containing at least about 70 weight percent
 19 methylvinylidene isomer and most preferably the polyisobutyl-substituted
 20 phenol is derived from polyisobutene containing at least about 90 weight
 21 percent methylvinylidene isomer.

22 Suitable polyisobutenes may be prepared using boron trifluoride (BF₃)
 23 alkylation catalyst as described in U.S. Patent Nos. 4,152,499 and 4,605,808.

1 Commercially available polyisobutenes having a high alkylvinylidene content
2 include Glissopal® 1000, 1300 and 2300, available from BASF.

3 The preferred polyisobutyl-substituted phenol for use in the preparation of the
4 Mannich condensation products of the present invention is a mono-substituted
5 phenol, wherein the polyisobutyl substituent is attached at the para-position to
6 the phenol ring. However, other polyisobutyl-substituted phenols that may
7 undergo the Mannich condensation reaction may also be used for preparation
8 of the Mannich condensation products of the present invention.

9 Solvent

10 Solvents may be employed to facilitate handling and reaction of the
11 polyisobutyl-substituted phenols in the preparation of the Mannich
12 condensation products of the present invention. Examples of suitable
13 solvents are hydrocarbon compounds such as heptane, benzene, toluene,
14 chlorobenzene, aromatic solvent, neutral oil of lubricating viscosity, paraffins
15 and naphthenes. Examples of other commercially available suitable solvents
16 that are aromatic mixtures include Chevron® Aromatic 100N, neutral oil,
17 Exxon® 150N, neutral oil.

18 If the Mannich condensation product sequestering agent prepared by the
19 above process is to be used as an additive in lubricating oil, then the
20 polyisobutyl-substituted phenol may be first dissolved in an alkyl-substituted
21 aromatic solvent. Preferably the alkyl substituent on the aromatic solvent has
22 from about 3 carbon atoms to about 15 carbon atoms. More preferably the
23 alkyl substituent on the aromatic solvent has from about 6 carbon atoms to
24 about 12 carbon atoms.

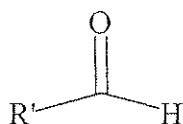
25 Base

26 Typical bases include alkali metal hydroxides and alkali metal alkoxides.
27 Preferably the base is an alkali metal hydroxide selected from the group

1 consisting of sodium hydroxide, lithium hydroxide or potassium hydroxide.
2 More preferably the alkali metal hydroxide is sodium hydroxide or potassium
3 hydroxide. Most preferably the base is sodium hydroxide. If the Mannich
4 condensation product sequestering agent is to be used as a fuel additive it
5 may be desirable to replace the alkali metal ion on the Mannich condensation
6 products with an ammonium ion. For other uses the alkali metal ion on the
7 Mannich condensation products may also be replaced with Group II metals of
8 the Periodic Table.

9 Aldehyde

10 Aldehydes contemplated for use in the process of the present invention are
11 formaldehyde or aldehydes having the formula



12
13 wherein R' is branched or linear alkyl, having from one carbon atom to
14 about 10 carbon atoms, cycloalkyl having from about 3 carbon atoms
15 to about 10 carbon atoms, aryl having from about 6 carbon atoms to
16 about 10 carbon atoms, alkaryl having from about 7 carbon atoms to
17 about 20 carbon atoms, or aralkyl having from about 7 carbon atoms to
18 about 20 carbon atoms..

19 Representative aldehydes for use in the preparation of the Mannich
20 condensation products of the present invention include, but are not limited to
21 aliphatic aldehydes such as formaldehyde, acetaldehyde, propionaldehyde,
22 butyraldehyde, valeraldehyde, caproaldehyde and heptaldehyde.

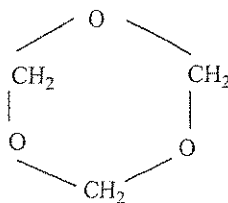
23 Aromatic aldehydes are also contemplated for use in the preparation of the
24 Mannich condensation products of the present invention, such as

1 benzaldehyde, alkylbenzaldehyde and hydroxybenzaldehyde. Para-
2 tolualdehyde is an example of an alkylbenzaldehyde.

3 Also useful are formaldehyde producing reagents, such as paraformaldehyde
4 and aqueous formaldehyde solutions such as formalin. Aldehydes most
5 preferred for use in the in the preparation of the Mannich condensation
6 products of the present invention are paraformaldehyde and formalin.

7 Aldehydes most preferred for use in the in the preparation of the Mannich
8 condensation products of the present invention are paraformaldehyde and
9 formalin.

10 Preferably the aldehyde is formaldehyde. By formaldehyde is meant all its
11 forms, including gaseous, liquid and solid. Examples of gaseous
12 formaldehyde is the monomer CH_2O and the trimer, $(\text{CH}_2\text{O})_3$ (trioxane) having
13 the formula given below.



14

15 Examples of liquid formaldehyde are the following:

16 4. Monomer CH_2O in ethyl ether.

17 5. Monomer CH_2O in water which has the formulas $\text{CH}_2(\text{H}_2\text{O})_2$ (methylene
18 glycol) and $\text{HO}(-\text{CH}_2\text{O})_n\text{-H}$.

19 6. Monomer CH_2O in methanol which has the formulas $\text{OHCH}_2\text{OCH}_3$ and
20 $\text{CH}_3\text{O}(-\text{CH}_2\text{O})_n\text{-H}$.

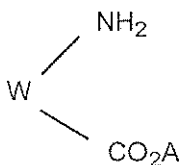
21

1 Formaldehyde solutions are commercially available in water and various
2 alcohols. In water it is available as a 37% - 50% solution. Formalin is a 37%
3 solution in water.

4 Formaldehyde is also commercially available as linear and cyclic (trioxane)
5 polymers. Linear polymers may be low molecular weight or high molecular
6 weight polymers.

7 Amino Acid

8 The amino acid or the ester derivative thereof used in the above process has
9 the formula



10
11 W is $-\text{[CHR]}_m-$ wherein each R is independently H, alkyl having one
12 carbon atom to about 15 carbon atoms, or a substituted-alkyl having
13 one carbon atom to about 10 carbon atoms and one or more
14 substituents selected from the group consisting of amino, amido,
15 benzyl, carboxyl, hydroxyl, hydroxyphenyl, imidazolyl, imino, phenyl,
16 sulfide, or thiol; and m is an integer from one to 4 and A is hydrogen or
17 alkyl having one carbon atoms to about 6 carbon atoms.

18 Preferably A is hydrogen in the above formula. The preferred alkyl in the
19 above formula is methyl or ethyl.

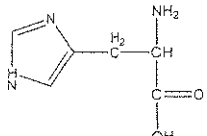
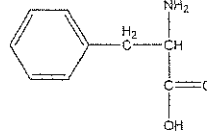
20 Preferably the amino acid is glycine.

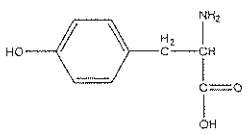
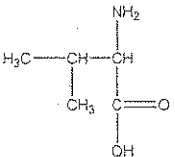
21 Some examples of alpha amino acids contemplated for use in the
22 preparation of the Mannich condensation products of the present invention
23 are given below in Table II.

1
2
3
4

Table II

Name	Formula	Log K ^{25°C, 0 ionic strength}
Alanine	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{H}_3\text{C}-\text{CH} \\ \\ \text{C}=\text{O} \\ \\ \text{OH} \end{array} $	9.87
Arginine	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{H}_2\text{N}-\text{C}(=\text{NH})-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH} \\ \qquad \qquad \qquad \\ \text{OH} \qquad \qquad \qquad \text{C}=\text{O} \\ \qquad \qquad \qquad \\ \qquad \qquad \qquad \text{OH} \end{array} $	8.99
Asparagine	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{H}_2\text{N}-\text{C}(=\text{O})-\text{CH}_2-\text{CH} \\ \qquad \qquad \qquad \\ \qquad \qquad \qquad \text{C}=\text{O} \\ \qquad \qquad \qquad \\ \qquad \qquad \qquad \text{OH} \end{array} $	8.72 *
Aspartic Acid	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{HO}-\text{C}(=\text{O})-\text{CH}_2-\text{CH} \\ \qquad \qquad \qquad \\ \qquad \qquad \qquad \text{C}=\text{O} \\ \qquad \qquad \qquad \\ \qquad \qquad \qquad \text{OH} \end{array} $	10.0
Cysteine	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{HS}-\text{CH}_2-\text{CH} \\ \qquad \qquad \\ \qquad \qquad \text{C}=\text{O} \\ \qquad \qquad \\ \qquad \qquad \text{OH} \end{array} $	10.77
Cystine	$ \begin{array}{c} \text{NH}_2 \qquad \qquad \text{NH}_2 \\ \qquad \qquad \qquad \\ \text{CH}-\text{CH}_2-\text{S}-\text{S}-\text{CH}-\text{CH} \\ \qquad \qquad \qquad \\ \text{C}=\text{O} \qquad \qquad \text{C}=\text{O} \\ \qquad \qquad \qquad \\ \text{OH} \qquad \qquad \text{OH} \end{array} $	8.80 **
Glutamic Acid	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{HO}-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_2-\text{CH} \\ \qquad \qquad \qquad \\ \qquad \qquad \qquad \text{C}=\text{O} \\ \qquad \qquad \qquad \\ \qquad \qquad \qquad \text{OH} \end{array} $	9.95
Glutamine	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{H}_2\text{N}-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_2-\text{CH} \\ \qquad \qquad \qquad \\ \qquad \qquad \qquad \text{C}=\text{O} \\ \qquad \qquad \qquad \\ \qquad \qquad \qquad \text{OH} \end{array} $	9.01 *

Glycine	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{H}-\text{CH} \\ \\ \text{C}=\text{O} \\ \\ \text{OH} \end{array} $	9.78
Histidine	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{H}_2\text{C}-\text{CH} \\ \quad \quad \\ \text{C} \quad \quad \text{C}=\text{O} \\ \quad \quad \\ \text{OH} \quad \quad \text{OH} \end{array} $ 	9.08 *
Hydroxylysine	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{H}_2\text{N}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{CH}_2-\text{CH} \\ \quad \quad \quad \\ \text{OH} \quad \quad \quad \text{C}=\text{O} \\ \quad \quad \quad \\ \quad \quad \quad \text{OH} \end{array} $	
Isoleucine	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}-\text{CH} \\ \quad \quad \\ \text{CH}_3 \quad \quad \text{C}=\text{O} \\ \quad \quad \\ \quad \quad \text{OH} \end{array} $	9.75
Leucine	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{H}_3\text{C}-\text{CH}-\text{CH}_2-\text{CH} \\ \quad \quad \\ \text{CH}_3 \quad \quad \text{C}=\text{O} \\ \quad \quad \\ \quad \quad \text{OH} \end{array} $	9.75
Lysine	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH} \\ \\ \text{C}=\text{O} \\ \\ \text{OH} \end{array} $	10.69 *
Methionine	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{CH}_3-\text{S}-\text{CH}_2-\text{CH}_2-\text{CH} \\ \\ \text{C}=\text{O} \\ \\ \text{OH} \end{array} $	9.05
Phenylalanine	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{C}_6\text{H}_5-\text{CH}_2-\text{CH} \\ \\ \text{C}=\text{O} \\ \\ \text{OH} \end{array} $ 	9.31
Serine	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{HO}-\text{CH}_2-\text{CH} \\ \\ \text{C}=\text{O} \\ \\ \text{OH} \end{array} $	9.21
Threonine	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{H}_2\text{N}-\text{C}(=\text{NH})-\text{H}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH} \\ \\ \text{C}=\text{O} \\ \\ \text{OH} \end{array} $	9.10

Tyrosine		10.47
Valine		9.72

1
2
3
4
5

* 0.1 ionic strength.

** 20°C and 0.1 ionic strength.

6 The present invention is also directed to a lubricating oil additive composition
7 comprising a major amount of an oil of lubricating viscosity and a minor
8 amount of the Mannich condensation product sequestering agent of the
9 present invention. A mixture of Mannich condensation product sequestering
10 agents are also contemplated in the lubricating oil additive composition of the
11 present invention. Typically the lubricating oil composition will contain
12 Mannich condensation product sequestering agents of this invention in the
13 range of from about 0.01 weight percent to about 10 weight percent,
14 preferably in the range of from about 0.1 weight percent to about 5 weight
15 percent and more preferably in the range of from about 0.3 weight percent to
16 about 2 weight percent. The lubricating oil additive composition will generally
17 contain other additives including detergents (overbased and non-overbased),
18 dispersants, extreme pressure agents, wear inhibitors, rust inhibitors, foam
19 inhibitors, corrosion inhibitors, pour point depressants, antioxidants, zinc di-
20 thiophosphates and a variety of other well known additives.

21 The present invention is also directed to a lubricating oil concentrate.
22 Lubricating oil additive concentrates usually include from 90 weight percent to
23 10 weight percent of an organic liquid diluent and from 10 weight percent to
24 90 weight percent (on a dry polymer basis) of the additive of this invention.
25 Typically, the concentrates contain sufficient diluent to make them easy to
26 handle during shipping and storage. Generally, the lubricating oil concentrate

1 will contain the Mannich condensation product sequestering agents of this
2 invention in the range of from about 10 weight percent to about 90 weight
3 percent dry polymer Mannich condensation product, preferably in the range of
4 from about 30 weight percent to about 70 weight percent dry polymer Mannich
5 condensation product, and more preferably about 50 weight percent dry
6 polymer Mannich condensation product.

7 The present invention is also directed to a fuel additive composition
8 comprising a major amount of hydrocarbons boiling in the gasoline or diesel
9 range and a minor effective amount of the Mannich condensation product
10 sequestering agent of the present invention. A mixture of Mannich
11 condensation product sequestering agents are also contemplated in the fuel
12 composition of the present invention. Typically the fuel composition will
13 contain the Mannich condensation product sequestering agents of this
14 invention in the range of from about 25 parts per million to about 2,500 parts
15 per million, preferably in the range of from about 50 parts per million to about
16 1,500 parts per million, and more preferably in the range of from about 70
17 parts per million to about 1,000 parts per million. The gasoline fuel additive
18 composition of the present invention may include other fuel additives,
19 including oxygenates, anti-knock agents, dispersants, detergents, lead
20 scavengers, anti-oxidants, pour point depressants, corrosion inhibitors and
21 demulsifiers. The gasoline fuels may also contain amounts of other fuels, for
22 example, methanol. The diesel fuel additive composition of the present
23 invention may also contain other additives, including pour point depressants,
24 flow improvers and cetane improvers. The diesel fuels may also contain
25 amounts of other fuels, for example, methanol.

26 A further embodiment of the present invention is also directed to a fuel
27 concentrate comprising an inert stable oleophilic organic solvent boiling in the
28 range of from about 65°C to about 204°C and from about 10 weight percent to
29 about 90 weight percent of one or more Mannich condensation product
30 sequestering agents of the present invention. Generally the fuel concentrate
31 will contain Mannich condensation product sequestering agents of the present

1 invention in the range of from about 10 weight percent to about 70 weight
2 percent, preferably in the range of from about 10 weight percent to about 50
3 weight percent and more preferably in the range of from about 20 weight
4 percent to about 40 weight percent.

5 A fuel-soluble, non-volatile carrier fluid or oil may also be used with the fuel
6 additive composition of this invention. The carrier fluid is a chemically inert
7 hydrocarbon-soluble liquid vehicle which substantially increases the non-
8 volatile residue, or the solvent-free liquid fraction of the fuel additive
9 composition while not overwhelmingly contributing to octane requirement
10 increase. The carrier fluid may be a natural or a synthetic oil, such as mineral
11 oil or refined petroleum oils.

12 Typically, an engine lubricating oil composition may contain the following
13 components:

- 14 (a) A major amount of oil of lubricating viscosity;
- 15 (b) 0.01 weight percent to 10.0 weight percent of at least one Mannich
16 condensation product of the present invention;
- 17 (c) 1.0 weight percent to 10.0 weight percent of at least one borated or
18 non-borated succinimide ashless detergent;
- 19 (d) 0.05 weight percent to 0.5 weight percent, as calcium, of at least
20 one calcium sulfonate, phenate or salicylate detergent;
- 21 (e) 0.02 weight percent to 0.2 weight percent, as phosphorus, of at
22 least one secondary or mixture of primary and secondary alkyl zinc
23 dithiophosphate;
- 24 (f) 0.0 weight percent to 5.0 weight percent of at least one diphenyl
25 amine oxidation inhibitor;

- 1 (g) 0.0 weight percent to 0.5 weight percent of, as molybdenum, of at
2 least one molybdenum succinimide oxidation inhibitor;
- 3 (h) 0.0 weight percent to 5.0 weight percent of at least one partial;
4 carboxylic ester or borated ester friction modifier;
- 5 (i) 0.0 weight percent to 0.05 weight percent of at least one
6 supplemental anti-wear/extreme pressure agent, such as
7 molybdenum dithiocarbamate;
- 8 (j) 0.0 weight percent to 0.1 weight percent of at least one foam
9 inhibitor; and
- 10 (k) 0.0 weight percent to 2.0 weight percent of at least one olefin
11 copolymer viscosity index improver.

12 The Mannich condensation products of the present invention may also be
13 employed as dispersants in lubricating oil. For use as dispersants in fuels the
14 alkali metal ions in Mannich condensation products are replaced with
15 ammonium ions.

16 EXAMPLES

17 Example 1

18 Preparation of Mannich condensation product using
19 1,000 molecular weight polyisobutyl-substituted phenol

20 To a 1.0 liter three-neck flask equipped with a temperature probe, mechanical
21 stirrer and reflux condenser were added 4.0 grams of sodium hydroxide in 3.0
22 milliliters of water (0.1 moles), 300 milliliters of methanol (boiling point 65°C),
23 7.5 grams (0.1 moles) of glycine and 6.59 grams (0.2 moles) of
24 paraformaldehyde. The reaction mixture was gently warmed (40°C) for 30

1 minutes. To this was added, at a reflux temperature, 134.8 grams (0.1 moles)
2 of 1,000 molecular weight polyisobutyl-substituted phenol, prepared as
3 described in U.S. Patent Nos. 5,300,701 and 6,274,777, (hydroxyl number
4 41.6 milligrams KOH per gram sample) diluted in C₉ aromatic solvent. The
5 reaction mixture was heated at reflux temperature for 17 hours. Next the
6 methanol was removed under vacuum and the product obtained.

7
8 This product was soluble in diluent oil. The product had a viscosity of 1,653
9 centistokes at 100°C.

10 11 Comparative Example A

12 13 Preparation of Mannich condensation product using 14 C₁₂ alkyl substituted phenol

15 To a 2.0 liter three-neck flask equipped with a temperature probe, mechanical
16 stirrer and reflux condenser were added 40 grams of sodium hydroxide in 20
17 milliliters of water (0.1 moles) and 700 milliliters of methanol (boiling point
18 65°C). The reaction mixture was heated gently (40°C) for 15 minutes to
19 dissolve the sodium hydroxide. To the reaction mixture was added 75.07
20 grams (1.0 mole) of glycine and 60.06 grams (2.0 moles) of paraformaldehyde
21 with gentle heating (40°C). To this was added 286.29 grams (0.1 moles) of
22 C₁₂ propylene tetramer substituted phenol, OLOA 200® (hydroxyl number 196
23 milligrams KOH per gram sample), available from Chevron Oronite Company
24 LLC. The reaction mixture was heated at reflux temperature for 17 hours.
25 Next the methanol was removed under vacuum. The product obtained was
26 dissolved in toluene. The product had to be dissolved in toluene because it
27 was only slightly soluble in hexane. The product was filtered through Celite®
28 and the solvent (toluene) removed under vacuum and the product was
29 obtained.

1 Comparative Example B

2
3 Solubility of Mannich condensation product prepared from
4 C₉ alkyl substituted phenol

5 Mannich condensation product, 15.1 grams, was prepared from C₉ alkyl-
6 substituted phenol as described in U.S. Patent No. 4,387,244. The product
7 was dissolved in 50 milliliters toluene at elevated temperature (100°C). To
8 this was added 35 grams Citcon® 100N, neutral diluent oil. Next most of the
9 toluene was removed under vacuum. A total of 52 grams of product (30
10 product and 70 percent diluent oil) was obtained. The product was cloudy
11 indicating that Mannich condensation product was poorly soluble in diluent oil.

12
13 Example 2

14
15 High Temperature PCDO Performance VW TDI-1 Engine Test
16 Using 10w40 Oil
17

18 The performance of a sample of the Mannich condensation product prepared
19 in Example 1 was evaluated in a VW TD-1 Engine Test and compared to a
20 fully formulated oil without the Mannich condensation product. The product
21 prepared in Example 1 was added at a 1.0 percent treat rate to a fully
22 formulated oil containing typical amounts of ashless dispersant, phenate,
23 overbased sulfonate, LOB sulfonate zinc di-thiophosphate, wear inhibitors,
24 etc., in a SAE grade 10W40, partial synthetic oil. The results of the VW TDI-
25 1 Engine Test are summarized below in Table II. The data show that the oil
26 containing the Mannich condensation product of the present invention had
27 significantly better performance than the baseline oil. The baseline oil ran for
28 only 42 hours and was terminated early. The average piston merit was 60.6,
29 and the average ring sticking was 2.0. This was a failing engine test. The oil
30 containing the Mannich condensation product of the present invention
31 completed the 60 hour test and gave average piston merit of 66.7, and

1 average ring sticking of 0.63. This was a passing engine test result. It is
2 believed that the oil containing the Mannich condensation product of the
3 present invention performed better than the baseline oil alone because of the
4 Mannich condensation product's ability to sequester metal ions, thus
5 preventing metal ion catalyzed oxidation and polymerization reactions from
6 occurring.

7 Table II

Example	Test Hours	Average Piston Merit	Average Ring Sticking
Baseline	42	60.6	2.00
Example 2	60	66.7	0.63

8

9 Example 3

10 High Temperature PCDO Performance VW TDI-2 Engine Test
11 Using 5w30 Oil

12 The performance of a sample of the Mannich condensation product, prepared
13 in Example 1 dissolved at 1.0 percent level in a fully formulated Group III
14 5w30 baseline oil, was determined in a VW TD-2 Engine Test. This was
15 compared to the baseline oil without the Mannich condensation product. The
16 results of the VW TDI Engine Test are summarized below in Table III. The
17 data show that the oil containing the Mannich condensation product of the
18 present invention had significantly better performance than the baseline. The
19 oil containing the Mannich condensation product of the present invention
20 performed better for average piston cleanliness and there was no ring

1 sticking. It is believed that the Mannich condensation product of the present
2 invention performed better than the Group III Base Oil alone because of the
3 product's ability to sequester metal ions, thus preventing metal ion catalyzed
4 oxidation and polymerization reactions in the hydrocarbon base oil.

5 Table III

Example	Test Hours	Average Piston Merit	Average Ring Sticking
Baseline	54	55	none
Example 3	54	60	none

6
7 Example 4

8 High Temperature PCDO Performance VW TDI-2 Engine Test

9 Using 10w40 Oil

10 The performance of a sample of the Mannich condensation product, prepared
11 in Example 1 dissolved at 1.0 percent level in a fully formulated 5w40 baseline
12 oil, was measured in a VW TD-2 Engine Test. This was compared to the
13 baseline oil without the Mannich condensation product. The results of the VW
14 TDI Engine Test are summarized below in Table IV. The data show that the
15 oil containing the Mannich condensation product of the present invention had
16 significantly better performance than the baseline. The oil containing the
17 Mannich condensation product of the present invention performed better for,
18 average piston merit and average ring sticking, than the baseline. It is
19 believed that the oil containing the Mannich condensation product of the
20 present invention performed better than the baseline because of the product's

- 1 ability to sequester metal ions, thus preventing metal ion catalyzed oxidation
2 and polymerization reactions in the hydrocarbon base oil.

3 Table IV

Example	Test Hours	Average Piston Merit	Average Ring Sticking
Baseline	54	42	1.875
Example 4	54	54.8	0.625

4

5

6

Example 5

7

8 Preparation of Mannich condensation product using 550 molecular weight
9 polyisobutyl-substituted phenol

10

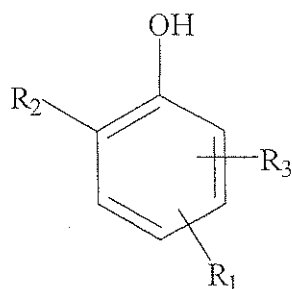
11 To a 2 liter 3 neck glass round bottom flask equipped with a reflux condenser,
12 nitrogen inlet, mechanical stirrer, heating mantle, and thermocouple, was
13 added NaOH, 8.00 grams (50 percent aqueous solution), (0.10 moles) and
14 300 milliliters methanol. This was stirred and heated to about 50°C for 15
15 minutes. To this was added glycine, 7.51 grams (0.100 moles) and
16 paraformaldehyde, 6.59 grams 0.220 moles. The solution was then heated to
17 reflux and to this was added 66.50 grams (0.101 moles) polyisobutyl-
18 substituted phenol (prepared using the procedure described in U.S. Patent
19 Nos. 5,300,701 and 6,274,777 using Glissopal®, $M_n = 550$, methylvinylidene
20 content greater than 50 weight percent). This was heated at reflux for 20
21 hours. The resulting oil and methanol phases were dissolved in hexane,
22 filtered through Celite® 521, and diluted with toluene. The solvent was then
23 removed in vacuo to yield a glassy yellow solid, melting point 110°C.

- 1 This example shows that 550 molecular weight polyisobutyl-substituted
- 2 phenol can also be used to make the Mannich condensation products of this
- 3 invention.

WHAT IS CLAIMED IS:

1. A Mannich condensation product prepared by the Mannich condensation of:
 - (a) a polyisobutyl-substituted hydroxyaromatic compound, wherein the polyisobutyl group is derived from polyisobutene containing at least 50 weight percent methylvinylidene isomer and has a number average molecular weight in the range of from about 400 to about 5,000;
 - (b) an aldehyde;
 - (c) an amino acid or ester derivative thereof; and
 - (d) an alkali metal base.
2. The Mannich condensation product of claim 1, wherein the polyisobutyl group of the polyisobutyl-substituted hydroxyaromatic compound in (a) is derived from polyisobutene containing at least 70 weight percent methylvinylidene isomer.
3. The Mannich condensation product of claim 2, wherein the polyisobutyl group is derived from polyisobutene containing at least 90 weight percent methylvinylidene isomer.
4. The Mannich condensation product of any one of the preceding claims, wherein the polyisobutyl group has a number average molecular weight in the range of from about 500 to about 2,500.
5. The Mannich condensation product of claim 4, wherein the polyisobutyl group has a number average molecular weight in the range of from about 700 to about 1,500.

6. The Mannich condensation product of claim 5, wherein the polyisobutyl group has a number average molecular weight in the range of from about 700 to about 1,100.
7. The Mannich condensation product of anyone of the preceding claims, wherein the aldehyde is formaldehyde or paraformaldehyde.
8. The Mannich condensation product of claim 7, wherein the aldehyde is paraformaldehyde.
9. The Mannich condensation product of any one of the preceding claims, wherein the polyisobutyl-substituted hydroxyaromatic compound is present in a diluent.
10. The Mannich condensation product of claim 9, wherein the diluent is an alkanol having one carbon atom to about 10 carbon atoms.
11. The Mannich condensation product of claim 10, wherein the alkanol is methanol.
12. The Mannich condensation product of anyone of the preceding claims, wherein the base is an alkali metal hydroxide.
13. The Mannich condensation product of claim 12, wherein the alkali metal hydroxide is sodium hydroxide.
14. The Mannich condensation product of anyone of the preceding claims, wherein the amino acid is glycine.
15. A Mannich condensation product prepared by the Mannich condensation of:
 - (a) a polyisobutyl-substituted hydroxyaromatic compound having the formula



1

2

3

4

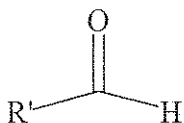
5

6

wherein R_1 is polyisobutyl derived from polyisobutene containing at least 50 weight percent methylvinylidene isomer and having a number average molecular weight in the range of about 400 to about 5,000, R_2 is hydrogen or lower alkyl having one carbon atom to about 10 carbon atoms, and R_3 is hydrogen or $-OH$;

7

(b) a formaldehyde or an aldehyde having the formula



8

9

10

11

12

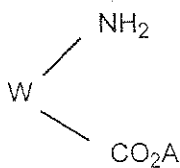
13

14

wherein R' is branched or linear alkyl having one carbon atom to about 10 carbon atoms, cycloalkyl having from about 3 carbon atoms to about 10 carbon atoms, aryl having from about 6 carbon atoms to about 10 carbon atoms, alkaryl having from about 7 carbon atoms to about 20 carbon atoms, or aralkyl having from about 7 carbon atoms to about 20 carbon atoms;

15

(c) an amino acid or ester derivative thereof having the formula

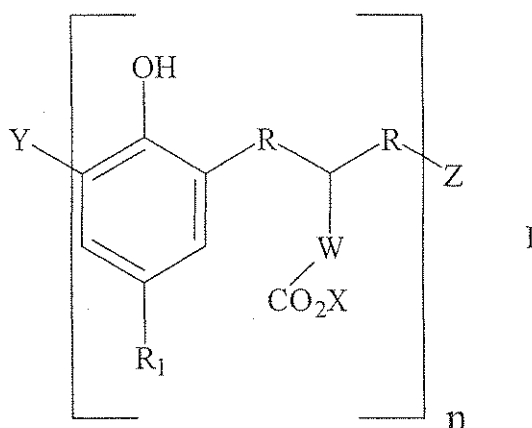


16

1 wherein W is $-[\text{CHR}']_m$ wherein each R' is independently H,
 2 alkyl having one carbon atom to about 15 carbon atoms, or a
 3 substituted-alkyl having one carbon atom to about 10 carbon
 4 atoms and one or more substituents selected from the group
 5 consisting of amino, amido, benzyl, carboxyl, hydroxyl,
 6 hydroxyphenyl, imidazolyl, imino, phenyl, sulfide, or thiol; and m
 7 is an integer from one to 4, A is hydrogen or alkyl having one
 8 carbon atom to about 6 carbon atoms; and

9 (d) an alkali metal base.

10 16. A Mannich condensation product having the formula



11

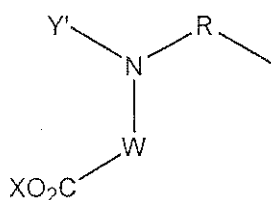
12 wherein each R is independently $-\text{CHR}'-$, wherein R' is branched or
 13 linear alkyl having one to about 10 carbon atoms, cycloalkyl having
 14 from about 3 carbon atoms to about 10 carbon atoms, aryl having from
 15 about 6 carbon atoms to about 10 carbon atoms, alkaryl having from
 16 about 7 carbon atoms to about 20 carbon atoms, or aralkyl having from
 17 about 7 carbon atoms to about 20 carbon atoms, R₁ is a polyisobutyl
 18 group derived from polyisobutene containing at least 50 weight percent
 19 methylvinylidene isomer and having a number average molecular
 20 weight in the range of about 400 to about 5,000;

1 X is hydrogen, an alkali metal ion, or alkyl having one carbon atom to
2 about 6 carbon atoms;

3 W is $-[\text{CHR}']_m$ wherein each R' is independently H, alkyl having one
4 carbon atom to about 15 carbon atoms, or a substituted-alkyl having
5 one carbon atom to about 10 carbon atoms and one or more
6 substituents selected from the group consisting of amino, amido,
7 benzyl, carboxyl, hydroxyl, hydroxyphenyl, imidazolyl, imino, phenyl,
8 sulfide, or thiol; and m is an integer from one to 4;

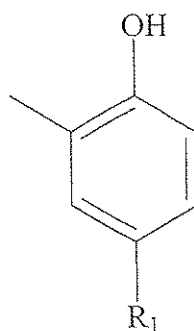
9 Y is hydrogen, alkyl having one carbon atom to about 10 carbon atoms,
10 $-\text{CHR}'\text{OH}$, wherein R' is as defined above,

11 or

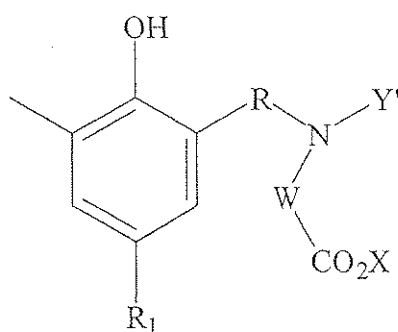


12
13 wherein Y' is $-\text{CHR}'\text{OH}$, wherein R' is as defined above; and R, X, and
14 W are as defined above;

15 Z is hydroxyl, a hydroxyphenyl group of the formula



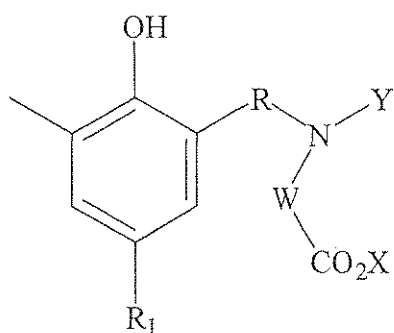
16
17 or



1

2 wherein R, R₁, Y', X, and W are as defined above,

3 and n is an integer from 0 to 20, with the proviso that when n = 0, Z
4 must be:

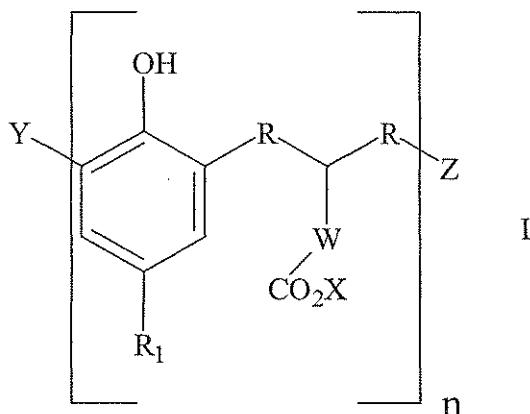


5

6 wherein R, R₁, Y', X, and W are as defined above.

- 7 17. The Mannich condensation product of claim 16, wherein the
8 polyisobutyl group of the polyisobutyl-substituted hydroxyaromatic
9 compound in (a) is derived from polyisobutene containing at least 70
10 weight percent methylvinylidene isomer.
- 11 18. The Mannich condensation product of claim 17, wherein the
12 polyisobutyl group is derived from polyisobutene containing at least 90
13 weight percent methylvinylidene isomer.

19. The Mannich condensation product of any one of claims 16 to 18, wherein R_1 is a polyisobutyl group having a number average molecular weight of about 500 to about 2,500.
20. The Mannich condensation product of claim 19, wherein R_1 is a polyisobutyl group having a number average molecular weight of about 700 to about 1,500.
21. The Mannich condensation product of claim 20, wherein R_1 is a polyisobutyl group having a number average molecular weight of about 700 to about 1,100.
22. 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 a compound having the formula



wherein each R is independently $-CHR'$ -, wherein R' is branched or linear alkyl having one to about 10 carbon atoms, cycloalkyl having from about 3 carbon atoms to about 10 carbon atoms, aryl having from about 6 carbon atoms to about 10 carbon atoms, alkaryl having from about 7 carbon atoms to about 20 carbon atoms, or aralkyl having from about 7 carbon atoms to about 20 carbon atoms R_1 is a polyisobutyl

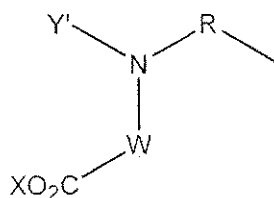
1 group derived from polyisobutene containing at least 50 weight percent
2 methylvinylidene isomer and having a number average molecular
3 weight in the range of about 400 to about 5,000;

4 X is hydrogen, an alkali metal ion, or alkyl having one carbon atom to
5 about 6 carbon atoms;

6 W is $-[\text{CHR}']_m$ wherein each R' is independently H, alkyl having one
7 carbon atom to about 15 carbon atoms, or a substituted-alkyl having
8 one carbon atom to about 10 carbon atoms and one or more
9 substituents selected from the group consisting of amino, amido,
10 benzyl, carboxyl, hydroxyl, hydroxyphenyl, imidazolyl, imino, phenyl,
11 sulfide, or thiol; and m is an integer from one to 4;

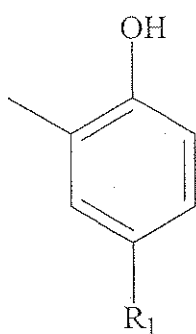
12 Y is hydrogen, alkyl having one carbon atom to about 10 carbon atoms,
13 $-\text{CHR}'\text{OH}$, wherein R' is as defined above,

14 or



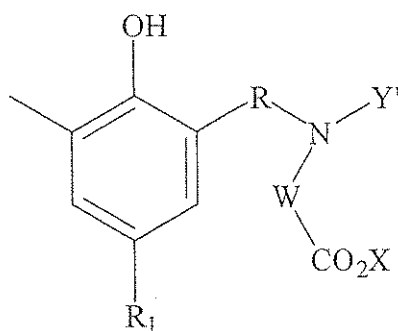
15
16 wherein Y' is $-\text{CHR}'\text{OH}$, wherein R' is as defined above; and R, X, and
17 W are as defined above;

18 Z is hydroxyl, a hydroxyphenyl group of the formula



1

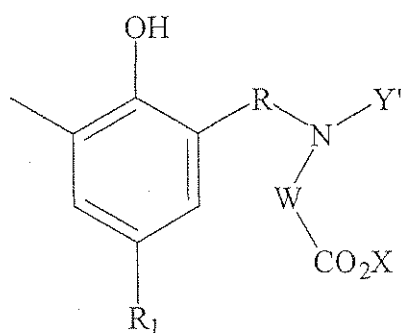
2 or



3

4 wherein R, R₁, Y', X, and W are as defined above,

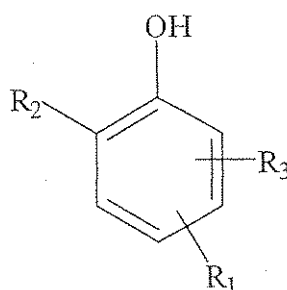
5 and n is an integer from 0 to 20, with the proviso that when n = 0, Z
6 must be



7

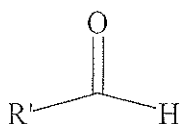
8 wherein R, R₁, Y', X, and W are as defined above.

- 1 23. The method of claim 22, wherein R is CH₂, R₁ is a polyisobutyl group
2 derived from polyisobutene containing at least 50 weight percent
3 methylvinylidene isomer and having a number average molecular
4 weight of about 700 to about 1,100, W is CH₂, X is a sodium ion and n
5 is an integer between 0 and 20.
6
- 7 24. A method for preventing metal ion catalyzed oxidation and
8 polymerization reactions in a hydrocarbon medium comprising
9 sequestering the metal ion by the addition of an effective amount of the
10 Mannich condensation product of claim 15.
11
- 12 25. A process for preparing a Mannich condensation product comprising:
13 mixing under reaction conditions,
14
15 (a) a polyisobutyl-substituted hydroxyaromatic compound having
16 the formula



17

- 18 wherein R₁ is polyisobutyl derived from polyisobutene containing
19 at least 50 weight percent methylvinylidene isomer and a
20 number average molecular weight in the range of about 400 to
21 about 5,000, R₂ is hydrogen or lower alkyl having one carbon
22 atom to about 10 carbon atoms, and R₃ is hydrogen or -OH;
23 (b) a formaldehyde or an aldehyde having the formula



1

2

3

4

5

6

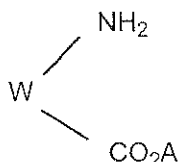
7

8

9

or polymers thereof, wherein R' is branched or linear alkyl having one carbon atom to about 10 carbon atoms, cycloalkyl having from about 3 carbon atoms to about 10 carbon atoms, aryl having from about 6 carbon atoms to about 10 carbon atoms, alkaryl having from about 7 carbon atoms to about 20 carbon atoms, or aralkyl having from about 7 carbon atoms to about 20 carbon atoms;

(c) an amino acid or ester derivative thereof having the formula



10

11

12

13

14

15

16

17

18

wherein W is $-\text{[CHR]}_m$ wherein each R'' is independently H, alkyl having one carbon atom to about 15 carbon atoms, or a substituted-alkyl having one carbon atom to about 10 carbon atoms and one or more substituents selected from the group consisting of amino, amido, benzyl, carboxyl, hydroxyl, hydroxyphenyl, imidazolyl, imino, phenyl, sulfide, or thiol; and m is an integer from one to 4, A is hydrogen or alkyl having one carbon atom to about 6 carbon atoms;

19

20

(d) in the presence of an alkali metal base to obtain the Mannich condensation product.

21

22

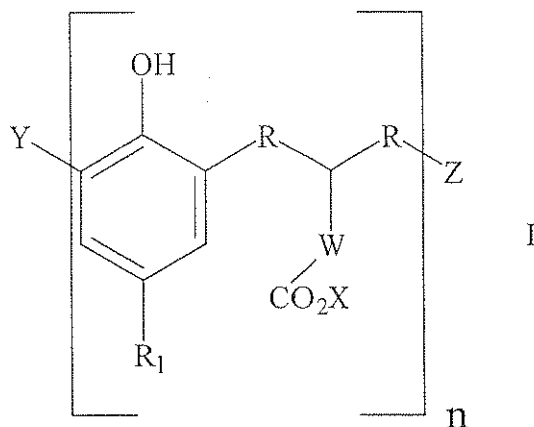
23

24

26. The process of claim 25, wherein the polyisobutyl group of the polyisobutyl-substituted hydroxyaromatic compound in (a) is derived from polyisobutene containing at least 70 weight percent methylvinylidene isomer.

27. The process of claim 26, wherein the polyisobutyl group is derived from polyisobutene containing at least 90 weight percent methylvinylidene isomer.
28. The process of any one of claims 25 to 27, wherein the R₁ polyisobutyl in (a) has a number average molecular weight of about 500 to about 2,500.
29. The process of claim 28, wherein the R₁ polyisobutyl in (a) has a number average molecular weight of about 700 to about 1,500.
30. The process of claim 29, wherein the R₁ polyisobutyl in (a) has a number average molecular weight of about 700 to about 1,100.
31. The process of anyone of claims 25 to 29, wherein the aldehyde (b) is formaldehyde or paraformaldehyde.
32. The process of claim 31, wherein the aldehyde is paraformaldehyde.
33. The process of anyone of claims 25 to 32, wherein the polyisobutyl-substituted hydroxyaromatic compound (a) is in a diluent.
34. The process of claim 33, wherein the diluent is an alkanol having one carbon atom to about 10 carbon atoms.
35. The process of claim 34, wherein the alkanol is methanol.
36. The process of anyone of claims 25 to 35, wherein the base in (d) is an alkali metal hydroxide.
37. The process of claim 36, wherein the alkali metal hydroxide is sodium hydroxide.
38. The process of anyone of claims 25 to 37, wherein the amino acid (c) is glycine.

- 1 39. A lubricating oil composition comprising a major amount of an oil of
 2 lubricating viscosity and a minor effective amount of one or more
 3 Mannich condensation products having the formula



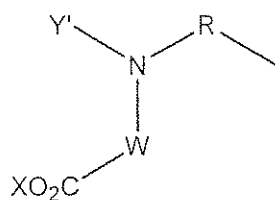
4
 5 wherein each R is independently -CHR'-, wherein R' is branched or
 6 linear alkyl having one to about 10 carbon atoms, cycloalkyl having
 7 from about 3 carbon atoms to about 10 carbon atoms, aryl having from
 8 about 6 carbon atoms to about 10 carbon atoms, alkaryl having from
 9 about 7 carbon atoms to about 20 carbon atoms, or aralkyl having from
 10 about 7 carbon atoms to about 20 carbon atoms, R₁ is a polyisobutyl
 11 group derived from polyisobutene containing at least 50 weight percent
 12 methylvinylidene isomer and having a number average molecular
 13 weight in the range of about 400 to about 5,000;

14 X is hydrogen, an alkali metal ion, or alkyl having one carbon atom to
 15 about 6 carbon atoms;

16 W is -[CHR'']-_m wherein each R'' is independently H, alkyl having one
 17 carbon atom to about 15 carbon atoms, or a substituted-alkyl having
 18 one carbon atom to about 10 carbon atoms and one or more
 19 substituents selected from the group consisting of amino, amido,
 20 benzyl, carboxyl, hydroxyl, hydroxyphenyl, imidazolyl, imino, phenyl,
 21 sulfide, or thiol; and m is an integer from one to 4;

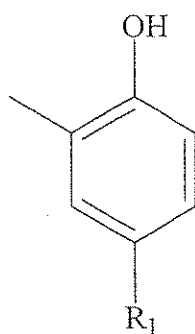
1 Y is hydrogen, alkyl having one carbon atom to about 10 carbon atoms,
2 -CHR'OH, wherein R' is as defined above,

3 or



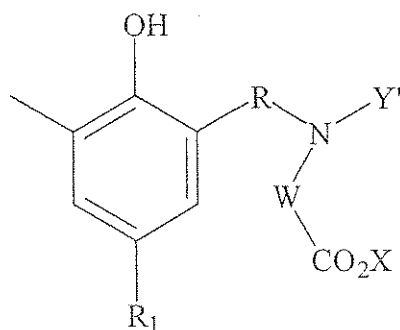
4
5 wherein Y' is -CHR'OH, wherein R' is as defined above; and R, X, and
6 W are as defined above;

7 Z is hydroxyl, a hydroxyphenyl group of the formula



8

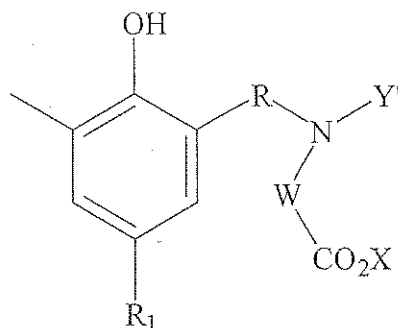
9 or



10

11 wherein R, R₁, Y', X, and W are as defined above,

1 and n is an integer from 0 to 20, with the proviso that when n = 0, Z
2 must be



3

4 wherein R, R₁, Y', X, and W are as defined above.

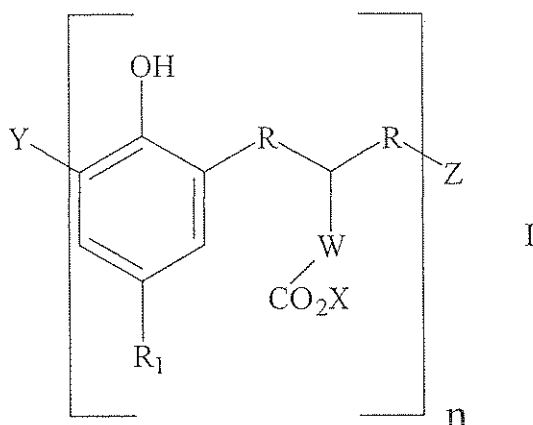
5 40. The lubricating oil composition of claim 39, wherein R is CH₂, R₁ is
6 polyisobutyl group derived from polyisobutene containing at least 50
7 weight percent methylvinylidene isomer and having a number average
8 molecular weight of about 700 to about 1,100, W is CHR'', wherein R''
9 is H, X is a sodium ion and n is an integer between 0 and 20.

10

11 41. A lubricating oil composition comprising a major amount of an oil of
12 lubricating viscosity and a minor effective amount of one or more
13 Mannich condensation products of claim 15.

14

15 42. A lubricating oil concentrate comprising from about 90 weight percent
16 to about 10 weight percent of an oil of lubricating viscosity and from
17 about 10 weight percent to about 90 weight percent of one or more
18 lubricating Mannich condensation products having the formula



1

2

3

4

5

6

7

8

9

10

wherein each R is independently -CHR'-, wherein R' is branched or linear alkyl having one to about 10 carbon atoms, cycloalkyl having from about 3 carbon atoms to about 10 carbon atoms, aryl having from about 6 carbon atoms to about 10 carbon atoms, alkaryl having from about 7 carbon atoms to about 20 carbon atoms, or aralkyl having from about 7 carbon atoms to about 20 carbon atoms, and R₁ is a polyisobutyl group containing at least 50 weight percent methylvinylidene isomer and having a number average molecular weight in the range of about 400 to about 5,000;

11

12

X is hydrogen, an alkali metal ion, or alkyl having one to about 6 carbon atoms;

13

14

15

16

17

18

W is -[CHR'']-_m wherein each R'' is independently H, alkyl having one carbon atom to about 15 carbon atoms, or a substituted-alkyl having one carbon atom to about 10 carbon atoms and one or more substituents selected from the group consisting of amino, amido, benzyl, carboxyl, hydroxyl, hydroxyphenyl, imidazolyl, imino, phenyl, sulfide, or thiol; and m is an integer from one to 4;

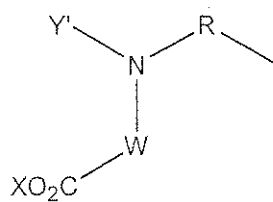
19

20

Y is hydrogen, alkyl having one carbon atom to about 10 carbon atoms, -CHR'OH, wherein R' is as defined above,

21

or



1

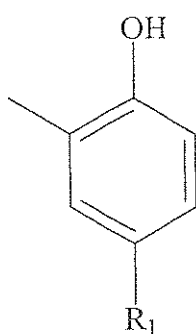
2

wherein Y' is -CHR'OH, wherein R' is as defined above; and R, X, and W are as defined above;

3

4

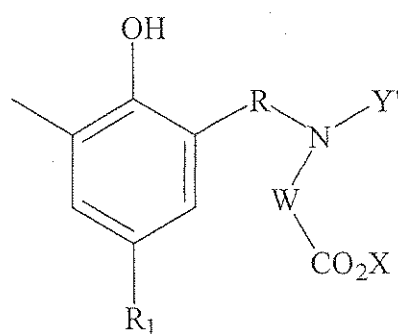
Z is hydroxyl, a hydroxyphenyl group of the formula



5

6

or



7

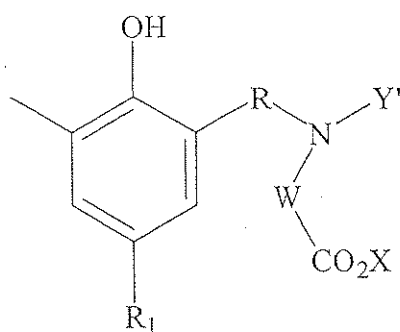
8

wherein R, R₁, Y', X, and W are as defined above,

9

and n is an integer from 0 to 20, with the proviso that when n = 0, Z must be

10



1

2

wherein R, R₁, Y', X, and W are as defined above.

3

43. The lubricating oil concentrate of claim 42, wherein R is CH₂, R₁ is alkyl group having a number average molecular weight of about 700 to about 1,000, W is CHR'', wherein R'' is H, X is a sodium ion and n is an integer between 0 and 20.

7

8

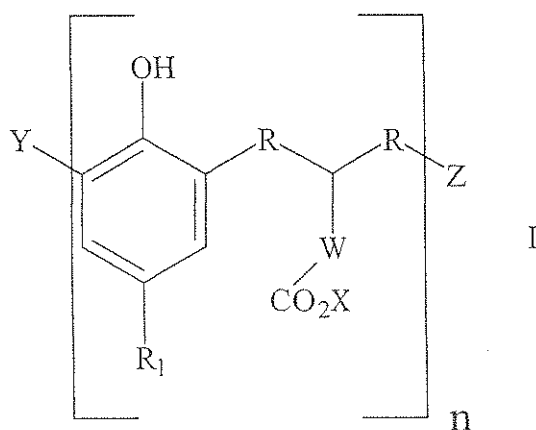
44. A lubricating oil concentrate comprising from about 90 weight percent to about 10 weight percent of an oil of lubricating viscosity and from about 10 weight percent to about 90 weight percent of one or more lubricating Mannich condensation products of claim 15.

12

13

45. 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 Mannich condensation products having the formula

16



17

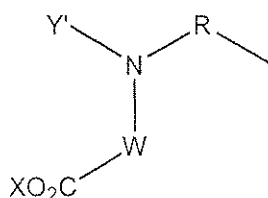
1 wherein each R is independently -CHR'-, wherein R' is branched or
2 linear alkyl having one to about 10 carbon atoms, cycloalkyl having
3 from about 3 carbon atoms to about 10 carbon atoms, aryl having from
4 about 6 carbon atoms to about 10 carbon atoms, alkaryl having from
5 about 7 carbon atoms to about 20 carbon atoms, or aralkyl having from
6 about 7 carbon atoms to about 20 carbon atoms, and R₁ is a
7 polyisobutyl group containing at least 50 weight percent
8 methylvinylidene isomer and having a number average molecular
9 weight in the range of about 400 to about 5,000;

10 X is hydrogen, an alkali metal ion or alkyl having one to about 6 carbon
11 atoms;

12 W is -[CHR'']-_m wherein each R'' is independently H, alkyl having one
13 carbon atom to about 15 carbon atoms, or a substituted-alkyl having
14 one carbon atom to about 10 carbon atoms and one or more
15 substituents selected from the group consisting of amino, amido,
16 benzyl, carboxyl, hydroxyl, hydroxyphenyl, imidazolyl, imino, phenyl,
17 sulfide, or thiol; and m is an integer from one to 4;

18 Y is hydrogen, alkyl having one carbon atom to about 10 carbon atoms,
19 -CHR'OH, wherein R' is as defined above,

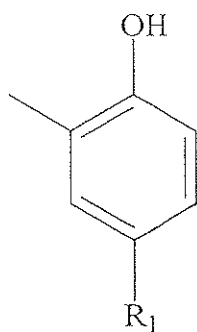
20 or



21

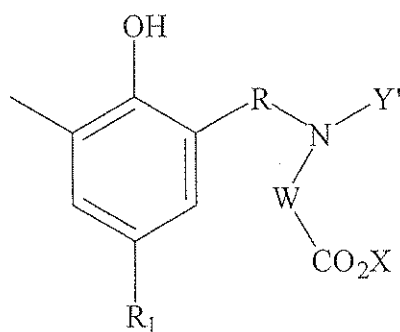
22 wherein Y' is -CHR'OH, wherein R' is as defined above; and R, X, and
23 W are as defined above;

24 Z is hydroxyl, a hydroxyphenyl group of the formula



1

2 or

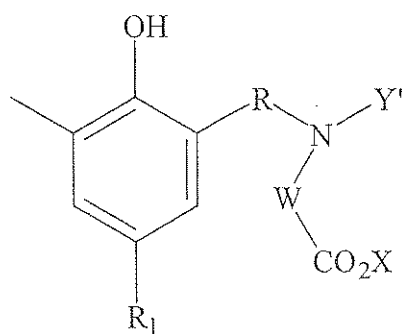


3

4 wherein R, R₁, Y', X, and W are as defined above,

5 and n is an integer from 0 to 20, with the proviso that when n = 0, Z

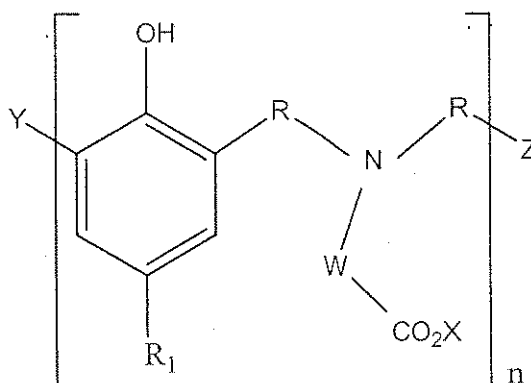
6 must be



7

8 wherein R, R₁, Y', X, and W are as defined above.

- 1 46. The fuel composition of claim 45, wherein R is CH₂, R₁ is polyisobutyl
 2 group derived from polyisobutene containing at least 50 weight percent
 3 methylvinylidene isomer and having a number average molecular
 4 weight of about 700 to about 1,000, W is CHR'', wherein R'' is H, X is a
 5 sodium ion and n is an integer between 0 and 20.
 6
- 7 47. A fuel composition comprising a major amount of hydrocarbons boiling
 8 in the gasoline or diesel range and a minor effective amount of one or
 9 more Mannich condensation products of claim 15.
 10
- 11 48. A fuel concentrate comprising an inert stable oleophilic organic solvent
 12 boiling in the range of from about 65°C to about 204°C and from about
 13 10 weight percent to about 90 weight percent of one or more Mannich
 14 condensation products having the formula

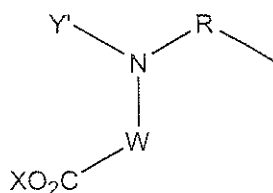


15
 16
 17 wherein R is either CH₂ or CHR' and wherein R' is branched or linear
 18 alkyl having one carbon atom to about 10 carbon atoms, cycloalkyl
 19 having from about 3 carbon atoms to about 10 carbon atoms, aryl
 20 having from about 6 carbon atoms to about 10 carbon atoms, alkaryl
 21 having from about 7 carbon atoms to about 20 carbon atoms, or aralkyl
 22 having from about 7 carbon atoms to about 20 carbon atoms, and R₁ is
 23 polyisobutyl derived from polyisobutene containing at least 50 weight
 24 percent methylvinylidene isomer and having a number average
 25 molecular weight in the range of about 400 to about 5,000,
 26

X is hydrogen, an alkali metal ion or alkyl having one carbon atom to about 6 carbon atoms,

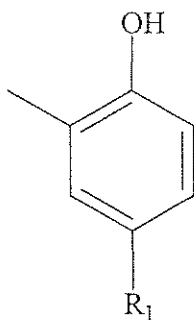
Y is hydrogen, alkyl having one carbon atom to about 10 carbon atoms, -CHR'OH, wherein R' is as defined above,

or

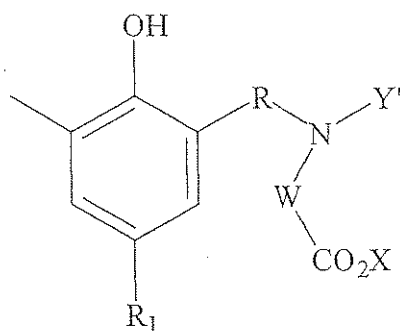


wherein Y' is -CHR'OH, wherein R' is as defined above; and R, X, and W is -[CHR'']_m wherein each R'' is independently H, alkyl having one carbon atom to about 15 carbon atoms, or a substituted-alkyl having one carbon atom to about 10 carbon atoms and one or more substituents selected from the group consisting of amino, amido, benzyl, carboxyl, hydroxyl, hydroxyphenyl, imidazolyl, imino, phenyl, sulfide, or thiol; and m is an integer from one to 4;

Z is hydroxyl, a hydroxyphenyl group of the formula



or



1

2

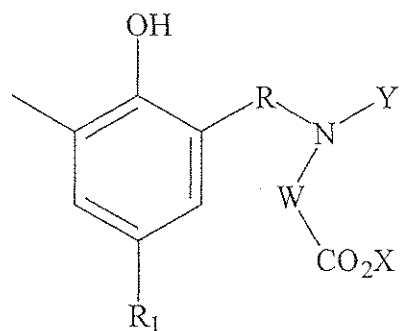
wherein R, R₁, Y', X, and W are as defined above,

3

and n is an integer from 0 to 20, with the proviso that when n = 0, Z

4

must be



5

6

wherein R, R₁, Y', X, and W are as defined above.

7

49. The fuel concentrate of claim 48, wherein R is CH₂, R₁ is polyisobutyl having a number average molecular weight of about 700 to about 1,000, W is CHRⁿ, wherein Rⁿ is H, X is a sodium ion and n is an integer between 0 and 20.

11

12

50. 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 Mannich condensation products of claim 15.

15