

1

2 PROCESS FOR PREPARATION OF MANNICH CONDENSATION
3 PRODUCTS USEFUL AS SEQUESTERING AGENTS

4

FIELD OF THE INVENTION

5 The present invention is directed to a process for preparing Mannich
6 condensation product sequestering agents or mixtures of Mannich
7 condensation product sequestering agents for use in fuels and lubricating oils.

8

BACKGROUND OF THE INVENTION

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

23 Metal ions can play an important role in the deterioration of lubricating oils.
24 Transition metals such as Fe^{+3} , Cu^{+2} , Pb^{+2} , and other metals, can catalyze the
25 oxidation of the oil resulting in the formation of the primary oxidation products
26 such as hydroperoxides, carboxylic acids, carbonyl compounds, hydroxyl
27 carbonyl compounds, and the like. In addition, metal ions such as Fe^{+3} , Cu^{+2} ,

1 Pb^{+2} , and other metals, can catalyze the polymerization of the primary
2 oxidation products resulting in the formation of sludge, lacquer, and varnish.

3 In order to prevent the metal catalyzed oxidation and polymerization of
4 lubricating oils, it would be desirable to find a way to complex or sequester the
5 metal ions to prevent the metal ions from acting as oxidation and
6 polymerization catalysts.

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

17 The conventional oil-soluble Mannich condensation products are useful in
18 internal combustion engine fuels. Non-volatile constituents of fuel, such as
19 additives, sometimes form deposits or varnish on inlet valves and on heating
20 elements. Such deposits and varnish impair the efficiency of these elements.
21 In addition, fuels are susceptible to chemical reactions, such as oxidation, on
22 aging. One effect of oxidation is to produce soluble and insoluble materials
23 that form deposits which interfere with the proper functioning of the internal
24 combustion engines. The conventional oil-soluble Mannich condensation
25 products help to reduce deposits.

26 Oil-soluble Mannich condensation products are also useful in internal
27 combustion engine lubricating oils. These products generally act as
28 dispersants to disperse sludge, varnish, and lacquer, and prevent the
29 formation of deposits. In general, conventional oil-soluble Mannich

1 condensation products are formed from the reaction of alkylphenols with
2 formaldehyde and an amine or a polyamine. These products have limited
3 ability to sequester Fe^{+3} and have limited ability to prevent the Fe^{+3} catalyzed
4 oxidation and polymerization that often occur.

5 Water-soluble Mannich condensation products are well known as
6 sequestering agents. However, such products cannot be used as
7 sequestering agents in fuels and lubricating oils.

8 The preparation of Mannich condensation products is well known in the art. A
9 number of patents have disclosed Mannich condensation products of
10 alkylphenols, aldehydes and amines. However, none of the known Mannich
11 condensation products contain both the needed oil solubility and the ability to
12 sequester Fe^{+3} to prevent Fe^{+3} catalyzed oxidation and polymerization
13 reactions in lubricating oil.

14 U. S. Patent No. 4,032,304 discloses an improved fuel composition containing
15 a normally liquid fuel, a carboxylic acid ester of lubricating viscosity and an oil-
16 soluble nitrogen-containing dispersant. The dispersant is characterized by
17 the presence therein of a substantially saturated hydrocarbon-based radical
18 having at least 50 carbon atoms. The dispersant is preferably a carboxylic
19 dispersant or a Mannich-type dispersant. The Mannich-type dispersant is for
20 example the reaction product of an alkylphenol with formaldehyde and a
21 polyethylene polyamine.

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

27 U. S. Patent No. 4,166,726 discloses a fuel additive and fuel composition. The
28 additive compound is a mixture of a polyalkylene amine and the reaction

1 product of an alkylphenol, an aldehyde and an amine. The additive provides
2 surprising stability in preventing thermal degradation of fuels, particularly fuels
3 for compression ignition engines.

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

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

12 U. S. Patent No. 4,197,091 discloses a composition for inhibiting the corrosion
13 of ferrous metal pipelines used to transport petroleum hydrocarbons
14 comprising a major portion of a mixture of C₃₆ dicarboxylic dimer acid and a
15 C₅₄ trimer acid, which mixture has an acid number of at least 110 and from
16 0.5% up to 5% of a composition from the group consisting of (a) an N,N'-
17 di(ortho-hydroxyarylidene)-1,2-alkyldiamine in which the arylidene radical
18 contains 6-7 carbon atoms and the alkylene radical contains 2-3 carbon
19 atoms; and (b) a polymeric condensation product obtained by the reaction of a
20 phenol having two reactive ring positions, a lower aliphatic aldehyde and a
21 polyamine.

22 U. S. Patent No. 4,225,502, a division of application Serial No. 630,792,
23 Patent No. 4,069,249 discussed above, discloses a novel Mannich
24 condensation product chelating agent for iron (III) or iron (II). The chelating
25 agent is a Mannich condensation product made from phenol or substituted-
26 phenol, formaldehyde, a di-amino di-acid and a diamine. The single claim is to
27 a cyano substituted compound.

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

12 U. S. Patent No. 4,387,244 discloses that alkyl-substituted hydroxy benzyl
13 amino acid oligomers are effective metal chelating agents in a broad range of
14 non-aqueous systems. The products claimed display surprisingly high
15 solubilities in a broad range of substituted and unsubstituted aliphatic and
16 aromatic solvents.

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

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

27 U. S. Patent No. 4,847,415 discloses certain Mannich reaction products (i.e.
28 alkylated phenol, polyoxyalkylenediamine, and an aldehyde) which are used
29 to deactivate iron species already present in hydrocarbon fluids. Left

1 untreated, such iron species lead to decomposition resulting in the formation
2 of gummy, polymer masses in the hydrocarbon liquid. The method for the
3 preparation of these Mannich condensation products are claimed in the
4 divisional U. S. Patent No. 4,883,580.

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

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

21 U. S. Patent No. 5,641,394 discloses a composition for use in deactivating
22 iron species in hydrocarbon fluids, comprising the products resulting from the
23 reaction of (I) a substituted-catechol, (II) a mixture of polyamines, and (III) an
24 aldehyde. The composition also functions as an anti-oxidant in hydrocarbon
25 fluids. The anti-oxidant function is separate from, and in addition to the metal
26 deactivating properties of the invention. These functional properties of the
27 invention can act either singly, or in concert, for stabilization of hydrocarbon
28 fluids.

1 U. S. Patent No. 6,126,837 discloses methods for removing suspended
2 particles from a solution. The methods generally comprise adding to the
3 solution to be treated an effective amount of a composition comprising a
4 Mannich derivatized polyether. The polyether is generally described as the
5 condensation polymer of Mannich derivatized bisphenol and a di-functional
6 monomer.

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

14 SUMMARY OF THE INVENTION

15 There is disclosed a process for preparing a Mannich
16 condensation product sequestering agent or mixtures of Mannich
17 condensation product sequestering agents for use in fuels and lubricating oils.

18 Unlike conventional processes for preparing Mannich condensation product
19 sequestering agents using amino acids as the source for the amine reactant
20 the process of the present invention involves a two step process that does not
21 require the use of alkanols, such as methanol, or aromatic solvents, such as
22 C₉ aromatic solvents, to assist in the handling of reactants and in conducting
23 the Mannich reaction.

24 In one aspect, there is provided a process for preparation of a Mannich
25 condensation product comprising the steps of:

- (a) reacting a polyalkyl-substituted hydroxyaromatic compound, wherein the polyalkyl group has a number average molecular weight of from 280 to 5,000 with an aldehyde in the presence of an alkali metal base; and
- (b) reacting the reaction mixture obtained from step (a) with an amino acid or ester derivative thereof and an alkali metal base.

In one embodiment, there is provided a process for preparing a Mannich condensation product sequestering agent comprising:

1 reacting

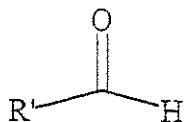
2 (a) a polyalkyl-substituted hydroxyaromatic compound, wherein the
3 polyalkyl group has a number average molecular weight of from
4 about 280 to about 5,000 and an aldehyde in the presence of an
5 alkali metal base; with

6 (b) an alkali metal base; and an amino acid or ester derivative
7 thereof and an alkali metal base.

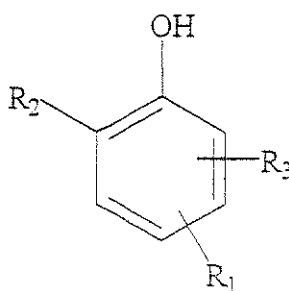
8 In another embodiment of the above process the reacting is conducted in the
9 absence of an alkanol.

10 Another embodiment of the process is directed to
11 preparing a Mannich condensation product sequestering agent comprising the
12 steps of:

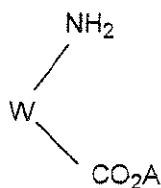
13 (a) forming a reaction mixture by combining formaldehyde or an
14 aldehyde having the formula



15
16 wherein R' is branched or linear alkyl having one carbon atom to
17 about 10 carbon atoms, cycloalkyl having from about 3 carbon
18 atoms to about 10 carbon atoms, aryl having from about 6 carbon
19 atoms to about 10 carbon atoms, alkaryl having from about 7
20 carbon atoms to about 20 carbon atoms, or aralkyl having from
21 about 7 carbon atoms to about 20 carbon atoms; with a polyalkyl-
22 substituted hydroxyaromatic compound having the formula



- wherein R_1 is polyalkyl of 280 to 5,000 molecular weight, R_2 is hydrogen or lower alkyl having one carbon atom to about 10 carbon atoms, and R_3 is hydrogen or $-OH$, in the presence of a base; and
- (b) contacting the reaction mixture with an amino acid or the ester derivative thereof having the formula



wherein 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, and A is hydrogen or alkyl having one carbon atom to about 6 carbon atoms; and

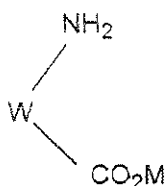
a base to form the Mannich condensation product.

Preferably in the above formula A is hydrogen.

In another preferred embodiment, in the above formula, A is alkyl selected from methyl or ethyl.

1 In an alternate embodiment of the process water
2 may be added in Step (b).

3 In a further embodiment of the process Step (b)
4 involves contacting the reaction mixture of Step (a) with an amino acid salt
5 having the formula



6
7 wherein w is as defined above and M is an alkali metal ion.

8 In the formula in the above process M is preferably a sodium ion or potassium
9 ion, more preferably M is a sodium ion.

10 In the above processes, preferably the R_1 polyalkyl group has a number
11 average molecular weight of about 400 to about 3,000. More preferably the
12 R_1 polyalkyl group has a number average molecular weight of about 500 to
13 about 2,000. Even more preferably the R_1 polyalkyl group has a number
14 average molecular weight of about 700 to about 1,500. Most preferably the
15 R_1 polyalkyl group has a number average molecular weight of about 700 to
16 about 1,100.

17 In the above processes, the polyalkyl substituent on the polyalkyl-substituted
18 hydroxyaromatic compound in step (a) is preferably derived from
19 polypropylene, polybutene, or a polyalpha olefin oligomer of 1-octene or 1-
20 decene. The polyalkyl-substituted hydroxyaromatic compound in step (a) in
21 the above process is more preferably polypropyl or polyisobutyl. In the above
22 process in step (a), preferably the polyalkyl-substituted hydroxyaromatic
23 compound is polyisobutyl-substituted phenol or polyisobutyl-substituted o-
24 cresol. More preferably the polyalkyl-substituted hydroxyaromatic compound
25 is polyisobutyl-substituted phenol.

1 Preferably, in the above processes the polyisobutyl-substituted phenol is
2 derived from polyisobutene containing at least about 20 weight percent
3 methylvinylidene isomer. More preferably the polyisobutyl-substituted phenol
4 is derived from polyisobutene containing at least about 50 weight percent
5 methylvinylidene isomer and most preferably the polyisobutyl-substituted
6 phenol is derived from polyisobutene containing at least about 70 weight
7 percent methylvinylidene isomer.

8 The aldehyde in step (a) in the above processes is preferably formaldehyde,
9 paraformaldehyde or formalin. More preferably the aldehyde in step (a) is
10 paraformaldehyde.

11 In the above processes, preferably the base in each of steps (a) and (b) is
12 independently an alkali metal hydroxide. More preferably the alkali metal
13 hydroxide is sodium hydroxide base in each of steps (a) and (b).

14 In another preferred embodiment, before performing
15 step (b), the amino acid, base and water are first combined separately at a
16 temperature in the range of about 15°C to about 100°C to form a concentrated
17 amino acid salt solution and then added to the reaction mixture formed in step
18 (a). Preferably before performing step (b) the amino acid, base and water are
19 first combined separately at a temperature in the range of about 30°C to about
20 70°C to form a concentrated amino acid salt solution and then added to the
21 reaction mixture formed in step (a). More preferably before performing step
22 (b) the amino acid, base and water are first combined separately at a
23 temperature in the range of about 40°C to about 60°C to form a concentrated
24 amino acid salt solution and then added to the reaction mixture formed in step
25 (a).

26 The amino acid employed in step (b) in the above processes is preferably
27 glycine and the preferred salt is the sodium glycine salt.

1 In yet another embodiment of the above processes
2 each of Steps (a) and (b) is independently conducted in the absence of an
3 alkanol.

4 If the Mannich condensation product sequestering agent prepared by the
5 above process is to be used as an additive in lubricating oil, then in step (a)
6 the polyalkyl-substituted hydroxyaromatic compound may be first dissolved in
7 an oil of lubricating viscosity. Preferably the oil of lubricating viscosity is a
8 neutral oil.

9 The Mannich condensation products prepared by the process disclosed herein
10 may also be employed as dispersants in lubricating oil. For use as dispersants in
11 fuels the alkali metal ions in Mannich condensation products are replaced with
12 ammonium ions.

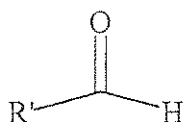
13 Among other factors, the disclosure herein is based upon the discovery that the
14 Mannich condensation products described herein can be obtained by the unique
15 two-step process as disclosed herein. Such Mannich
16 condensation products are effective in sequestering metals, especially Fe^{+3} ,
17 and preventing metal ion catalyzed oxidation and polymerization reactions,
18 while maintaining sufficient oil solubility for use in lubricating oils and fuels.

19 DETAILED DESCRIPTION OF THE INVENTION

20 DEFINITIONS

21 As used herein, the following terms have the following meanings unless
22 expressly stated to the contrary:

23 The term "aldehydes" as used herein refers to formaldehyde or aldehydes
24 having the formula



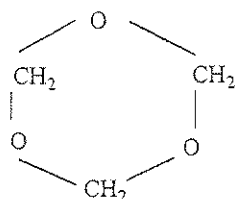
1

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

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

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

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



1

2 Examples of liquid formaldehyde are the following:

3 1. Monomer CH_2O in ethyl ether.

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

6 3. Monomer CH_2O in methanol which has the formulas $\text{OHCH}_2\text{OCH}_3$ and
7 $\text{CH}_3\text{O}(-\text{CH}_2\text{O})_n\text{H}$.

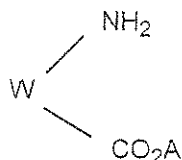
8

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

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

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

17 The term "amino acid or ester derivative thereof" as used herein refers to
18 amino acids and their esters having the formula



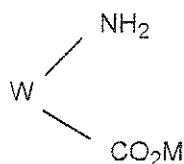
19

20 wherein W is $-\text{[CHR]}_m-$ wherein each R is independently H, alkyl
21 having one carbon atom to about 15 carbon atoms, or a substituted-

1 alkyl having one carbon atom to about 10 carbon atoms and one or
2 more substituents selected from the group consisting of amino, amido,
3 benzyl, carboxyl, hydroxyl, hydroxyphenyl, imidazolyl, imino, phenyl,
4 sulfide, or thiol; and m is an integer from one to 4 and A is hydrogen or
5 alkyl having one carbon atom to about 6 carbon atoms.

6 Preferably A is hydrogen. Preferred alkyl is methyl or ethyl.

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



10 wherein W is as defined above and M is an alkali metal ion. Preferably
11 M is a sodium ion or a potassium ion. More preferably M is a sodium
12 ion.

13 The term "aromatic solvent" as used herein refers to a mixture of aromatic
14 hydrocarbons, typically each having approximately from about 7 carbon atoms
15 to about 14 carbon atoms.

16 The term "base" as used herein refers to any alkali metal base having a pK_a
17 greater than 7, preferably the base pK_a is between 10 and 30. Typical bases
18 include alkali metal hydroxides and alkali metal alkoxides. Preferably the
19 base is an alkali metal hydroxide selected from the group consisting of sodium
20 hydroxide, lithium hydroxide or potassium hydroxide. More preferably the
21 alkali metal hydroxide is sodium hydroxide or potassium hydroxide. Most
22 preferably the base is sodium hydroxide.

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

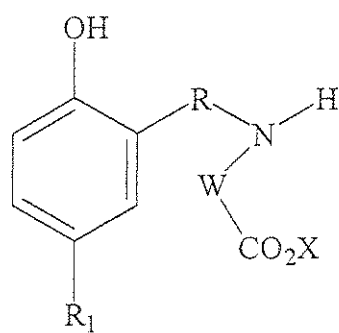
4 Test for Iron Sequestering Ability

5 The test used for iron sequestering ability was similar to that described in U.S.
6 Patent No. 4,387,244. A 0.15 to 0.25 gram sample of the Mannich
7 condensation product of the present invention is placed into an 8 dram vial to
8 which is added 15 milliliters toluene and shaken to homogeneity. Next 15
9 milliliters 0.05 molar aqueous solution of FeCl_3 is added to the vial and the vial
10 is mechanically shaken for one hour. The contents of the vial are allowed to
11 separate and the toluene layer changed color from yellow to purple, as
12 evidence of iron being chelated, in the presence of the Mannich condensation
13 product sequestering agents of the present invention.

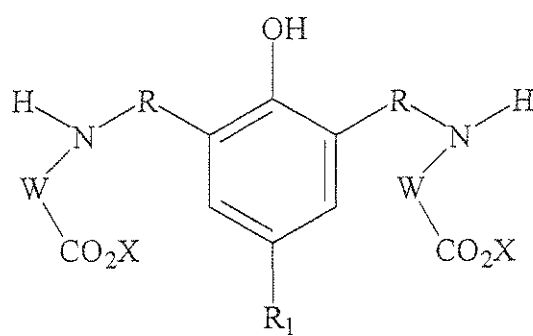
14 The term "hydroxyl number" as used herein refers to the amount of potassium
15 hydroxide required to neutralize the polyalkyl-substituted phenol per gram of
16 sample (mg KOH/g sample) as measured by tetrabutylammonium hydroxide
17 titration.

18 The term "Mannich condensation product" as used herein refers to a mixture
19 of products obtained by the condensation of a polyalkyl-substituted phenol
20 with an aldehyde and an amino acid or ester thereof, such as, glycine, in the
21 presence of a base, to form condensation products having the formulas given
22 below. The formula given below are provided only as some examples of the
23 Mannich condensation products of the present invention and are not intended
24 to exclude other possible Mannich condensation products that may be formed
25 using the methods of the present invention.

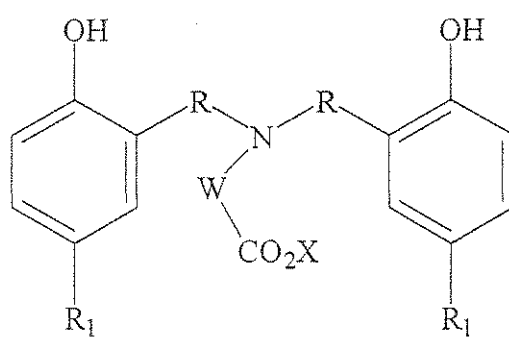
26



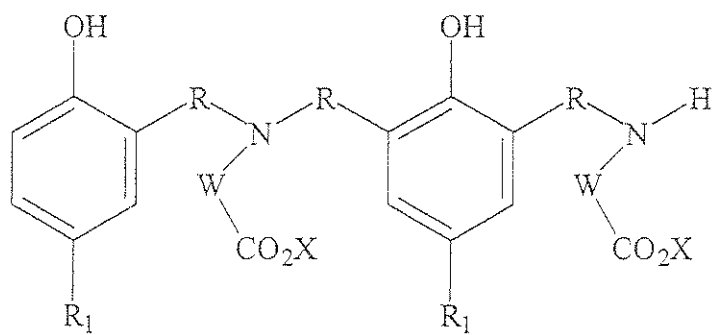
1



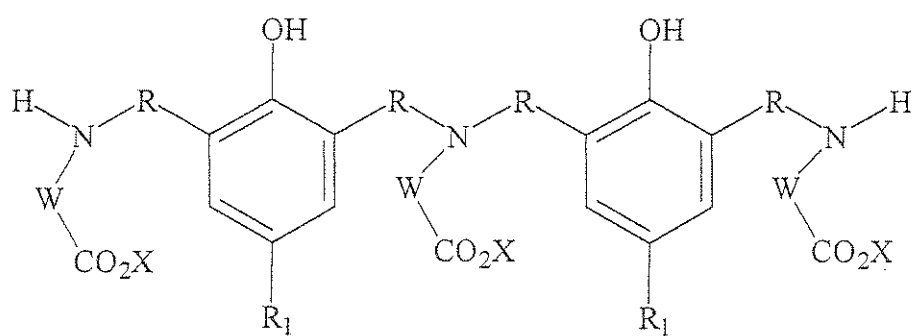
2



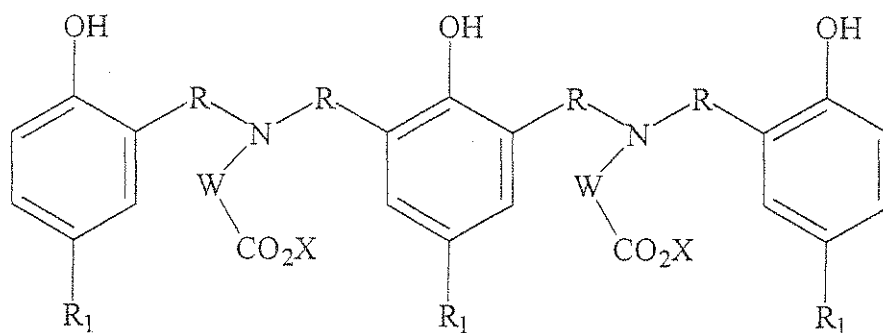
3



4



1

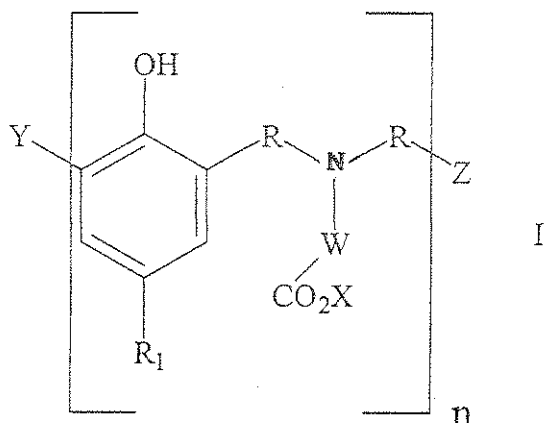


2

3 wherein each R is independently -CHR'-, wherein R' is as defined
 4 above and R₁ and W are as defined above, and X is hydrogen, an alkali
 5 metal ion or alkyl having one to about 6 carbon atoms;

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

1 In general, the principal Mannich condensation product prepared by the
 2 process of the present invention can be represented by the formula:



3

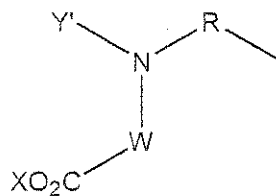
4 wherein each R is independently -CHR'-, wherein R' is as defined above, R₁
 5 is a polyalkyl group having a number average molecular weight in the range
 6 of about 280 to about 5,000;

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

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

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

17 or



1

2

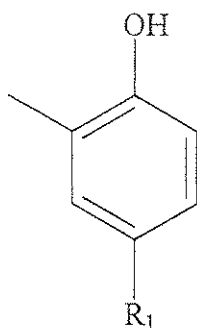
wherein Y' is -CHR'OH, wherein R' is as defined above; and R, X,

3

and W are as defined above;

4

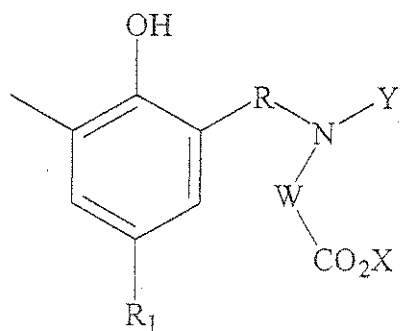
Z is hydroxyl, a hydroxyphenyl group of the formula:



5

6

or



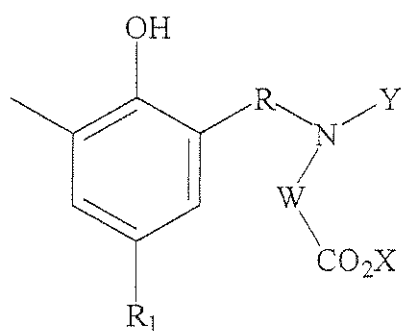
7

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:



1

2

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

3

Preferably the R₁ polyalkyl group has a number average molecular weight of

4

about 400 to about 3,000. More preferably the R₁ polyalkyl group has a

5

number average molecular weight of about 500 to about 2,000. Even more

6

preferably the R₁ polyalkyl group has a number average molecular weight of

7

about 700 to about 1,500. Most preferably the R₁ polyalkyl group has a

8

number average molecular weight of about 700 to about 1,100.

9

In the compound of formula I above, X is preferably hydrogen or alkali metal

10

ion, more preferably X is an alkali metal ion and most preferably a sodium ion.

11

In another embodiment of the invention, in the compound of formula I above,

12

X is alkyl selected from methyl or ethyl.

13

In a preferred embodiment of the Mannich condensation product of the

14

present invention R is CH₂, R₁ has a number average molecular weight in the

15

range of about 700 to about 1,100, W is CH₂, X is sodium ion and n is 0 to 20.

16

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

17

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

18

preferably useful in the crankcase of an internal combustion engine.

19

Crankcase lubricating oils ordinarily have a viscosity of about 1300

20

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

21

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

1 oil in this invention includes paraffinic, naphthenic and other oils that are
2 ordinarily used in lubricating oil compositions. Synthetic oils include
3 hydrocarbon synthetic oils, synthetic esters and Fischer-Tropsch derived base
4 oil. Useful synthetic hydrocarbon oils include liquid polymers of alpha-olefins
5 having the proper viscosity. Especially useful are the hydrogenated liquid
6 oligomers of C₆ to C₁₂ alpha-olefins such as 1-decene trimer. Similarly, alkyl
7 benzenes of proper viscosity, such as didodecyl benzene, may be used.
8 Useful synthetic esters include the esters of both mono-carboxylic acids and
9 polycarboxylic acids as well as mono-hydroxy alkanols and polyols. Typical
10 examples are didodecyl adipate, pentaerthritol tetracapoate, di-2-ethylhexyl
11 adipate, di-laurylsebacate and the like. Complex esters prepared from
12 mixtures of mono- and di-carboxylic acid and mono- and di-hydroxy alkanols
13 can also be used. Blends of hydrocarbon oils and synthetic oils may also be
14 used. For example, blends of 10 weight percent to 25 weight percent
15 hydrogenated 1-decene trimer with 75 weight percent to 90 weight percent
16 683 centistokes at 37.8°C mineral oil gives an excellent oil base.

17 The term "polyalkyl or polyalkyl substituent" as used herein refers to the
18 polyalkyl substituent on the hydroxyaromatic compound. The polyalkyl
19 substituent has a number average molecular weight in the range of about 280
20 to about 5,000. Preferably the polyalkyl moiety has a number average
21 molecular weight in the range of about 400 to about 5,000. More preferably
22 the polyalkyl moiety has a number average molecular weight in the range of
23 about 500 to about 2,000 and even more preferably the polyalkyl moiety has a
24 number average molecular weight in the range of about 700 to about 1,500.
25 Most preferably the polyalkyl moiety has a number average molecular weight
26 in the range of about 700 to about 1,100. Preferably the polyalkyl group is
27 polypropyl or polyisobutyl. Most preferably the polyalkyl group is polyisobutyl.

28 Preferably the attachment of the polyalkyl substituent to the phenol ring is
29 para to the hydroxyl moiety in at least 60 percent of the total polyalkylphenol
30 molecules, more preferably the attachment of the polyalkyl substituent to the
31 phenol ring is para to the hydroxyl moiety in at least 80 percent of the total

1 polyalkylphenol molecules, and most preferably the attachment of the
2 polyalkyl substituent to the phenol ring is para to the hydroxyl moiety on the
3 phenol ring in at least 90 percent of the total polyalkylphenol molecules.

4 The term "polyisobutyl-substituted phenol" as used herein refers to a
5 polyisobutyl-substituted phenol ring. The polyisobutyl substituent is defined
6 above. Preferably the polyisobutyl-substituted phenol is derived from
7 polyisobutene containing at least 20 weight percent methylvinylidene isomer.
8 More preferably the polyisobutyl-substituted phenol is derived from
9 polyisobutene containing at least about 50 weight percent methylvinylidene
10 isomer and most preferably the polyisobutyl-substituted phenol is derived from
11 polyisobutene containing at least about 70 weight percent methylvinylidene
12 isomer.

13 The term "sequestering agent" as used herein refers to compounds that hold
14 a metal atom between two or more atoms of the compound, thereby
15 neutralizing or controlling harmful metal ions, such as Fe^{+3} , in lubricating oil or
16 fuel.

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

19 Process For Preparing The Mannich Condensation Product

20 In its broadest aspect the present invention is directed to a process for
21 preparing Mannich condensation products, which process comprises the
22 steps of (a) forming a reaction mixture by combining an aldehyde with a
23 polyalkylphenol in the presence of a base, and (b) contacting the reaction
24 mixture with an amino acid or ester thereof, a base, and optionally water, to
25 form a product.

26 Conventional processes for preparing Mannich condensation product
27 sequestering agents using amino acids as the source for the amine employ

1 the use of alkanols, such as methanol, to assist in the handling of reactants
2 and in conducting the Mannich reaction. The Mannich reaction in such
3 processes is carried out with all the reactants simultaneously present in the
4 reaction mixture without any apparent significant effect of the order of addition
5 of individual reactants. The relatively large amounts of alkanol in the final
6 reaction mixture must be separated from the waste water and either disposed
7 off at great cost or recycled.

8 We have discovered a novel process for preparing Mannich condensation
9 product sequestering agents using amino acids as the source for the amine.
10 This process does not require the use of an alkanol. The process of the
11 present invention also allows for flexibility in the type of solvent used in the
12 Mannich reaction.

13 The novel process of the present invention for preparing Mannich
14 condensation product sequestering agents using amino acids surprisingly has
15 very strict limitations imposed on the Mannich reaction when an alkanol is not
16 used. These limitations have not been observed in the prior art processes.
17 The Mannich reaction in the present process does not proceed when all the
18 reactants are simultaneously added to the reaction flask as in the prior art
19 processes. The process of the present invention using an amino acid
20 requires two specific and separate steps for preparing the Mannich
21 condensation oligomer product sequestering agent.

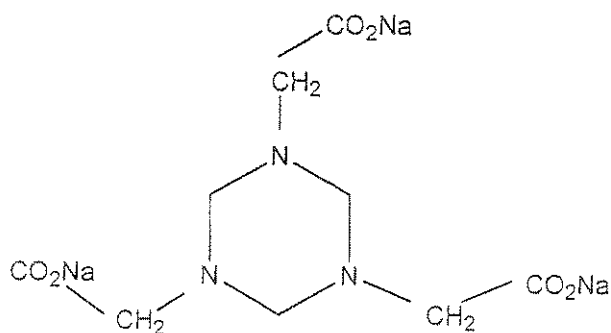
22 In addition, conventional processes for preparing Mannich condensation
23 product sequestering agents using amino acids as the source for the amine
24 employ aromatic solvents, such as C₉ aromatic solvents, for solubilizing the
25 polyalkyl-substituted hydroxyaromatic compound. The aromatic solvent must
26 also be separated and recycled in many cases where the Mannich
27 condensation product sequestering agent is to be used in a formulation using
28 mineral oil because of viscosity and flash point specifications required for
29 such formulations. We have discovered that the process of the present
30 invention may be carried out without the use of an aromatic solvent. The

1 process may be carried out using mineral oil or a relatively lower boiling, low
2 flash point aromatic solvent, thus, permitting the sequestering agent to be
3 prepared for applications requiring the sequestering agent in a mineral oil,
4 such as Exxon® 150N, neutral oil or Chevron® 100N, neutral oil.

5 In addition, the process of the present invention does not require a
6 neutralization step as used in some conventional processes for obtaining
7 Mannich condensation products.

8 Without being limited to any particular theory, it is believed that in the first step
9 of the present process a methylol intermediate is formed between
10 polyalkylphenol and aldehyde in the presence of a of base at about 65°C to
11 about 95°C.

12 Evidence for the absolute requirement of two separate and discrete steps for
13 carrying out the Mannich reaction in the process of the present invention was
14 observed when a precipitate was obtained instead of the Mannich
15 condensation product when all the reactants were simultaneously added, as
16 in the prior art processes. The precipitate had the following formula



18 The Mannich reaction for the preparation of the Mannich condensation
19 products of the present invention are believed to proceed as shown below.

1 General Procedure for Preparation of Mannich Condensation Product

2 Sequestering agents

3

4 A typical procedure for the preparation of Mannich condensation product
5 sequestering agents of the present invention is given below:

6 The method of the present invention may be conducted as a batch process, a
7 continuous process, a semi-batch process or by any process known to
8 persons skilled in the art.

9 Generally, the Mannich condensation reaction is carried out under inert gas
10 and atmospheric pressure, under basic conditions, in two steps. However,
11 higher and lower than atmospheric pressure may be used.

12 Step (a)

13 In Step (a) are charged with the following reactants:

14 1. a polyalkylphenol diluted in an inert solvent. The polyalkylphenol is
15 stirred and heated to allow for proper agitation. To the polyalkylphenol
16 is added

17 2. a base,

18 3. an aldehyde,

19 Typically, the reactants may be allowed to react over a broad period of time
20 and at a broad temperature range. In Table I below are summarized the
21 temperature and hold time ranges for conducting Step (a).

22 Step (b)

23 In Step (b) are added

24 3. one or more amino acids

25 4. water, and

1 5. a base;

2 Typically, Step (b) is conducted in two stages. In Stage 1 of Step (b) the
3 reactants may be allowed to react over a broad period of time and at a broad
4 temperature range. In Stage 2 of Step (b) the temperature is increased and
5 pressure is reduced to remove water. In Table I below are summarized the
6 temperature and hold times ranges for conducting Step (b).

7 Although, the concentration of the reactants may be varied to obtain the
8 desired product, it has been found that certain charge mole ratios of the
9 reactants are important for obtaining high yields of the Mannich condensation
10 products of the present invention. The charge mole ratios are described below
11 and summarized in Table I:

12 Charge Mole Ratio of Polyalkyl-Substituted Phenol to Aldehyde and Base to
13 Polyalkyl-substituted phenol

14 In Step (a) the charge mole ratio of base to the polyalkyl-substituted phenol is
15 present in the range of about 0.01:1.0 to about 1.0:1.0 and the charge mole
16 ratio of aldehyde to the polyalkyl-substituted phenol is present in the range of
17 about 0.5:1.0 to about 4.0:1.0. Preferably in step (a) the charge mole ratio of
18 base to the polyalkyl-substituted phenol is present in the range of about
19 0.03:1.0 to about 0.5:1.0 and the charge mole ratio of aldehyde to the
20 polyalkyl-substituted phenol is present in the range of about 1.0:1.0 to about
21 3.0:1.0. More preferably in step (a) the charge mole ratio of base to the
22 polyalkyl-substituted phenol is present in the range of about 0.05:1.0 to about
23 0.15:1.0 and the charge mole ratio of aldehyde to the polyalkyl-substituted
24 phenol is present in the range of about 1.5:1.0 to about 2.5:1.0. These charge
25 mole ratios are also summarized in Table I below.

1 Charge Mole Ratio of Base to Polyalkyl-Substituted Phenol and Amine to
2 Polyalkyl-Substituted Phenol

3 In Step (b) the charge mole ratio of base to the polyalkyl-substituted phenol is
4 present in the range of about 0:01 to about 1.5:1 and the charge mole ratio of
5 amine to the polyalkyl-substituted phenol is present in the range of about
6 0.01:1 to about 3:1. Preferably in step (b) the charge mole ratio of base to the
7 polyalkyl-substituted phenol is present in the range of about 0.5:1.0 to about
8 1.3:1 and the charge mole ratio of amine to the polyalkyl-substituted phenol is
9 present in the range of about 0.0.5:1.0 to about 2:1.0. More preferably in step
10 (b) the charge mole ratio of base to the polyalkyl-substituted phenol is present
11 in the range of about 0.9:1.0 to about 1.0:1.0 and the charge mole ratio of
12 amine to the polyalkyl-substituted phenol is present in the range of about
13 0.75:1.0 to about 1.5:1.0. These charge mole ratios are also summarized in
14 Table I below.

Table I

<u>Parameter</u>	<u>Ranges</u>	<u>Preferred Ranges</u>	<u>More Preferred Ranges</u>
Charge Mole ratio			
Aldehyde:Hydroxyaromatic in step (a)	0.5:1 - 4:1	1:1 - 3:1	1.5:1 - 2.5:1
Base:Hydroxyaromatic in step (a)	0.01:1 - 1:1	0.03:1 - 0.5:1	0.05:1 - 0.15:1
Base:Hydroxyaromatic in step (b)	0.01:1 - 1.5:1	0.5:1 - 1.3:1	0.9:1 - 1:1
Amino Acid:Hydroxyaromatic in step (b)	0.01:1 - 3:1	0.5:1 - 2:1	0.75:1 - 1.5:1
Water:Hydroxyaromatic in step (b)	0:1 - 20:1	0.1:1 - 15:1	1:1 - 7:1
Temperature Range (°C)			
Step (a)	50 – 120	60 – 100	70 – 95
Stage 1 * of Step (b)	50 – 120	60 – 100	70 – 95
Stage 2 ** of Step (b)	120 – 190	140 – 180	150 – 175
Hold time			
Step (a) (hours)	0.2 - 8	0.5 - 4	0.5 - 2.5
Stage 1 of Step (b) (hours)	0 - 8	0.5 - 4	0.5 - 2.5
Stage 2 of Step (b) (hours)	0.2 - 8	0.5 - 4	0.5 - 2.5

2

3 * Stage 1 is described above under Step (b).

4 ** Stage 2 is described above under Step (b).

5 If the Mannich condensation product sequestering agent is to be used as a
6 fuel additive it may be desirable to replace the alkali metal ion on the Mannich
7 condensation products with an ammonium ion. For other uses the alkali metal
8 ion on the Mannich condensation products may also be replaced with Group II
9 metals of the Periodic Table.

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

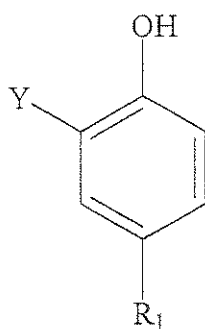
3 Polyalkyl-substituted hydroxyaromatic compound

4 A variety of polyalkyl-substituted hydroxyaromatic compounds can be utilized
5 in the synthesis of the Mannich condensation products of this invention. The
6 critical feature is that the polyalkyl substituent be large enough to impart oil
7 solubility to the finished Mannich condensation product. In general the
8 number of carbon atoms that are required to allow for oil solubility of the
9 Mannich condensation product is on the order of about C₂₀ and higher. This
10 corresponds to a molecular weight of 280 to 5,000. It is desirable that the C₂₀
11 or higher alkyl substituent on the phenol ring be located in the position para to
12 the OH group on the phenol.

13 In general, one unsubstituted ortho position to the hydroxyl group on the
14 phenol ring is required in order to synthesize the Mannich condensation
15 products of this invention. For example phenol substituted in the para position
16 with a substituent that contains greater than C₂₀ is a preferred polyalkylphenol
17 raw material for 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 alkyl substituent and the like.

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



1

2 wherein R_1 is polyalkyl having a number average molecular weight in the
3 range of about 280 to about 5,000, Y is hydrogen.

4 Preferably the R_1 polyalkyl group has a number average molecular weight of
5 about 400 to about 3,000. More preferably the R_1 polyalkyl group has a
6 number average molecular weight of about 500 to about 2,000. Even more
7 preferably the R_1 polyalkyl group has a number average molecular weight of
8 about 700 to about 1,500. Most preferably the R_1 polyalkyl group has a
9 number average molecular weight of about 700 to about 1,100.

10 In the above process the polyalkyl substituent on the polyalkylphenol is
11 derived from polypropylene, polybutene, or a polyalphaolefin oligomer of 1-
12 octene or 1-decene.

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

21 Suitable polyisobutenes may be prepared using boron trifluoride (BF_3)
22 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 2200, available from BASF.

3 The preferred polyalkylphenol for use in the preparation of the Mannich
4 condensation products of the present invention is a mono-substituted phenol,
5 wherein the polyalkyl substituent is attached at the para-position to the phenol
6 ring. However, other polyalkylphenols that may undergo the Mannich
7 condensation reaction may also be used for preparation of the Mannich
8 condensation products of the present invention. Some examples of such
9 polyalkylphenols are mono-substituted and di-substituted ortho-substituted
10 polyalkylphenols.

11 Inert Solvent

12 Inert solvents may be employed to facilitate handling and reaction of the
13 polyalkylphenols in the preparation of the Mannich condensation products of
14 the present invention. Examples of suitable inert solvents are hydrocarbon
15 compounds such as heptane, benzene, toluene, chlorobenzene, aromatic
16 solvent, neutral oil of lubricating viscosity, paraffins and naphthenes.
17 Examples of other commercially available suitable solvents include Chevron®
18 100N, neutral oil and Exxon® 150N, neutral oil.

19 If the Mannich condensation product sequestering agent prepared by the
20 above process is to be used as an additive in lubricating oil, then in step (a)
21 the polyalkylphenol may be first dissolved in a suitable solvent, such as
22 Chevron® 100Neutral Oil.

1 Base

2 Bases useful for the preparation of the Mannich condensation products of the
3 present invention may be any alkali metal base having a pK_a greater than 7,
4 preferably the base pK_a is between 10 and 30. Typical bases include alkali
5 metal hydroxides and alkali metal alkoxides. Preferably the base is an alkali
6 metal hydroxide selected from the group consisting of sodium hydroxide,
7 lithium hydroxide or potassium hydroxide. More preferably the alkali metal
8 hydroxide is sodium hydroxide or potassium hydroxide. Most preferably the
9 base is sodium hydroxide.

10 Aldehyde

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



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

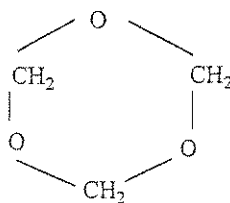
23 Aromatic aldehydes are also contemplated for use in the preparation of the
24 Mannich condensation products of the present invention, such as

1 benzaldehyde and alkylbenzaldehyde. Para-tolualdehyde is an example of an
2 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 $\text{CH}_3\text{O}(-\text{CH}_2\text{O})_n\text{-H}$.

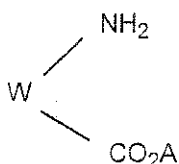
21

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 ester derivative thereof in the above process has the
9 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 atom 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.

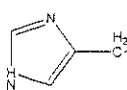
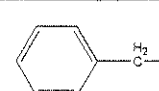
20 Preferably the amino acid is glycine.

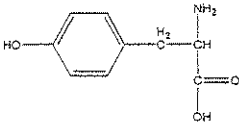
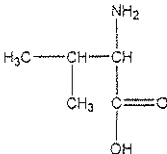
21 Some examples of alpha amino acids contemplated for use in the
22 preparation of the Mannich condensation products of the present invention
23 are given below in Table II.

1
2
3
4
5

Table II

Name	Structure	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{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH} \\ \quad \quad \quad \quad \quad \quad \\ \text{C}=\text{O} \quad \quad \quad \text{C}=\text{O} \quad \quad \quad \text{C}=\text{O} \\ \quad \quad \quad \quad \quad \quad \\ \text{OH} \quad \quad \quad \text{OH} \quad \quad \quad \text{OH} \end{array} $	8.99
Asparagine	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{H}_2\text{N}-\text{C}=\text{O} \\ \\ \text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{CH} \\ \quad \quad \quad \\ \text{C}=\text{O} \quad \quad \quad \text{C}=\text{O} \\ \quad \quad \quad \\ \text{OH} \quad \quad \quad \text{OH} \end{array} $	8.72 *
Aspartic Acid	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{HO}-\text{C}=\text{O} \\ \\ \text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{CH} \\ \quad \quad \quad \\ \text{C}=\text{O} \quad \quad \quad \text{C}=\text{O} \\ \quad \quad \quad \\ \text{OH} \quad \quad \quad \text{OH} \end{array} $	10.0
Cysteine	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{HS}-\text{C}-\text{CH} \\ \quad \quad \quad \\ \text{C}=\text{O} \quad \quad \quad \text{C}=\text{O} \\ \quad \quad \quad \\ \text{OH} \quad \quad \quad \text{OH} \end{array} $	10.77
Cystine	$ \begin{array}{c} \text{NH}_2 \quad \quad \quad \text{NH}_2 \\ \quad \quad \quad \\ \text{CH}-\text{CH}_2-\text{S}-\text{S}-\text{CH}_2-\text{CH} \\ \quad \quad \quad \\ \text{C}=\text{O} \quad \quad \quad \text{C}=\text{O} \\ \quad \quad \quad \\ \text{OH} \quad \quad \quad \text{OH} \end{array} $	8.80 **
Glutamic Acid	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{HO}-\text{C}=\text{O} \\ \\ \text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{CH}_2-\text{CH}_2-\text{CH} \\ \quad \quad \quad \quad \quad \quad \\ \text{C}=\text{O} \quad \quad \quad \text{C}=\text{O} \quad \quad \quad \text{C}=\text{O} \\ \quad \quad \quad \quad \quad \quad \\ \text{OH} \quad \quad \quad \text{OH} \quad \quad \quad \text{OH} \end{array} $	9.95
Glutamine	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{H}_2\text{N}-\text{C}=\text{O} \\ \\ \text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{CH}_2-\text{CH}_2-\text{CH} \\ \quad \quad \quad \quad \quad \quad \\ \text{C}=\text{O} \quad \quad \quad \text{C}=\text{O} \quad \quad \quad \text{C}=\text{O} \\ \quad \quad \quad \quad \quad \quad \\ \text{OH} \quad \quad \quad \text{OH} \quad \quad \quad \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} \\ \\ \text{C}=\text{O} \\ \\ \text{OH} \end{array} $ 	9.08 *
Hydroxylysine	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{CH}_2-\text{CH} \\ \\ \text{C}=\text{O} \\ \\ \text{OH} \end{array} $	
Isoleucine	$ \begin{array}{c} \text{NH}_2 \\ \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}-\text{CH} \\ \quad \\ \text{CH}_3 \quad \text{C}=\text{O} \\ \\ \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 \\ \text{CH}_3 \quad \text{C}=\text{O} \\ \\ \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{H}_3\text{C}-\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{NH}-\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 * 0.1 ionic strength.

4

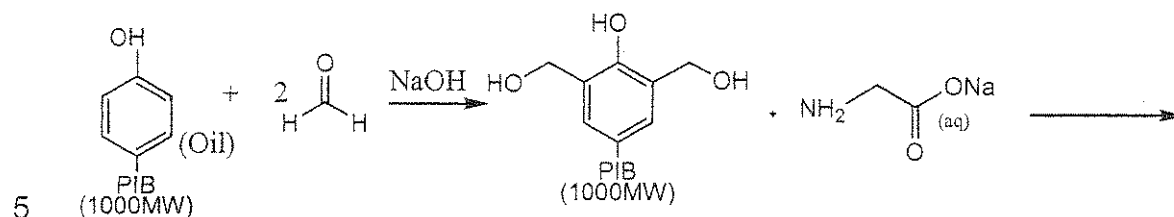
5 ** 20°C and 0.1 ionic strength.

6 In a preferred embodiment of the present process, before performing step (b),
7 the amino acid, base and water are first combined separately at a
8 temperature in the range of about 15°C to about 100°C to form a concentrated
9 amino acid salt solution and then added to the reaction mixture formed in step
10 (a). Preferably before performing step (b) the amino acid, base and water are
11 first combined separately at a temperature in the range of about 30°C to about
12 70°C to form a concentrated amino acid salt solution and then added to the
13 reaction mixture formed in step (a). More preferably before performing step
14 (b) the amino acid, base and water are first combined separately at a
15 temperature in the range of about 40°C to about 60°C to form a concentrated
16 amino acid salt solution and then added to the reaction mixture formed in step
17 (a).

EXAMPLES

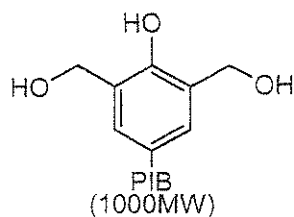
Example 1

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



PRODUCT

7 In a one liter round-bottom flask was added 351.09 grams (0.23 moles) of
8 1,000 molecular weight polyisobutyl substituted phenol as defined in the
9 Definitions section. The polyisobutyl-substituted phenol used in this Example
10 and in the following Examples in the present patent application was prepared
11 as described in U.S. Patent Nos. 5,300,701 and 6,274,777. The polyisobutyl-
12 substituted phenol, diluted in 31 percent Chevron® 100N, neutral oil (hydroxyl
13 number = 36.77 milligram KOH per gram sample) was combined with 2.88
14 grams (0.036 moles) aqueous sodium hydroxide (Aldrich® 50% solution).
15 The mixture was stirred and heated at about 35°C under nitrogen. After
16 approximately 15 minutes, when the mixture was homogenized, 14.99 grams
17 (0.46 moles) paraformaldehyde (Celanese® prills 92.56%) was added to the
18 reaction flask. Temperature of the reaction mixture was increased to about
19 75°C and the pressure was reduced from atmospheric to 250 millimeters Hg.
20 The reaction mixture in the flask was maintained at a temperature of about
21 75°C and a pressure of 250 millimeters Hg for about 1.5 hours. A sample of
22 less than 0.2 grams was removed for determination of the formula of the
23 product by ¹H-NMR. The intermediate product primarily formed had the
24 following formula



1

2 In a four ounce bottle was prepared a solution by mixing 18.02 grams (0.24
3 moles) glycine (Fisher Biotech® 98.5%), 15.94 grams (0.2 moles) sodium
4 hydroxide (Aldrich® 50% aqueous solution) and 2.72 grams deionized water.
5 The bottle was shaken until the contents formed a mostly homogeneous
6 solution with some particles suspended.

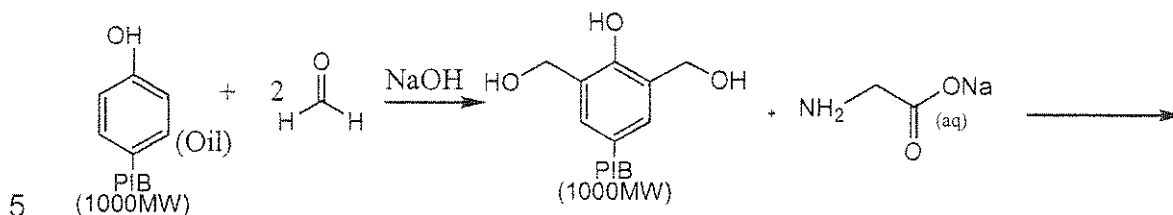
7 Next 34.98 grams of the above sodium glycine solution was added to the
8 flask. Pressure in the flask was reduced from atmospheric pressure to 300
9 millimeters Hg. The contents of the flask were held at about 75°C and a
10 pressure of 300 millimeters Hg for about 2 hours. Next the temperature of the
11 contents of the flask was increased to about 85°C and held at this
12 temperature for an additional 3 hours. The vacuum was released, the
13 contents of the flask were returned to atmospheric pressure, and three drops
14 of defoamer (Dow Corning® 200 Fluid) were added to the flask. After the
15 addition of the defoamer, water was removed by heating the contents of the
16 flask to 160°C and reducing the pressure to 50 millimeters Hg. A hazy, light
17 amber colored product 375.31 grams was obtained. The product was filtered
18 to yield a clear, light amber colored Mannich condensation product, which
19 sequestered Fe⁺³ as determined by the color test, namely the Test for Iron
20 Sequestering Ability, as described in the Definitions section.

21

Example 2

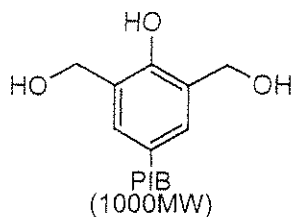
Preparation of Mannich condensation product using 1,000 molecular weight polyisobutyl-substituted phenol

Mannich condensation product was prepared in a 4 liter reactor.



PRODUCT

To a 4 liter reactor equipped with a temperature probe, an overhead system and a mechanical stirrer was added 2,500.5 grams (1.638 moles) of 1,000 molecular weight polyisobutyl-substituted phenol. The polyisobutyl-substituted phenol was diluted 31% in Chevron® 100N, neutral oil (hydroxyl number = 36.77 milligram KOH per gram sample) and heated to 80°C. When the temperature of the contents of the reactor had reached 80°C, 13.2 grams (0.164 moles) sodium hydroxide solution (Aldrich® 49.4% aqueous solution) was added to the reactor, followed quickly with the addition of 109.7 grams (3.277 moles) paraformaldehyde (Celanese® prills 92.56%). The reaction mixture was maintained at a temperature between about 80°C to about 90°C for 1.5 hours. A ¹H NMR was taken on a sample at this point in the reaction. The intermediate was determined to have the following formula:



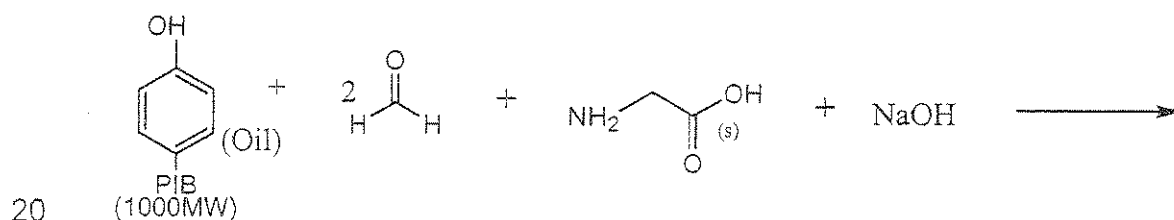
1 Next 270.2 grams sodium glycine solution, as prepared in Example 1, was
2 added to the reaction mixture. This solution was made by mixing 122.2 grams
3 (1.53 moles) sodium hydroxide solution (Aldrich® 49.4% aqueous solution)
4 with 128.5 grams (1.71 moles) glycine (Fisher Biotech® 100.3%) and 25
5 grams deionized water. This solution, along with 2 drops defoamer (Dow
6 Corning® 200 Fluid), was added to the reaction mixture at about 80°C. The
7 temperature was held at about 80°C for 1.5 hours. Next the temperature was
8 slowly increased to 160°C. When the temperature had reached 160°C, the
9 pressure was reduced from atmospheric to 50 millimeters Hg to remove any
10 remaining water from the product. These reaction conditions were held for
11 one hour. A Mannich condensation product was obtained which sequestered
12 Fe^{+3} as determined by the color test, Test for Iron Sequestering Ability,
13 described in the Definitions section.

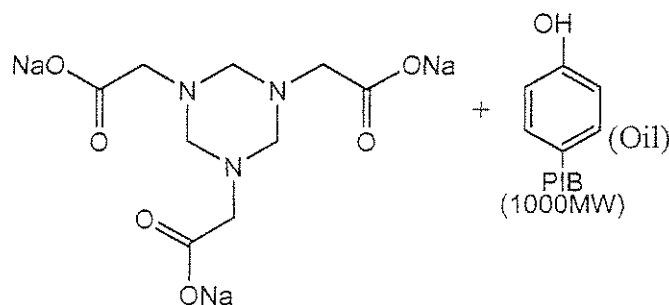
14 Comparative Example A

15 Attempted Preparation of Mannich condensation product using
16 1,000 molecular weight polyisobutyl-substituted phenol

17 The process of Example 1 was carried out, except paraformaldehyde was
18 added last.

19





1

2 To a 1 liter Morton flask was added 429.17 grams (0.281 moles) 1,000

3 molecular weight polyisobutyl-substituted phenol, as defined in the Definitions

4 section, diluted in Chevron 100Neutral® oil (hydroxyl number = 36.77

5 milligrams KOH per gram sample) and 11.92 grams (0.29 moles) sodium

6 hydroxide pellets (Fisher® 98.1%). The reaction mixture was warmed to

7 50°C and allowed to mix for approximately one hour. To the reaction mixture

8 was added 21.4 grams (0.281 moles) glycine (Fisher Biotech® 100.3%, solid),

9 quickly followed by 18.82 grams (0.58 moles) paraformaldehyde (Celanese®

10 prills 92.56%). To the reaction mixture two drops of defoamer (Dow Corning

11 200 Fluid®) was added to reduce foaming. The reaction mixture was stirred

12 and heated to about 90°C under nitrogen and held between the temperatures

13 of about 70°C to about 90°C for approximately one hour. An additional two

14 drops of defoamer (Dow Corning® 200 Fluid) was added to reduce foaming.

15 The temperature was then slowly increased over 1.5 hours to about 160°C.

16 Pressure was reduced from atmospheric pressure to 250 millimeters Hg using

17 a vacuum pump. These reaction conditions were held for about 2 hours.

18 Next stirring was stopped and the mixture was allowed to separate into two

19 phases, a solid phase and a liquid phase. A sample of the reaction mixture

20 analyzed by ¹H-NMR showed the liquid phase to be primarily unreacted

21 polyisobutyl-substituted phenol. The reaction mixture was then heated to

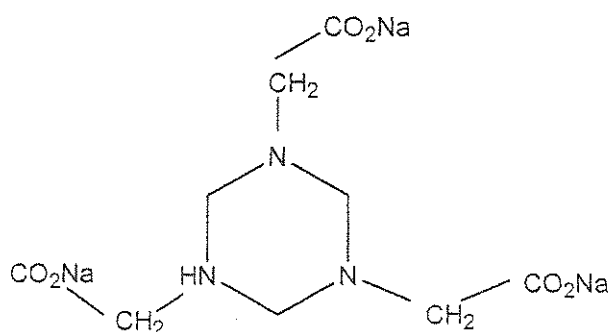
22 175°C and the pressure was reduced to approximately 400 millimeters Hg.

23 These reaction conditions were held for 3 hours. Again, the mixture was

24 allowed to separate into two phases. As determined by ¹H-NMR, the liquid

25 phase was still primarily unreacted polyisobutyl-substituted phenol and the

26 solid phase primarily had the formula below.



Comparative Example B

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

The process of Example 1 was carried out, except that sodium glycine was added to the reaction mixture before the paraformaldehyde.

A 488.87 gram (0.281 moles) 1,000 molecular weight polyisobutyl-substituted phenol sample, as defined in the Definitions section, diluted in 25% aromatic solvent, (hydroxyl number = 46.1 milligrams KOH per gram sample) was stripped by taking the sample to 160°C at a pressure of 5 millimeters Hg on a Buchi Rotovap®. This process yielded 389.96 grams of the stripped material. To a 1 liter round-bottom flask was added 161.62 grams (0.15 moles) of the stripped product and 75.86 grams Chevron® 100N, neutral oil. In a 400 milliliter beaker was prepared a solution of 5.97 grams (0.13 moles) sodium hydroxide pellets (Fisher® 98.1%), 21.4 grams (0.281 moles) solid glycine (Fisher Biotech® 100.3%) and 56.5 grams deionized water. To the reaction mixture in the round-bottom flask was added 65.84 grams of the homogeneous solution from the 400 milliliter beaker. The combined reaction mixture in the flask was heated to 110°C and held for about 30 minutes. The reaction mixture was further heated to 115°C and the pressure was reduced to 200 millimeters Hg using a vacuum pump. Next one drop of defoamer (Dow Corning 200 Fluid®) was added to the reaction mixture. Next 8.12

1 grams (0.26 moles) paraformaldehyde (Celanese® prills, 92.58%) was added
2 to the reaction mixture. The reaction mixture was heated to 170°C and held
3 at this temperature for 3 hours. A sample of the reaction mixture analyzed by
4 ¹H NMR showed the liquid phase to be primarily unreacted polyisobutyl-
5 substituted phenol.

6 A Mannich condensation product was not obtained from this Example. This
7 Example shows that the addition of sodium glycine before the addition of
8 paraformaldehyde does not provide a Mannich condensation product, and did
9 not sequester Fe⁺³ as determined by the color test described in the Definitions
10 section.

11 Comparative Example C

12 Attempted Preparation of Mannich condensation product using 13 1,000 molecular weight polyisobutyl-substituted phenol

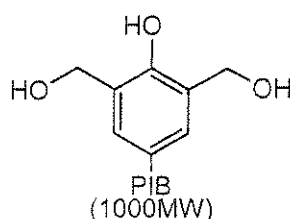
14 The process of Example 1 was carried out, except that sodium hydroxide and
15 glycine were added to the reaction mixture before the polyisobutyl-substituted
16 phenol and the paraformaldehyde.

17 To a 1 liter round-bottom flask were added 12.38 grams (0.31 moles) sodium
18 hydroxide (Fisher®, reagent grade), 22.91 grams (0.31 moles) glycine (Fisher
19 Biotech®, culture grade) and 77.95 grams deionized water. The reaction
20 mixture was stirred under nitrogen and heated to about 35°C. The reaction
21 mixture exothermed to 55°C as the solutes went into solution. After
22 approximately 20 minutes, 422.36 grams (0.31 moles) 1,000 molecular weight
23 polyisobutene-substituted phenol sample, as defined in the Definitions
24 section, diluted in about 25% aromatic solvent (hydroxyl number = 41.3
25 milligrams KOH per gram sample) was added to the reaction mixture, quickly
26 followed by 18.96 grams (0.62 moles) paraformaldehyde (Celanese® prills,
27 92.56%). The reaction mixture in the flask was heated to 120°C and allowed
28 to reflux for 2 hours. The solvent was then distilled off by attaching a Dean-

1 Starke® trap and heating the reaction mixture to 170°C and holding at this
2 temperature for 6 hours. To the reaction mixture was added 82.22 grams
3 Chevron® 100N, neutral oil, as the reaction mixture cooled to room
4 temperature. A sample of the reaction mixture analyzed by ¹H NMR showed
5 the liquid phase to be primarily unreacted polyisobutyl-substituted phenol.

6 A Mannich condensation product was not obtained from this Example. This
7 Example shows that the addition of sodium hydroxide and glycine before the
8 addition of polyisobutyl-substituted phenol and paraformaldehyde does not
9 provide the desired Mannich condensation product.

10 Without being bound by any theory, it is believed that the Mannich
11 condensation product was not formed because the order of addition of the
12 reactants did not permit the formation of the required intermediate as shown
13 below.



14

15 Comparative examples were conducted to determine whether excluding the
16 alkanol from the present process would still permit the addition of the
17 reactants in any order as in conventional processes. Comparative Examples
18 A-C described above and summarized in Table III show that when alkanol is
19 excluded from the present process, the present process must be conducted in
20 two steps and the order of the addition of the reactants is important for
21 obtaining a Mannich condensation product.

1

Table III

Example	Addition of polyisobutyl-phenol*	Addition of formaldehyde	Addition of glycine	Mannich Condensation Product
Example 1	First	Second	Third	Yes
Example 2	First	Second	Third	Yes
Comparative A	First	Second		No
Comparative B	First	Third	Second	No
Comparative C	Second	Third **	First	No

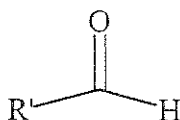
2

3 * Polyisobutyl-substituted phenol in Chevron® 100N, neutral oil.

4 ** The formaldehyde was quickly added after the polyisobutyl-substituted-
 5 phenol.

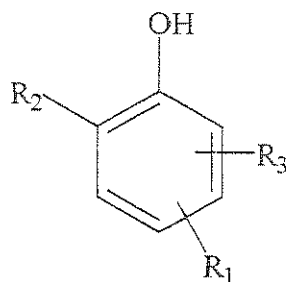
WHAT IS CLAIMED IS:

1. A process for preparation of a Mannich condensation product comprising the steps of:
 - (a) reacting a polyalkyl-substituted hydroxyaromatic compound, wherein the polyalkyl group has a number average molecular weight of from 280 to 5,000 with an aldehyde in the presence of an alkali metal base; and
 - (b) reacting the reaction mixture obtained from step (a) with an amino acid or ester derivative thereof and an alkali metal base.
2. The process of claim 1, wherein each of steps (a) and (b) is independently conducted in the absence of an alkanol.
3. The process according to claim 1 for preparing a Mannich condensation product sequestering agent comprising the steps of:
 - (a) reacting formaldehyde or an aldehyde having the formula



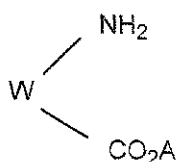
wherein R' is branched or linear alkyl having one carbon atom to 10 carbon atoms, cycloalkyl having from 3 carbon atoms to 10 carbon atoms, aryl having from 6 carbon atoms to 10 carbon atoms, alkaryl having from 7 carbon atoms to 20 carbon atoms, or aralkyl having from 7 carbon atoms to 20 carbon atoms;

with a polyalkyl-substituted hydroxyaromatic compound having the formula



wherein R_1 is polyalkyl of 280 to 5,000 molecular weight, R_2 is hydrogen or lower alkyl having one carbon atom to 10 carbon atoms, and R_3 is hydrogen or $-OH$, in the presence of an alkali metal base; and

- (b) reacting the reaction mixture obtained from step (a) with an amino acid or the ester derivative thereof having the formula



wherein W is $-[CHR'']_m$ wherein each R'' is independently H, alkyl having one carbon atom to 15 carbon atoms, or a substituted-alkyl having one carbon atom to 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; m is an integer from one to 4, and A is hydrogen or alkyl having one carbon atom to 6 carbon atoms; and

an alkali metal base to form the Mannich condensation product.

4. The process of claim 3, wherein the polyalkyl substituent on the polyalkyl-substituted hydroxyaromatic compound in Step (a) has a number average molecular weight of 400 to 3,000.
5. The process of claim 4, wherein the polyalkyl substituent on the polyalkyl-substituted hydroxyaromatic compound in Step (a) has a number average molecular weight of 500 to 2,000.
6. The process of claim 5, wherein the polyalkyl substituent on the polyalkyl-substituted hydroxyaromatic compound in Step (a) has a number average molecular weight of 700 to 1,500.
7. The process of claim 6, wherein the polyalkyl substituent on the polyalkyl-substituted hydroxyaromatic compound in Step (a) has a number average molecular weight of 700 to 1,100.
8. The process of any one of claims 3 to 7, wherein the polyalkyl substituent on the polyalkyl-substituted hydroxyaromatic compound in Step (a) is derived from polypropylene, polybutene, or a polyalphaolefin oligomer of 1-octene or 1-decene.
9. The process of any one of claims 3 to 7, wherein the polyalkyl-substituted hydroxyaromatic compound in Step (a) is polypropyl-substituted phenol or polyisobutyl-substituted phenol.
10. The process of claim 9, wherein the polyalkyl-substituted hydroxyaromatic compound in Step (a) is polyisobutyl-substituted phenol.
11. The process of claim 10, wherein the polyisobutyl-substituted phenol is derived from polyisobutene containing at least 20 weight percent methylvinylidene isomer.

12. The process of any one of claims 3 to 11, wherein the aldehyde in Step (a) is formaldehyde, paraformaldehyde or formalin.
13. The process of claim 12, wherein the aldehyde in Step (a) is paraformaldehyde.
14. The process of any one of claims 3 to 13, wherein Step (a) is conducted for a period of 0.2 hours to 8 hours at a temperature in the range of 50°C to 120°C.
15. The process of any one of claims 3 to 14, wherein the reaction mixture formed in Steps (a) is contacted with an amino acid salt.
16. The process of claim 15, wherein the amino acid salt is prepared by first separately combining the amino acid, base and water at a temperature in the range of 15°C to 100°C to form a concentrated amino acid salt solution and then added to the reaction mixture formed in Step (a).
17. The process of claim 16, wherein the amino acid salt is prepared by first separately combining the amino acid, base and water at a temperature in the range of 30°C to 70°C to form a concentrated amino acid salt solution and then added to the reaction mixture formed in Step (a).
18. The process of claim 17, wherein the amino acid salt is prepared by first separately combining the amino acid, base and water at a temperature in the range of 40°C to 60°C to form a concentrated amino acid salt solution and then added to the reaction mixture formed in Step (a).
19. The process of any one of claims 3 to 18, wherein the base in each of Steps (a) and (b) is independently an alkali metal hydroxide selected from the group

consisting of sodium hydroxide, lithium hydroxide or potassium hydroxide.

20. The process of claim 19, wherein the base is sodium hydroxide.
21. The process of any one of claims 3 to 20, wherein in Step (b) the amino acid is glycine.
22. The process of any one of claims 3 to 21, wherein Step (b) is conducted in two stages, Stage 1 and Stage 2, wherein Stage 1 of Step (b) is conducted for a period of 0.2 hours to 8 hours at a temperature in the range of 50°C to 120°C, and then Stage 2 of Step (b) is conducted for an additional period of 0.2 hours to 8 hours at a final temperature in the range of 120°C to 190°C.
23. The process of any one of claims 3 to 22, wherein in Step (a) the molar ratio of base to the polyalkyl-substituted hydroxyaromatic compound is in the range of 0.01:1 to 1:1 and the molar ratio of aldehyde to the polyalkyl-substituted hydroxyaromatic compound is present in the range of 0.5:1 to 4:1.
24. The process of any one of claims 3 to 22, wherein in Step (a) the molar ratio of base to the polyalkyl-substituted hydroxyaromatic compound is in the range of 0.01:1 to 1.5:1 and the molar ratio of amine to the polyalkyl-substituted hydroxyaromatic compound is present in the range of 0.01:1 to 3:1.
25. The process of any one of claims 3 to 24, wherein each of Steps (a) and (b) is independently conducted in the absence of an alkanol.

26. The process of any one of claims 3 to 25, wherein in Step (a) the polyalkyl-substituted hydroxyaromatic compound is first dissolved in an oil of lubricating viscosity.
27. The process of claim 26, wherein the oil of lubricating viscosity is neutral oil.