

FUEL ADDITIVE COMPOUNDS AND METHOD OF MAKING THE COMPOUNDS

DESCRIPTION OF THE DISCLOSURE

Field of the Disclosure

[0001] The present application is directed to a novel process for making detergents and fuel compositions comprising the detergents.

Background of the Disclosure

[0002] Over the years considerable work has been devoted to additives for controlling (preventing or reducing) deposit formation in the fuel induction systems of spark-ignition internal combustion engines. In particular, additives that can effectively control fuel injector deposits, intake valve deposits and combustion chamber deposits represent the focal point of considerable research activities in the field, and despite these efforts, further improvements are desired.

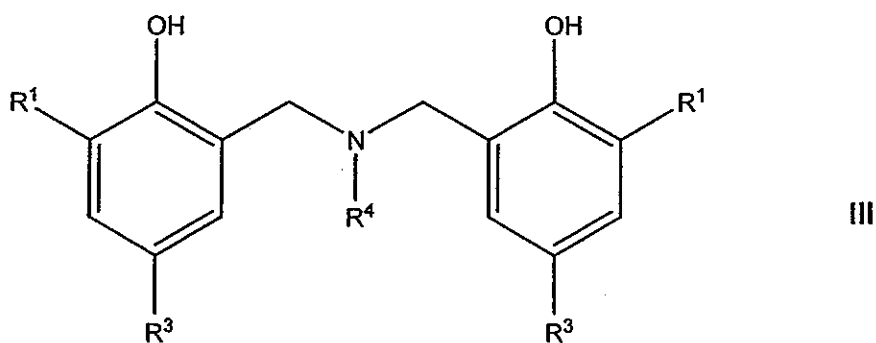
[0003] Conventional port-fuel injection (PFI) engines form a homogeneous pre-mixture of gasoline and air by injecting gasoline into the intake port. Direct injection gasoline (DIG) engines inject gasoline directly into the combustion chamber like a diesel engine so that it becomes possible to form a stratified fuel mixture which contains greater than the stoichiometric amount of fuel in the neighborhood of the spark plug but highly lean in the entire combustion chamber.

[0004] The major fuel-related deposit problem areas for PFI and DIG engines are injectors, intake valves, and the combustion chamber. Mannich base fuel additives are well known in the petroleum industry for controlling such deposit problems. However, while Mannich base additives traditionally provide excellent control for intake valve deposits, they may not control deposits to a desired degree for injectors in PFI and/or DIG engines. There is, therefore, a desire in the petroleum industry to produce fuel additives suitable for use in PFI and/or DIG engines that can provide improved control of engine deposits, and to develop methods for producing such fuel additives.

SUMMARY OF THE DISCLOSURE

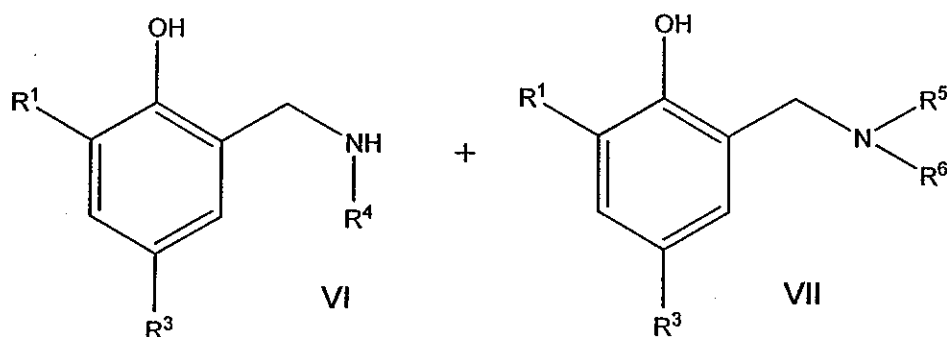
[0005] In accordance with the disclosure, an embodiment of the present application is directed to a process for forming a detergent base product. The process comprises forming a bis-Mannich intermediate compound by reacting (i) at least one hydroxyl substituted aromatic ring compound having on the ring an aliphatic hydrocarbyl substituent derived from a polyolefin having a number average molecular weight of about 500 to about 3000; (ii) at least one primary amine; and (iii) at least one aldehyde. The resulting bis-Mannich intermediate compound is then reacted with at least one second amine compound chosen from primary and secondary amines to form the detergent base product.

[0006] Another embodiment of the present application is directed to a process for forming a Mannich reaction product. The process comprises reacting at least one amine compound chosen from primary and secondary amines with a bis-Mannich compound having a formula II,



where R^1 is chosen from a hydrogen radical and C_{1-6} alkyl; R^3 is a hydroxyaromatic compound having on the ring an aliphatic hydrocarbyl substituent derived from a polyolefin having a number average molecular weight of about 500 to about 3000; and R^4 is a linear; branched, or cyclic, substituted or unsubstituted, saturated or unsaturated alkyl amine group.

[0007] Another embodiment of the present application is directed to a fuel composition comprising: a base fuel; and a detergent base product comprising a mixture of formulae (VI) and (VII),



where R^1 and R^3 are substituents independently chosen from a hydrogen radical, C_{1-6} alkyls and hydrocarbyl substituents having a number average molecular weight in the range of about 500 to about 3000, with the proviso that at least one of R^1 and R^3 is a hydrocarbyl substituent; R^4 is a substituent chosen from alkyl, aryl, alkenyl, alkyl amino, dialkyl amino, alkylaminoalkyl, and dialkylaminoalkyl groups; R^5 and R^6 are each independently chosen from a hydrogen radical, alkyl, cycloalkyl, aryl, alkaryl, and aralkyl groups, with the proviso that at least one of R^5 and R^6 is not a hydrogen radical.

[0008] Additional objects and advantages of the disclosure will be set forth in part in the description which follows, and can be learned by practice of the disclosure. The objects and advantages of the disclosure will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims.

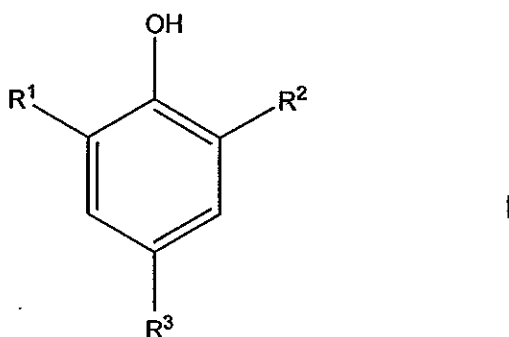
[0009] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the disclosure, as claimed.

DESCRIPTION OF THE EMBODIMENTS

[0010] The process of the present application involves formation of a detergent base product using a bis-Mannich intermediate. In embodiments, the reaction mechanism can include a two stage process, wherein the bis-Mannich intermediate is formed during the first stage, and then reacted with an amine during the second stage to form the detergent base product. The reactions of the first and second stage will now be described.

Formation of the Bis-Mannich Intermediate

[0011] In embodiments of the present application, the bis-Mannich intermediate compounds can be formed by reacting (i) at least one hydroxyl substituted aromatic ring compound having on the ring an aliphatic hydrocarbyl substituent derived from a polyolefin having a number average molecular weight of about 500 to about 3000; (ii) at least one primary amine; and (iii) at least one aldehyde. Any hydroxyl substituted aromatic ring compound readily reactive in the Mannich condensation reaction may be employed. Representative hydroxyl substituted aromatic ring compounds used in forming the bis-Mannich intermediates of the present application are represented by the following formula I:



where R^1 , R^2 and R^3 can each be independently chosen from a hydrogen radical, a C_{1-6} alkyl, or a hydrocarbyl substituent having a number average molecular weight in the range of about 500 to about 3000, with the proviso that at least one of R^1 , R^2 and R^3 is a hydrocarbyl substituent. Representative C_{1-6} alkyl groups include methyl, ethyl, propyl, isopropyl, butyl, and isobutyl.

[0012] Representative hydrocarbyl substituents can include polypropylene groups; polybutene groups; polyisobutylene groups; polyalpha-olefin groups, such as poly 1-octene

groups; and ethylene/alpha-olefin copolymer groups. Other similar long-chain hydrocarbyl substituents may also be used. Examples include copolymer groups having at least one monomer chosen from butylene, isobutylene, and propylene, and at least one monomer chosen from mono-olefinic comonomers copolymerizable therewith, such as ethylene, 1-pentene, 1-hexene, i-octene, i-decene, etc., where the copolymer molecule contains at least 50% by weight, of butylene and/or isobutylene and/or propylene units. The comonomers polymerized with propylene or such butenes may be aliphatic and can also contain non-aliphatic groups, e.g., styrene, o-methylstyrene, p-methylstyrene, divinyl benzene and the like. The resulting polymers and copolymers used in forming the compound of formula (I) are substantially aliphatic hydrocarbon polymers. In some embodiments, the hydrocarbyl substituents may be substantially saturated, containing only residual unsaturation.

[0013] In one embodiment, the hydrocarbyl substituent is a polybutylene group. Unless otherwise specified herein, the term "polybutylene" is used in a generic sense to include polymers made from "pure" or "substantially pure" 1-butene or isobutene, and polymers made from mixtures of two or all three of 1-butene, 2-butene and isobutene. Commercial grades of such polymers may also contain insignificant amounts of other olefins.

[0014] In some embodiments, high reactivity polyisobutenes having relatively high proportions of polymer molecules with a terminal vinylidene group can be used to form the hydrocarbyl substituent. In embodiments, at least 20% of the total terminal olefinic double bonds in such high reactivity polyisobutenes can comprise an alkylvinylidene isomer. For example, at least 50%, and in other examples, at least 70%, of the total terminal olefinic double bonds can comprise an alkylvinylidene isomer. Suitable high reactivity polyisobutenes are disclosed, for example, in U.S. Pat. No. 4,152,499 and W. German Offenlegungsschrift 29 04 314, the disclosures of which are herein incorporated by reference in their entirety. In other embodiments, ethylene alpha-olefin copolymers having a number average molecular weight of 500 to 3000, wherein at least about 30% of the polymer's chains contain terminal ethylidene unsaturation, can be used to form the hydrocarbyl substituent.

[0015] In one embodiment the compound of formula (I) can be obtained by alkylating o-cresol with the high molecular weight hydrocarbyl polymers described above. For example, an o-cresol, such as ortho methyl phenol, can be reacted with polyisobutylene (PIS) to form an ortho methyl phenol substituted at the para position with a PIS group.

Suitable methods of alkylating the hydroxyaromatic compounds of the present disclosure are well known in the art. Examples of some suitable well known methods for forming hydroxyl substituted aromatic ring compounds are taught in GS 1,159,368 and U.S. Pat. Nos. 4,238,628; 5,300,701, 5,876,468, and 6,800,103, the disclosures of all of which are herein incorporated by reference in their entirety.

[0016] In one embodiment, R^1 of the hydroxyl substituted aromatic ring compound of formula I can be a C_{1-4} alkyl, R^2 can be a hydrogen radical, and R^3 can be a hydrocarbyl substituent chosen from the hydrocarbyl substituents described above. For example, R^1 can be methyl, R^2 can be a hydrogen radical, and R^3 can be a polyisobutylene group. In other embodiments, both R^1 and R^2 are hydrogen radicals, and R^3 is a hydrocarbyl substituent chosen from the hydrocarbyl substituents described above.

[0017] Amines which may be employed in the first stage of the reaction include any primary amines suitable for use in Mannich reactions for forming the bis-Mannich intermediate. In embodiments, the primary amine can have the formula (II):



where R^4 can be any substituent chosen from alkyl, aryl, alkenyl, alkyl amine, dialkyl amine, alkylaminoalkyl, and dialkylaminoalkyl groups.

[0018] Representative examples of suitable secondary amines include dimethylamine, diethylamine, dipropylamine, dibutylamine, and dipentylamine. Representative examples of suitable primary amines include cyclohexaneamine; 1,3-propanediamine; 1,2-ethane diamine; 1,4-butanediamine; 1,6-hexanediamine; 1,2-cyclohexanediamine; 1,2-diamino-3-methyl cyclohexane; 1,2-diamino-4-methyl cyclohexane; N-aminomethyl-1,1-methanediamine and 3,3-dimethyl amino propyl amine.

[0019] In some embodiments, the amine of formula (II) may be a hydrocarbon chain substituted at one end with a primary amino group, and substituted at the other end with a primary, secondary, or tertiary amino group. For example, R^4 of the compound of formula (II) can be $-C_{1-6}NR'R''$, where the C_{1-6} portion of the substituent is a straight or branched chain alkyl, and R' and R'' can be independently chosen from H, methyl, ethyl, propyl and butyl substituents. Examples of such compounds include dialkylaminoalkyl amines, such as dimethylaminopropyl amine, diethylaminopropyl amine, and

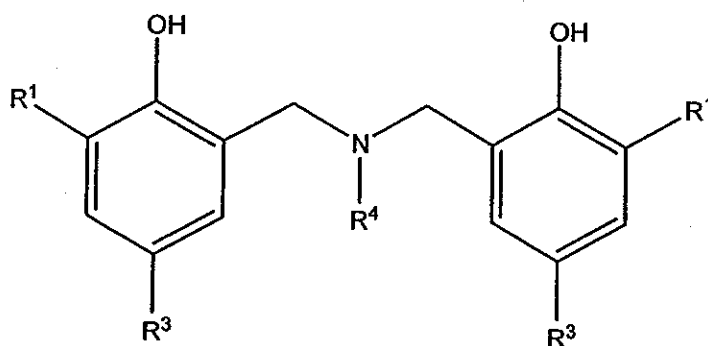
dimethylaminobutyl amine.

[0020] Any aldehydes suitable for use in a Mannich reaction can be employed in the preparation of the bis-Mannich intermediate. Non-limiting examples of suitable aldehydes include aliphatic aldehydes; such as formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, caproaldehyde, heptaldehyde, and stearaldehyde. Aromatic aldehydes which may be used include benzaldehyde and salicylaldehyde. Illustrative heterocyclic aldehydes for use herein are furfural and thiophene aldehyde, etc. Also useful are formaldehyde-producing reagents such as paraformaldehyde. In one embodiment, the chosen aldehyde is formaldehyde.

[0021] Any suitable proportions of the reactants that will result in formation of the bis-Mannich intermediate can be used. In one embodiment, the reactants can be mixed in a ratio of about: 1 mole of hydroxyl substituted aromatic ring compound; about 0.3 to about 0.7 moles of primary amine; and from about 0.8 to about 1.5 moles aldehyde. For example, the reactants can be mixed in a ratio of about: 1 mole of hydroxyl substituted aromatic ring compound; about 0.5 moles of primary amine; and about 1 mole aldehyde.

[0022] The condensation reaction among the hydroxyl substituted aromatic ring compounds, the primary amines and the aldehydes is conducted at a temperature in the range of about 40°C to about 200°C. The reaction can be conducted with or without a diluent or solvent. Examples of suitable solvents include aromatic solvents, such as xylenes, toluene, mesitylene, Aromatic 100, and heptane, or mixtures of such solvents. Water is evolved during the reaction and can be removed by azeotropic distillation during the-course of the reaction. Typical reaction times range from 2 to 4 hours, although longer or shorter times can be used as necessary.

[0023] The resulting bis-Mannich intermediate compound is a compound of formula (III):

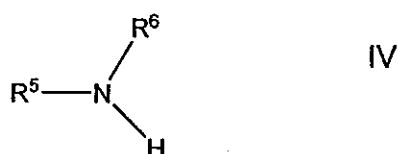


III

where R^1 , R^3 and R^4 are defined as above. As seen from formula (III), the bis-Mannich intermediate includes two hydroxyl substituted aromatic ring groups formed from the reactant compounds of formula (I) above, which are bridged together with a tertiary amine group. The bis-Mannich intermediate can be used to form the desired detergent base products in a second stage reaction, which will be described below.

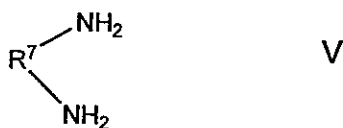
Formation of a Detergent Base from the Bis-Mannich Intermediate

[0024] In the second stage of the reaction process, the bis-Mannich intermediate of formula (III) can be reacted with a primary or secondary amine to form a desired detergent base product. The primary or secondary amine can be an amine of formula (IV):



wherein R^5 and R^6 are each independently chosen from a hydrogen radical, alkyl, cycloalkyl, aryl, alkaryl, and aralkyl groups, with the proviso that at least one of R^5 and R^6 is not a hydrogen radical. The alkyl, cycloalkyl, aryl, alkaryl, and aralkyl groups can be unsubstituted, or substituted with suitable functional groups, such as carbonyl groups, hydroxyl groups and amino groups. The alkyl, cycloalkyl, aryl, alkaryl, and aralkyl groups can have, for example, from 1 to 30 carbon atoms, such as from 1 to 18 carbon atoms, or in other examples, from 1 to 6 carbon atoms.

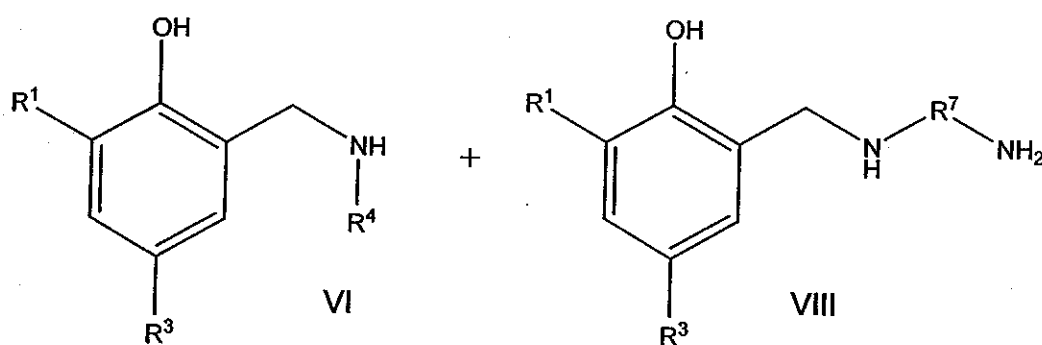
[0025] In some embodiments, R^6 is chosen to be a hydrogen radical, and R^5 is an alkyl group substituted with a primary amine. The resulting amine is a diamine of formula (V):



where R^7 is a linear, branched, or cyclic alkyl group having from 1 to 10 carbon atoms. For example, R^7 can be a saturated, straight chain hydrocarbon having 1 to 6 carbon atoms. In another embodiment, R^7 can be a substituted or unsubstituted cycloalkane having a 4 to 8 carbon member ring, which can optionally be substituted with one or more methyl, ethyl or propyl groups.

where R^1 , R^3 , R^4 , R^5 and R^6 are defined as set forth above. As seen from formulae (VI) and (VII), the reaction cleaves the bis-Mannich intermediate of Formula (III) to form two hydroxyl substituted aromatic ring compounds that are each substituted with an amine group, in addition to the R^1 , R^3 and hydroxyl substituents. Formula (VI) is substituted with an amine group formed from the primary amine reactant of the first stage of the reaction, while formula (VII) is substituted with an amine group formed from the primary or secondary amine reactant of the second stage of the reaction.

[0030] In an embodiment where a primary amine of formula (V) is used as the amine in the second stage, the products of the reaction include an amine substituted compound of formula (VI) as described above. However, in this embodiment, the product also comprises a primary amine substituent on one of the hydroxyl substituted aromatic ring compounds, as shown below in formula (VIII):



where R^1 , R^3 , R^4 and R^7 are defined as set forth above. The ratio of the compound of formula VI to the compound of formula VIII in the product mixture may vary depending on such things as reaction conditions and/or the reactants employed. For example, the ratio of the compound of formula VI to the compound of formula VIII may range from about 1:4 to about 4:1. In some embodiments, the ratio may be about 1:1.

[0031] The amine substituted products of the present application can be used as a detergent base in fuel compositions. In some embodiments, the detergent base can be used in fuel additive concentrates, which can be packaged and sold to consumers separately from the base fuel. The additive concentrates of this invention can contain, for example, from about 12 to about 69 wt %, and for example from about 22 to about 50 wt % of the detergent on an active ingredient basis. The additive concentrates may also contain carrier fluid, the level of which is determined by the desired carrier to detergent base ratio.

[0032] The carrier fluid can be of various types, such as for example liquid poly- α -olefin oligomers, liquid polyalkene hydrocarbons (e.g., polypropene, polybutene, polyisobutene, or the like), liquid hydrotreated polyalkene hydrocarbons (e.g., hydrotreated polypropene, hydrotreated polybutene, hydrotreated polyisobutene, or the like), mineral oils, hydrotreated mineral oils, liquid poly(oxyalkylene) compounds, liquid alcohols or polyols, liquid esters, and similar liquid carriers or solvents. Mixtures of two or more such carriers or solvents can be employed.

[0033] When formulating fuel compositions according to the present application, the detergent base and carrier fluid (with or without other additives) are employed in amounts sufficient to reduce or inhibit deposit formation in an internal combustion engine. Thus, the fuels can contain minor amounts of the detergent base and of the liquid carrier fluid proportioned as above that control or reduce formation of engine deposits, such as intake valve and injector deposits.

[0034] In some embodiments, the fuels of this disclosure can contain on an active ingredient basis, an amount of the Mannich base detergent in a range of about 5 to about 300 ptb (pounds by weight of additive per thousand barrels by volume of fuel), such as, for example, in the range of about 10 to about 200 ptb. The active ingredient basis excludes the weight of (i) unreacted components such as polyalkylene compounds associated and remaining in the product as produced and used, and (ii) diluents or solvents, if any, used in the manufacture of the detergent either during or after its formation, but before addition of a carrier, if a carrier is employed.

[0035] Other optional additives, such as one or more fuel-soluble antioxidants, demulsifying agents; antioxidants, such as hindered phenols and amines; rust or corrosion inhibitors, metal deactivators, combustion modifiers, alcohol cosolvents, octane improvers, emission reducers, friction modifiers, lubricity additives, ancillary

detergent/dispersant additives, markers, dyes and multifunctional additives (e.g., methylcyclopentadienyl manganese tricarbonyl and/or other cyclopentadienyl manganese tricarbonyl compounds) can also be included in the fuels and additive concentrates. These components can be present in the composition in any desired concentrations. For example, each component can be present in an amount at least sufficient for it to exert its intended function or functions in the finished fuel composition.

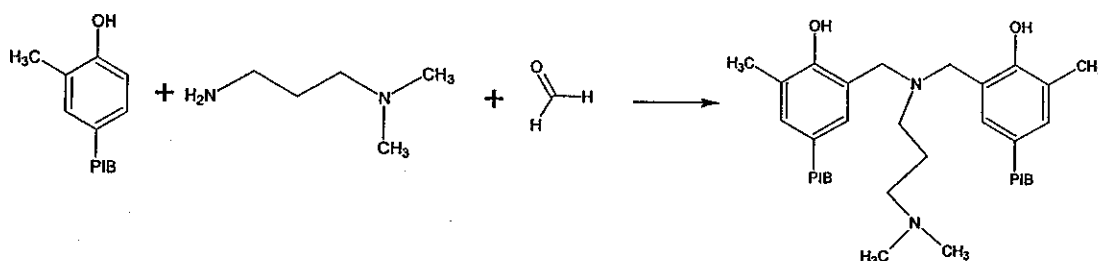
[0036] The base fuels used in formulating the fuels disclosed herein can be any and all base fuels suitable for use in the operation of spark ignition internal combustion engines, such as unleaded motor and aviation gasolines, and so-called reformulated gasolines which often contain both hydrocarbons of the gasoline boiling range and fuel-soluble oxygenated blending components ("oxygenates"). Examples of suitable oxygenates which may be used include alcohols, such as methanol and ethanol; fuel-soluble ethers, such as methyl tertiary butyl ether, ethyl tertiary butyl ether, and methyl tertiary amyl ether; and mixtures of such materials. Oxygenates, when used, can be present in the base fuel in any desired amount. Choosing an effective amount of oxygenates is within the ordinary skill of the art.

EXAMPLES

Example 1 - Process of Preparing the Intermediate

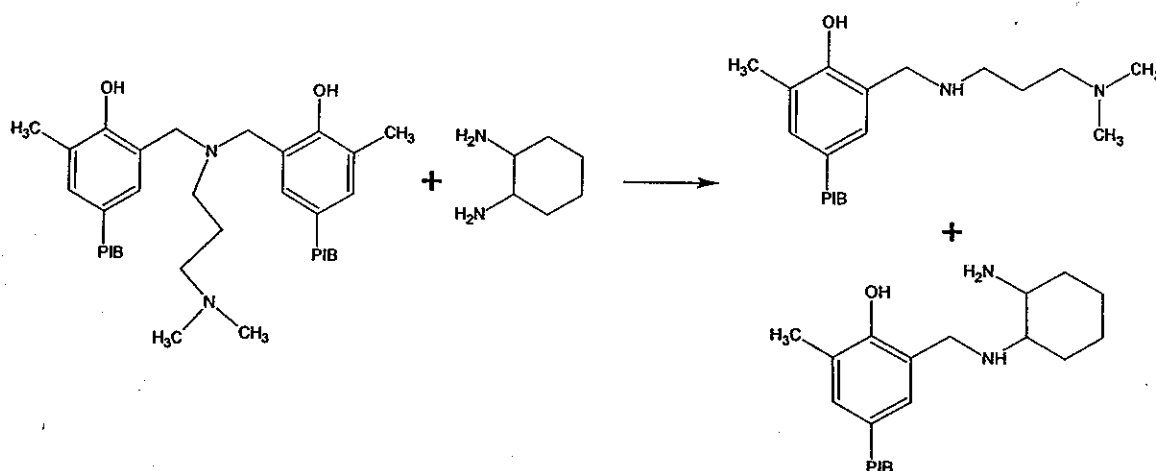
[0037] Exact quantities of the starting materials were pre-determined and calculated based upon a mole ratio of 2:1:2 of 2-methyl-4-polyisobutyl phenol, dimethylaminepropylamine (OMAPA), and formaldehyde, respectfully. The 2-methyl-4-polyisobutyl phenol was added to a round bottom flask, followed by the addition of approximately 75% of the total calculated amount of Aromatic 100 solvent to be used during the process. The mixture was stirred under a nitrogen blanket. Once the mixture was homogeneous, the calculated amount of DMAP A was added. The temperature of the mixture was about 40 to 45°C. Formaldehyde was added, and the temperature of the mixture increased to about 45 to 50°C. The mixture was heated and distilled under nitrogen using a Dean Stark trap set to 150°C. During distillation, the temperature of 150°C was maintained for about 2 to 2.5 hours. After distillation, sufficient Aromatic 100 solvent was added to the intermediate product to bring the final package composition to 25% solvent, taking into consideration the loss of water.

[0038] The above procedure theoretically resulted in the BIS product shown in the reaction below:



Example 2 - Process of Preparing the Final Product

[0039] Using the intermediate BIS product of Example 1 as a starting material, 1,2-diaminocyclohexane (DACH) was added at a 1:1 molar ratio while stirring at room temperature under a nitrogen blanket. The temperature was set to 90°C and held for 2 hours. The temperature was then set to 145°C with increased nitrogen flow and held for 2.5 hours. The process theoretically resulted in the following reaction.



Example 3

[0040] Gasoline fuel compositions employing the final product of Example 2 were subjected to engine tests whereby the substantial effectiveness of these compositions in reducing intake valve deposit weight was demonstrated. The above reaction products of

Example 2 were compared with several other detergent compounds, including a first comparative compound formed by a mannich reaction of a 1:1:1 mole ratio of 2-methyl-4-polyisobutyl phenol, dibutylamine, and formaldehyde ("Mannich 1 additive"); a second comparative compound formed by a mannich reaction of a 1:1:1 mole ratio of 2-methyl-4-polyisobutyl phenol, DMAPA, and formaldehyde ("Mannich 2 additive"); and a third comparative compound that was a PIS Amine. The compounds of example 2 and the comparative compounds were each blended with a base fuel to form fuel compositions that are referred to in Table 1 and Table 2 by the additive compound employed (Example 2 Compounds, Mannich 1, Mannich 2, and PIS Amine).

[0041] A first comparative IVD Engine test of the compounds of Example 1, Mannich 1, Mannich 2 and the base fuel without additive was run using a Ford 2.3-liter engine operated on a test stand under standard operating conditions for determination of deposit formation on intake valves. The results are reported in Table 1 below.

TASLE 1- 2.3L IVD Engine Test Results

<u>Example Composition</u>	<u>IVD (mg)</u>
Fuel Without Additive	478-527 mg
Mannich 1	53-56 mg
Mannich 2	67.9 mg
Example 2 Compound	64.6

Example 4

[0042] A second comparative IVD Engine test of the compounds of Example 2, Mannich 1, Mannich 2, PIB Amine and the base fuel without additive was run using an IVO Bench Simulator (Model L-2), which can be used to test gasoline detergent IVO performance. The test simulates the IVD deposition in an engine. During the test, the fuel compositions with detergent additives were run through an injector. A separate air flow was run through an air flow line to the injector. The air flow and gasoline flow were mixed at the tip of the injector, and the mixture was directed against a heated metal plate. Plate temperatures were controlled at around 174°C. Gasoline evaporated on the surface of the hot plate, leaving a deposit and stain behind.

[0043] At the end of the IVD Bench Simulator test, the deposit on the metal plate was weighted. The results are reported in Table 2 below.

TABLE 2~ IVO Bench Test From China

<u>Example Composition Fuel</u>	<u>IVD (mg)</u>
Without Additive	14 - 15 mg
Comparative Example 1	7.7mg
Comparative Example 2	1.3 mg
Example 2	1.0
PIB Amine	1.4 mg

[0044] It is clear, upon examination of the above Tables 1 and 2, that the reaction products of Example 2 exhibit improved performance over the base fuel without additive, and comparable performance to the additives of Comparative Examples 1 and 2, as demonstrated by the reduced amount of deposits in the Ford 2.3L Test. In addition, the reaction product of Example 2 exhibits improved performance over the base fuel without additive and the additives of Comparative Examples 1 and 2, as demonstrated by the reduced amount of deposits in the IVD Bench Test From China.

[0045] For the purposes of this specification and appended claims, unless otherwise indicated, all numbers expressing quantities, percentages or proportions, and other numerical values used in the specification and claims, are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by the present disclosure. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0046] It is noted that, as used in this specification and the appended claims, the singular forms "a," "an," and "the," include plural referents unless expressly and unequivocally limited to one referent. Thus, for example, reference to "an acid" includes two or more different acids. As used herein, the term "include" and its grammatical variants are intended to be non-limiting, such that recitation of items in a list is not to the exclusion of other like items that can be substituted or added to the listed items.

[0047] While particular embodiments have been described, alternatives, modifications, variations, improvements, and substantial equivalents that are or can be presently unforeseen can arise to applicants or others skilled in the art. Accordingly, the appended claims as filed and as they can be amended are intended to embrace all such alternatives, modifications variations, improvements, and substantial equivalents.

WHAT IS CLAIMED IS:

1. A process for forming a detergent base product, the process comprising:

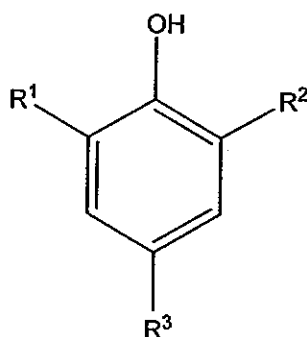
forming a bis-Mannich intermediate compound by reacting (i) at least one hydroxyl substituted aromatic ring compound having on the ring an aliphatic hydrocarbyl substituent derived from a polyolefin having a number average molecular weight of about 500 to about 3000;

(ii) at least one primary amine; and

(iii) at least one aldehyde; and

reacting the bis-Mannich intermediate compound with at least one second amine compound chosen from primary and secondary amines to form the detergent base product.

2. The process of claim 1, wherein at least one hydroxyl substituted aromatic ring compound has a formula I,



where R^1 , R^2 and R^3 are substituents independently chosen from a hydrogen radical, C_{1-6} alkyls and hydrocarbyl substituents having a number average molecular weight in the range of about 500 to about 3000, with the proviso that at least one of R^1 , R^2 and R^3 is a hydrocarbyl substituent.

3. The process of claim 2, wherein one of R^1 , R^2 and R^3 is a C_{1-6} alkyl chosen from methyl, ethyl, propyl, isopropyl, butyl, and isobutyl.

4. The process of claim 2, wherein the hydrocarbyl substituent is a group chosen from polypropylene groups, polybutylene groups, polyalphaolefin groups, and ethylene/alpha-olefin copolymer groups.

5. The process of claim 2, wherein the hydrocarbyl substituent is a copolymer group having at least one monomer chosen from butylene, isobutylene, and propylene, and at least one monomer chosen from mono-olefinic comonomers.

6. The process of claim 2, wherein the hydrocarbyl substituent is a polyisobutylene group.

7. The process of claim 2, wherein R^1 is methyl, R^2 is a hydrogen radical and R^3 is a polyisobutylene group.

8. The process of claim 1, wherein the at least one primary amine is a compound of formula (II),



where R^4 is a substituent chosen from alkyl, aryl, alkenyl, alkyl amino, dialkyl amino, alkylaminoalkyl, and dialkylaminoalkyl groups.

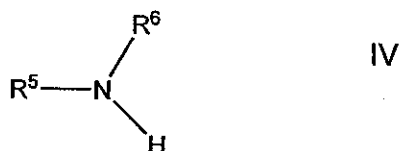
9. The process of claim 8, wherein R^4 is a $-C_{1-6}NR'R''$ group, where the C_{1-6} portion of the group is a straight or branched chain alkyl, and R' and R'' are independently chosen from hydrogen radicals, methyl, ethyl, propyl and butyl groups.

10. The process of claim 1, wherein at least one primary amine is chosen from dimethylaminopropyl amine, diethylaminopropyl amine, and dimethylaminobutyl amine.

11. The process of claim 1, wherein the at least one aldehyde is chosen from formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, caproaldehyde, heptaldehyde, stearaldehyde, benzaldehyde, salicylaldehyde, furfural aldehyde, thiophene aldehyde, and paraformaldehyde.

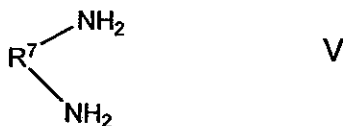
12. The process of claim 1, wherein at least one hydroxyl substituted aromatic ring compound, the at least one primary amine and the at least one aldehyde are mixed in a ratio of about 1 mole of hydroxyl substituted aromatic ring compound; about 0.3 to about 0.7 moles of primary amine; and from about 0.8 to about 1.5 moles aldehyde.

13. The process of claim 1, wherein at least one second amine is a compound of formula (IV),



wherein R^5 and R^6 are each independently chosen from a hydrogen radical, alkyl, cycloalkyl, aryl, alkaryl, and aralkyl groups, with the proviso that at least one of R^5 and R^6 is not a hydrogen radical.

14. The process of claim 1, wherein at least one second amine is a compound of formula (V):



where R^7 is a linear, branched, or cyclic alkyl group having from 1 to 10 carbon atoms.

15. The process of claim 14, where R^7 is a saturated, straight chain hydrocarbon having 1 to 6 carbon atoms.

16. The process of claim 14, where R^7 is a substituted or unsubstituted cycloalkane having a 4 to 8 carbon member ring that is optionally substituted with one or more methyl, ethyl or propyl groups.

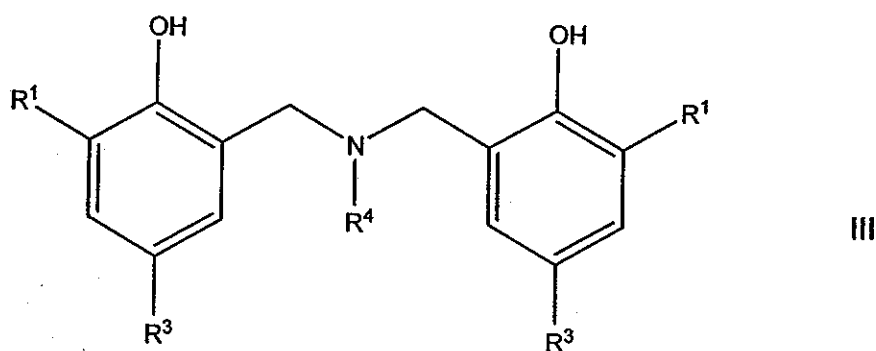
17. The process of claim 1, wherein the at least one second amine is chosen from dimethylamine, diethylamine, dipropylamine, dibutylamine, and dipentylamine.

18. The process of claim 1, wherein the at least one second amine is chosen from cyclohexaneamine; 1,3-propanediamine; 1,2 ethane diamine; 1,4-butanediamine; 1,6-hexanediamine; 1,2-diaminocyclohexane; 1,2-amino-3 methyl cyclohexane; 1,2 amino 4 methyl cyclohexane; N-methylamine methanediamine and 3,3 dimethyl amino propyl amine.

19. A detergent base product formed by the method of claim 1.

20. A process for forming a Mannich reaction product, the process comprising:

reacting at least one amine compound chosen from primary and secondary amines with a bis-Mannich compound having a formula III,



where R^1 is chosen from a hydrogen radical and C_{1-6} alkyl;

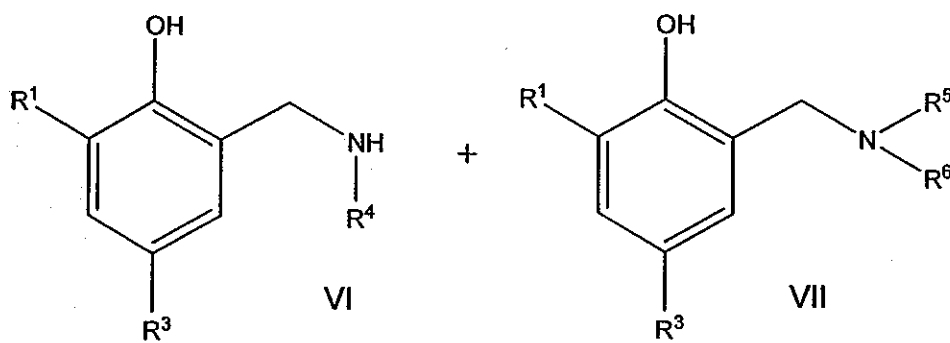
R^3 is a hydroxyaromatic compound having on the ring an aliphatic hydrocarbyl substituent derived from a polyolefin having a number average molecular weight of about 5pO to about 3000; and

R^4 is a linear, branched, or cyclic, substituted or unsubstituted, saturated or unsaturated alkyl amine group.

21. A fuel composition comprising:

a base fuel; and

a detergent base product comprising a mixture of formulae (VI) and (VII),



where R^1 and R^3 are substituents independently chosen from a hydrogen radical, C_{1-6} alkyls and hydrocarbyl substituents having a number average molecular weight in the range of about 500 to about 3000, with the proviso that at least one of R^1 and R^3 is a hydrocarbyl substituent, R^4 is a substituent chosen from alkyl, aryl, alkenyl, alkyl amino, dialkyl amino, alkylaminoalkyl, and dialkylaminoalkyl groups, R^5 and R^6 are each independently chosen from a hydrogen radical, alkyl, cycloalkyl, aryl, alkaryl, and aralkyl groups, with the proviso that at least one of R^5 and R^6 is not a hydrogen radical.