

# **PARTICULATE REDUCTION IN GDI ENGINES USING MANNICH DETERGENTS**

## **CROSS-REFERENCE TO RELATED APPLICATION**

**[0001]** The present disclosure claims priority under 35 U.S.C § 119 to US Provisional Application No 63/658,076 filed on June 10, 2024, which is incorporated herein by reference in its entirety.

## **TECHNICAL FIELD**

**[0002]** The present disclosure relates to compositions and methods for emission particulate reductions in gasoline direct injection (GDI) engines using select Mannich detergents.

## **BACKGROUND**

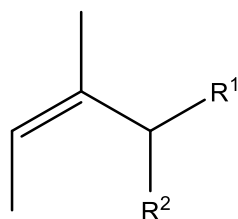
**[0003]** Gasoline direct injection (GDI) engines tend to produce higher levels of particulate emission when compared to port fuel injection (PFI) engines.

## **SUMMARY**

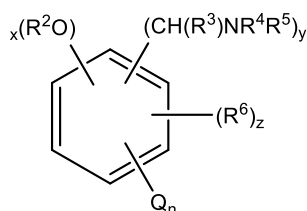
**[0004]** In one approach or embodiment, a method of reducing particulate emission in a gasoline direct injection engine is described herein. In one aspect of this embodiment, the method includes: combusting in the engine a gasoline composition including a Mannich detergent as an additive, wherein the Mannich detergent is produced by the reaction of hydrocarbyl-substituted phenol, an amine, and formaldehyde at a molar ratio of 1 : 1-2 : 2-3, and wherein the Mannich detergent is present in the gasoline composition at a concentration of about 40 to about 100 ppm.

**[0005]** In other approaches or embodiments, the method of the previous paragraph may be combined with one or more other features, steps, or embodiments in any combination. These other features, steps, or embodiments include one or more of the following: the molar ratio of the hydrocarbyl-substituted phenol, amine, and formaldehyde is 1 : 1-2 : 2; and/or wherein the molar ratio of the hydrocarbyl-substituted phenol, amine, and formaldehyde is 1 : 2 : 2; and/or wherein the hydrocarbyl substituent is derived from polyisobutylene and wherein at least 50 mol percent of polyisobutylene macromolecules have a tri-substituted alkene group, or wherein the hydrocarbyl substituent is derived from polyisobutylene and wherein at least 50 mol percent of polyisobutylene macromolecules have a tri-substituted

alkene group and a tetra-substituted alkene group; and/or wherein the polyisobutylene having a tri-substituted alkene group has the following stereochemistry:

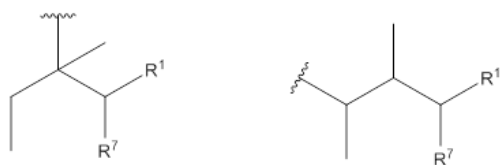


Wherein  $R^1$  is a polymer chain and  $R^2$  is -H or -CH<sub>3</sub>; and/or wherein the polyisobutylene has less than 50 mol percent of terminal double bonds; and/or wherein the polyisobutylene includes one or more of a  $\beta$ -olefin isomer structure, a  $\beta$ -olefin structure, or a tetra-substituted olefin structure; and/or wherein the Mannich detergent is an oligomer; and/or wherein the hydrocarbyl substituent is derived from polyisobutylene having a number average molecular weight of about 400 to about 1500; and/or wherein at least 50 mol percent of polyisobutylene macromolecules have a tri-substituted alkene group, or wherein the hydrocarbyl substituent is derived from polyisobutylene and wherein at least 50 mol percent of polyisobutylene macromolecules have a tri-substituted alkene group and a tetra-substituted alkene group; and/or wherein the Mannich detergent is a compound having a structure of Formula I:

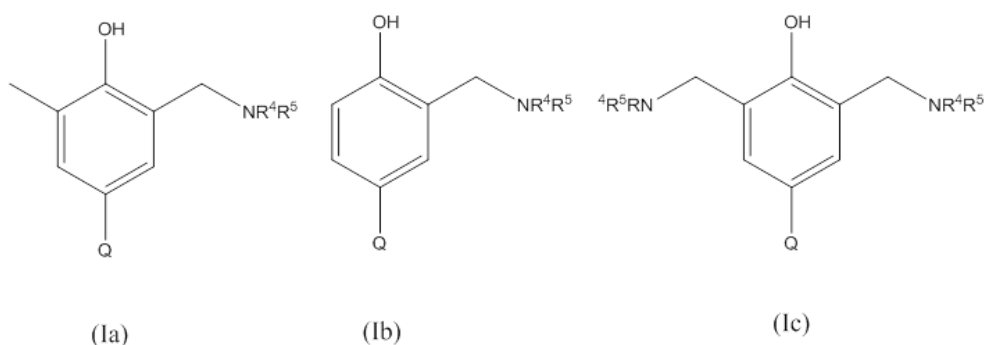


(Formula I)

Wherein each  $R^2$  is independently H or, together with the  $R^4$  or  $R^5$  moiety in an adjacent  $-\text{CH}(\text{R}^3)\text{NR}^4\text{R}^5$  group, is a divalent  $-\text{CH}(\text{R}^3)-$  group;  $x$  is an integer of 1, 2 or 3; each  $R^3$  is independently H or hydrocarbyl comprising 1 to 10 carbon atoms; each  $R^4$  and  $R^5$  is independently H, hydrocarbyl comprising 1 to 3000 carbon atoms which may be interrupted by one or more O, S and/or  $\text{NR}^3$  moieties, or together with  $R^2$  forms a divalent  $-\text{CH}(\text{R}^3)-$  group as defined above;  $y$  is an integer of 1, 2 or 3; each  $R^6$  is independently hydrocarbyl comprising 1 to 3000 carbon atoms which may be interrupted by one or more O, S and/or  $\text{NR}^3$  moieties;  $z$  is an integer of 0, 1 or 2;  $n$  is an integer of 1, 2 or 3; and  $Q$  is the hydrocarbyl substituent; and/or wherein, in at least 50 % of the compounds of formula (I), said  $Q$  group is bonded to the central benzene ring such that it has the structure:



Wherein  $R^1$  is a polymer chain, and together with the moiety  $-\text{CH}_2-\text{C}(\text{CH}_3)(\text{CH}_2\text{CH}_3)-$  through which it is attached to the central benzene ring, represents the Q group; and  $R^7$  is  $-\text{H}$  or  $-\text{CH}_3$ ; and/or wherein (1) any Q groups are para to an  $-\text{OR}^2$  group, (2) any  $-\text{CH}(\text{R}^3)\text{NR}^4\text{R}^5$  groups are ortho to at least one  $-\text{OR}^2$  group, and/or (3)  $-\text{R}^6$  (if present) is ortho to at least one  $-\text{OR}^2$  group; and/or wherein the hydrocarbyl substituent Q is derived from polyisobutylene and wherein at least 50 mol percent of polyisobutylene macromolecules have a tri-substituted alkene group, or wherein the hydrocarbyl substituent Q is derived from polyisobutylene and wherein at least 50 mol percent of polyisobutylene macromolecules have a tri-substituted alkene group and a tetra-substituted alkene group; and/or wherein the Mannich detergent is a compound having a structure of Formula (Ia), (Ib), and/or (Ic):



wherein the  $-\text{NR}^4\text{R}^5$  group of Formula (Ia), (Ib), and/or (Ic) is  $-\text{NH}(\text{CH}_2)_3\text{N}(\text{CH}_3)_2$ ; and/or wherein the hydrocarbyl substituent Q is derived from polyisobutylene and wherein at least 50 mol percent of polyisobutylene macromolecules have a tri-substituted alkene group, or wherein the hydrocarbyl substituent is derived from polyisobutylene and wherein at least 50 mol percent of polyisobutylene macromolecules have a tri-substituted alkene group and a tetra-substituted alkene group; and/or wherein the amine is an alkylene polyamine; and/or wherein the alkylene polyamine is ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, or mixtures of alkylene polyamines of the formula  $\text{H}_2\text{N}-(\text{A}-\text{NH})_n\text{H}$  where A is divalent ethylene or propylene and n is an integer of from 1 to 10.

**[0006]** In yet another approach or embodiment, the use of any embodiment of this Summary is provided to provide improved particulate emissions reduction in GDI engines. In aspect, the use provides combusting in an engine a gasoline composition including a Mannich detergent as an additive, wherein the Mannich detergent is produced by the

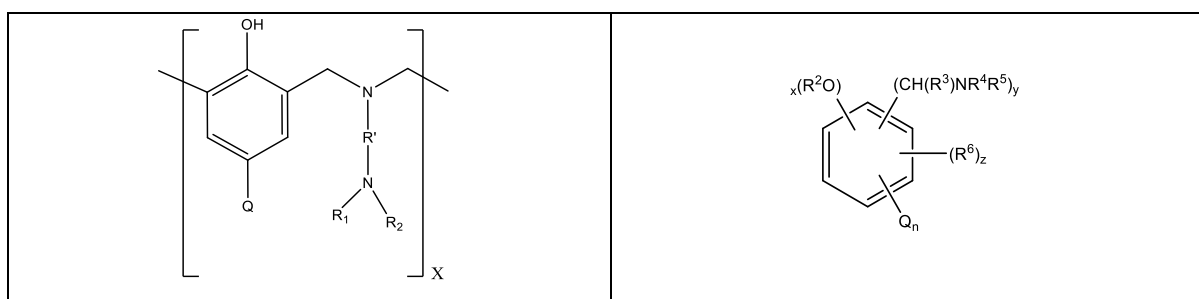
reaction of hydrocarbyl-substituted phenol, an amine, and formaldehyde at a molar ratio of 1 : 1-2 : 2-3, and wherein the Mannich detergent is present in the gasoline composition at a concentration of about 40 to about 100 ppm to provide improved particulate emissions.

### DETAILED DESCRIPTION

**[0007]** The present disclosure relates to fuel additive packages, fuels, and methods of achieving emission particulate reductions in gasoline direct injection (GDI) engines using select Mannich detergents (e.g., reaction products of a hydrocarbyl-substituted hydroxyaromatic compound, an aldehyde, and an amine). In one approach or embodiment, the select Mannich detergents herein for emissions particulate reductions include one or more of the following characteristics: (i) certain molar ratios of the hydroxyaromatic compound, the amine, and the aldehyde; (ii) select oligomer structures; and/or (iii) certain isomeric forms of polyisobutylene substituents on the hydroxyaromatic compound.

**[0008]** For instance and in one approach, the select Mannich detergent(s) of the fuel additive packages, fuels, and methods herein for improved particulate emissions reduction in GDI engines include (i) a molar ratio of the hydrocarbyl-substituted hydroxyaromatic compound (e.g., a hydrocarbyl-substituted phenol) to amine (e.g., dimethylamino propylamine) to formaldehyde of 1 : 0.9-2.0 : 1.5-3.0 and, more preferably, 1 : 1-2 : 2-3, and even more preferably, 1 : 1-2 : 2, and most preferably, 1 : 2 : 2.

**[0009]** In other approaches or embodiments, the select Mannich detergent(s) of the fuel additive packages, fuels, and methods herein for improved particulate emissions reductions in GDI engines include (ii) one or more compounds or oligomers having structures defined by the below formulas, which are defined further herein:



**[00010]** In yet other approaches or embodiments, the select Mannich detergent(s) of the fuel additive packages, fuels, and methods herein for particulate emissions reductions includes (iii) certain isomeric forms of a polyisobutylene (PIB) substituent of the hydroxyaromatic group in which, in one approach, at least 50 mol% of the PIB

macromolecules have a tri-substituted alkene group (e.g., a so-called conventional PIB). In another approach, the selected Mannich detergent of the compositions, fuels, or methods herein includes a Mannich reactant product having a isomeric forms of the polyisobutylene (PIB) substituent of the hydroxyaromatic comprising both (a) PIB macromolecules having a tri-substituted alkene group and (b) PIB macromolecules having a tetra-substituted alkene group, wherein the proportion of PIB macromolecules having both a tri-substituted and a tetra-substituted alkene group is at least 50 mol%, and wherein the Mannich reactant product and PIB substituent are subjected to conditions under which PIB macromolecules having a tetra-substituted alkene group will react to produce PIB macromolecules having a tri-substituted alkene group. Such PIB groups are referred to as conventional PIB, and Conventional PIB typically has less than 50 mol%, less than 40 mol%, less than 30 mol%, less than 20 mol%, or less than 10 mol% content of terminal double bonds.

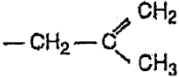
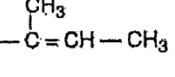
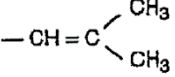
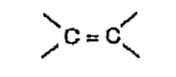
**[00011]** In yet alternative approaches, the isomeric forms of the polyisobutylene (PIB) substituent may have greater than 50 mol%, greater than 60 mol%, greater than 70 mol%, greater than 80 mol%, or greater than 90 mol% content of terminal double bonds. In such form, this alternative PIB substituent is referred to as highly reactive PIB (e.g., “HR-PIB”). HR-PIB having a number average molecular weight ranging from about 800 to about 5000, as determined by GPC, may be suitable for use in embodiments of the present disclosure. Such HR-PIB is commercially available, or can be synthesized by the polymerization of isobutene in the presence of a non-chlorinated catalyst such as boron trifluoride, as described in US 4,152,499 and/or US 5,739,355. When used in the aforementioned thermal ene reaction, HR-PIB may lead to higher conversion rates in the reaction, as well as lower amounts of sediment formation, due to increased reactivity. A suitable method is described in U.S. Patent No. 7,897,696.

**[00012]** In embodiments, a particular type of PIB has been developed for use in preparing lubricant and gasoline additives, namely PIB having an increased proportion of macromolecules in which the double bond is located at the end of the chain, to make the PIB more reactive. This can be achieved by using pure isobutene feedstock and a catalyst based on BF<sub>3</sub>, as reported by Mach et al (Lubrication Science 11-2, Feb 1999 (11) pp 175-185). More recently, it has also been achieved using AlCl<sub>3</sub> in a form of complex with ether (Kostjuk et al, Journal of Polymer Science, Part A: Polymer Chemistry 2013, 51, 471-486).

**[00013]** The structural differences between the more reactive HR-PIB and the conventional PIB substituents herein, and the implications for reactivity, are summarised in

by the following terms and shown in the chart below (Mach et al (Lubrication Science 11-2, Feb 1999 (11) pp 175-185)):

**Reactivity of PIB**

|                         | <i>α-Olefin</i>                                                                   | <i>β-Olefin isomer</i>                                                             | <i>β-Olefin</i>                                                                    | <i>Tetra-substituted olefin</i>                                                     |
|-------------------------|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
| Structure               |  |   |  |  |
| Reactivity              | high                                                                              |  |                                                                                    | low                                                                                 |
| Highly reactive PIB (%) | 85                                                                                | 1                                                                                  | 10                                                                                 | 2.5                                                                                 |
| Conventional PIB (%)    | 10                                                                                | 40                                                                                 | 2                                                                                  | 15                                                                                  |

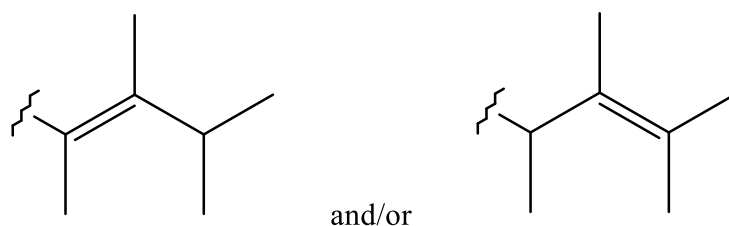
**[00014]** The structures indicated above are referred to herein using the following nomenclature:

| Structure in Table above: | Structure referred to herein as: |
|---------------------------|----------------------------------|
| <i>α-Olefin</i>           | Exo                              |
| <i>β-Olefin isomer</i>    | Tri                              |
| <i>β-Olefin</i>           | Endo                             |
| Tetra-substituted olefin  | Tetra                            |

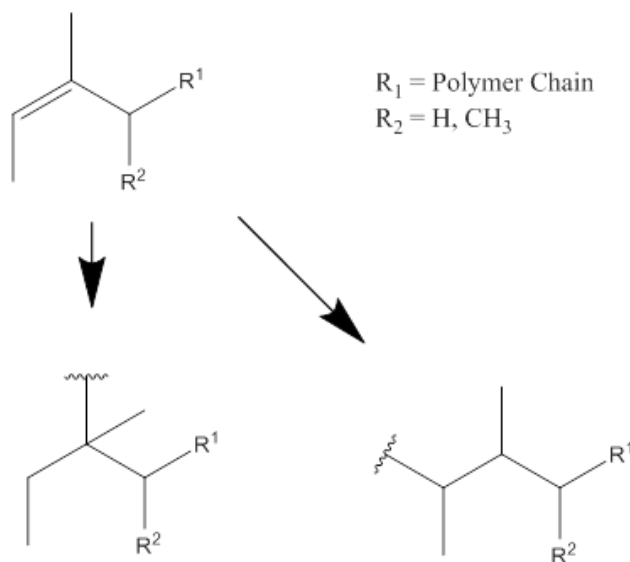
**[00015]** PIBs containing a high proportion of exo groups (i.e. vinylidene end groups) are generally referred to as high reactive PIB (e.g., HR-PIB). On the other hand, PIBs containing a high proportion of tri, endo, and tetra groups are generally referred to as conventional PIB. In one approach, the select Mannich detergents herein may include a high proportion of conventional PIB-based Mannich reaction products. In alternative approaches, the select Mannich detergents herein may include a high proportion of HR-PIB-based Mannich reaction products.

**[00016]** Such PIB macromolecules are produced with select conditions, and said conditions comprise contacting the Mannich reactants and the PIB substituent with a source of protons, such as BF<sub>3</sub>/HF. When using the approach with conventional PIB macromolecules, the PIB substituent is preferably one in which at least 60 mol% of the PIB macromolecules have a tetra-substituted alkene group, more preferably at least 70 mol%, more preferably still at least 80 mol%, and yet more preferably at least 90 mol%. Preferably, the tetra substituted alkene groups in the PIB macromolecules are located within or attached to a terminal C4 unit in the macromolecule. More preferably the PIB

macromolecules suitable for the detergent compositions, fuels, and particulate emission reduction methods of the present disclosure are of the structure:



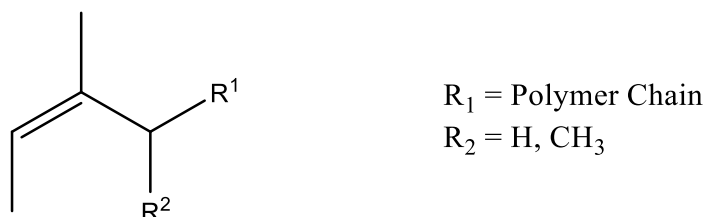
**[00017]** A preferred example of a Mannich detergent of the compositions, fuels, and methods herein is a product obtained or obtainable from a Mannich reaction between an aldehyde, an amine, and a select PIB-substituted hydroxyaromatic compound that has been prepared as described herein and having the noted PIB macromolecules. Such a PIB-substituted hydroxyaromatic reagent has been found to be enriched in compounds wherein the PIB substituent is bonded to the aromatic ring in the following manner:



**[00018]** Thus, the present disclosure provides a detergent obtained or obtainable from a Mannich reaction between the aldehyde, the amine, and the selected PIB-hydroxyaromatic compound wherein at least 70 mol% (such as at least 75 mol%, at least 80 mol%, at least 85 mol%, at least 90 mol% or at least 95 mol%) of the molecules has the structure depicted above.

**[00019]** In other approaches, the improved particulate emissions reductions of the Mannich detergents herein can be obtained using conventional PIB substituents prepared as follows and wherein the improved efficacy can be achieved by increasing the proportion of tri-PIB, i.e. the proportion of PIB wherein the alkene moiety appears at the end of the

molecule and has the structure  $-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CHCH}_3$ . Typically in this regard the tri group will have the following stereochemistry:



**[00020]** To prepare such a detergent having improved efficacy, PIB that is enriched in tri-PIB can be reacted with a reagent serving as a source of a group comprising a polar moiety, under conditions appropriate for the PIB to react with said reagent so as to form a compound in which the PIB is bonded to the group comprising a polar moiety.

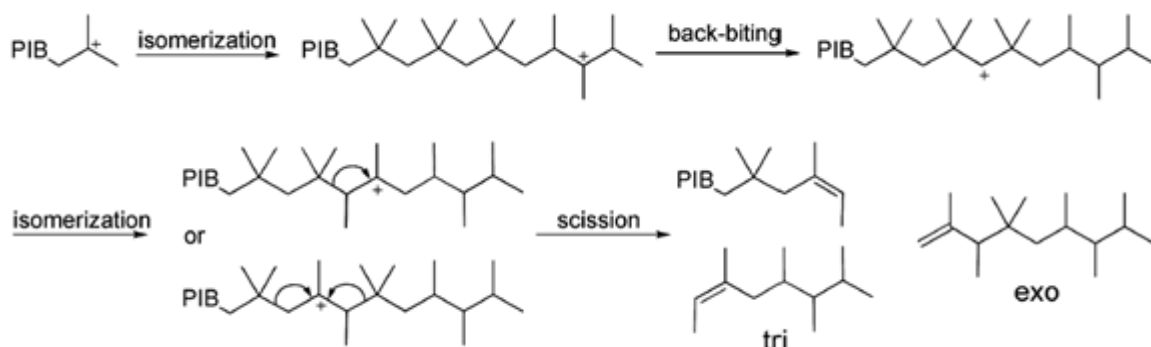
**[00021]** As for the PIB that is enriched in tri-PIB, this can be prepared directly. For instance, polymerisation of isobutylene in hexane with an initiator such as  $\text{H}_2\text{O}$ ,  $\text{MeOH}$ ,  $\text{tBuCl}$ ,  $\text{TMPCl}$  (2-chloro-2,4,4-trimethyl-pentane) or  $\text{CumCl}$  (cumyl chloride), in conjunction with EADC ( $\text{EtAlCl}_2$ ) in the temperature range of  $-40$  to  $25^\circ\text{C}$  can be used to prepare a PIB product having around 70 % tri-PIB and around 30 % tetra-PIB, with negligible exo- and endo-PIB. (Dimitrov et al., (Macromolecules 2011, 44, 1831-40). Alternatively, PIB that is enriched in to some extent in tri-PIB can be prepared from conventional PIB or HR PIB, e.g. by exposing the PIB sample to a Lewis acid or Bronsted-Lowry (protic) acid.

**[00022]** In relation to both of these approaches, though, it is noteworthy that due to the preference in the art to use HR PIB (with its high levels of exo-PIB), as a general rule the preparation of PIB enriched in tri-PIB is specifically avoided, particularly when the PIB is envisaged for use in preparing a detergent additive. The consequential loss of exo-PIB is seen as undesirable.

**[00023]** In situations where PIB contains both tri-PIB and tetra-PIB, the effective proportion of tri-PIB can be increased by reacting the PIB with said reagent having a group comprising a polar moiety under conditions in which the tetra-PIB will react to produce tri-PIB. This enhances the effective proportion of tri-PIB in situ. Thus, tri-PIB can be formed readily from tetra-PIB under suitable conditions, e.g. in the presence of a source of protons. A mechanism for this process, following cation formation, has been described by Dimitrov et al. (Macromolecules 2011, 44, 1831-1840). That reaction pathway has been summarised by Kostjuk et al. (citation details noted above) in the scheme reproduced below, in

connection with the formation of tri-substituted olefinic end groups during the EtAlCl<sub>2</sub>(AlCl<sub>3</sub>)-co-initiated cationic polymerisation of PIB.

**Scheme 1**



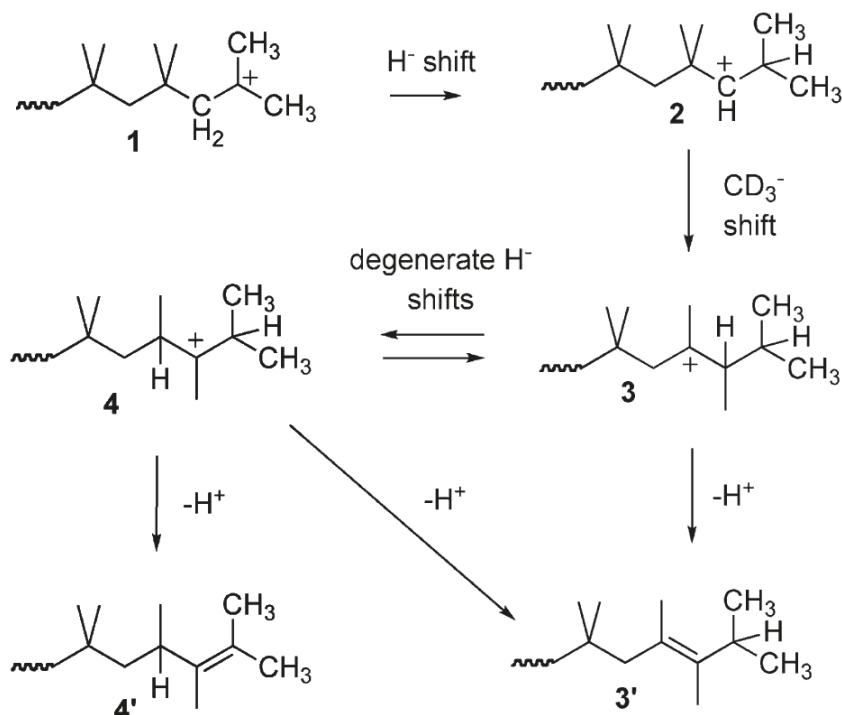
**[00024]** In this regard, the present invention also relates to a method of preparing PIB that is highly enriched with tetra-PIB. Such a highly enriched PIB can advantageously be used as a precursor for PIB that is highly enriched in other isomeric forms.

**[00025]** For instance, PIB that is highly enriched in tetra-PIB can be used to prepare a PIB reagent that is highly enriched in tri-PIB, or (if different conditions are used) a PIB reagent that is highly enriched in exo-PIB. Alternatively, PIB that is highly enriched with tetra-PIB can be used to form tri-PIB in situ during the preparation of a detergent product. In this regard, the fact that the tetra-PIB can be efficiently reacted to produce other types of PIB in this way means that the high levels of tetra-PIB enrichment possible in accordance with the present invention can effectively be transferred to provide similar levels of tri- and exo-PIB enrichment.

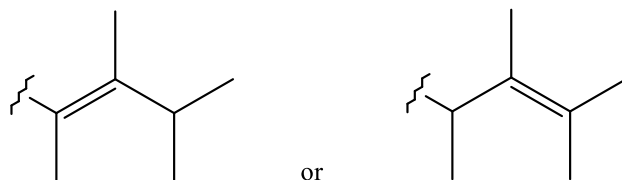
**[00026]** PIB that is highly enriched with tetra-PIB can be prepared by subjecting a sample of PIB containing a high proportion of exo- and endo-PIB (such as a typical HR PIB) to double bond isomerisation in circumstances in which the back-biting step depicted in Scheme 1 above is inhibited. For instance, the PIB sample can be subjected to double bond isomerisation in a molecular sieve, wherein the molecular sieve limits the extent to which the macromolecules can adopt the conformation that is needed in order for this intramolecular cyclic reaction to occur.

**[00027]** As regards the mechanism for the formation of tetra-PIB in this regard, Dimitrov et al. (citation details noted above) have proposed the reaction pathway set out below. In this regard, the isomer labelled 4' in the scheme below (i.e. one of the two tetra-PIB isomers) was reported to be most preferred.

**Scheme 2**

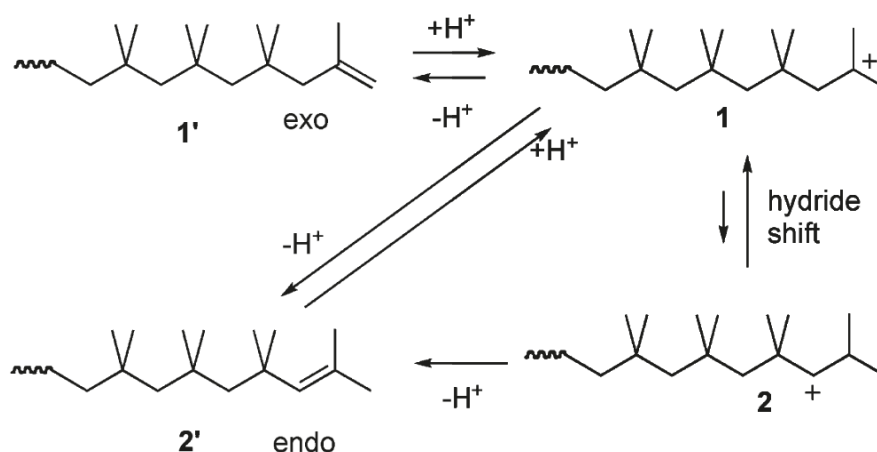


**[00028]** In line with the scheme set out above, in the PIB that is enriched with tetra-PIB (and optionally also enriched with tri-PIB, as discussed above), the alkene group having the tetra structure in tetra-PIB should be located within or attached to a terminal C4 unit in the macromolecule, and typically has one of the two structures noted below, with the second structure usually being more preferred:



**[00029]** Also, for completeness it is to be noted that cation 1 in scheme 2 can be formed from both exo- and endo-PIB. This is illustrated by the following further reaction scheme:

**Scheme 3**



**[00030]** As explained above, PIB that is highly enriched in tetra-PIB can advantageously be used, inter alia:

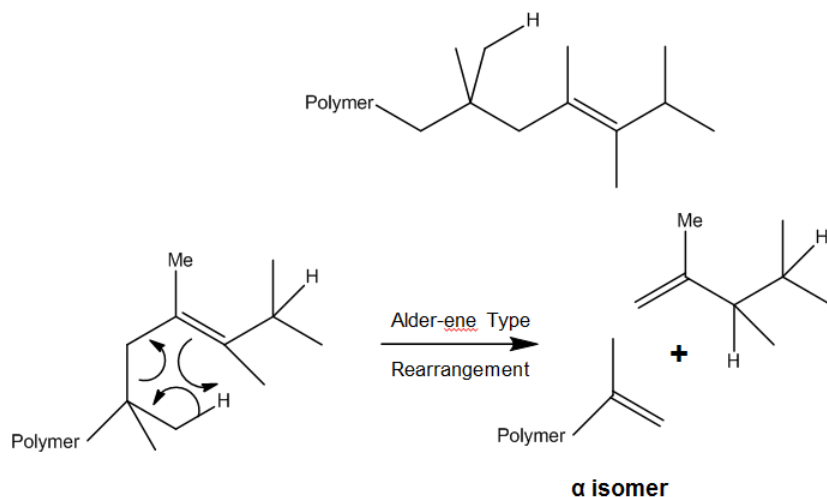
- (1) to prepare a PIB reagent that is highly enriched in tri-PIB,
- (2) to prepare a PIB reagent that is highly enriched in exo-PIB, or
- (3) to generate high levels of tri-PIB in situ, during the formation of a detergent compound.

**[00031]** In case (3), the PIB that is highly enriched in tetra-PIB can be combined with a reagent having a group comprising a polar moiety under conditions where back-biting (see Scheme 1 above) can arise and indeed is promoted (e.g. protic conditions), thus favouring the production of tri-PIB. The more reactive tri-PIB reacts preferentially with said reagent, so as to form detergent compounds having a structure which, as discussed above, imparts altered thermal stability, and has improved detergent activity.

**[00032]** In case (1), similar conditions to those identified in case (3) may be used to encourage back-biting so as to produce tri-PIB. This approach might be preferable to the formation of tri-PIB in situ as in approach (3), in instances where the PIB enriched in tri-PIB is intended for use in an application wherein the presence of tetra-PIB may be undesirable for some reason.

**[00033]** In case (2), rather than being subjected to conditions that will yield tri-PIB, the PIB that is highly enriched in tetra-PIB may be subjected to thermal treatment so as to form exo-PIB via a retro-Alder-ene reaction according to the mechanism depicted below in Scheme 4.

**Scheme 4**



**[00034]** This approach for preparing PIB that is highly enriched in the  $\alpha$  isomer, i.e. exo-PIB (although some tetra-PIB may still be present, depending on the extent to which the rearrangement step is carried out) can be particularly useful if the PIB is intended for reaction with maleic anhydride. That is because endo-PIB will not usually react with maleic anhydride at all. Thus, by converting the endo-PIB to either exo- or tetra-PIB, this approach enables the use of a component of the PIB reagent which would otherwise be wasted. Further, the extent to which the rearrangement step is carried out may if desired be varied so as to control the ratio of exo- to tetra-PIB in the end product

**[00035]** In one approach, the hydroxyaromatic compound of the Mannich detergents herein are based on phenol, resorcinol, hydroquinone, and/or phenethylphenol because it is believed two active sites on the aromatic ring (e.g. active ortho positions) are preferred. Most preferably, the hydroxyaromatic compound is based on phenol. Without wishing to be limited by theory, it is also believed that hydroxyaromatic compounds based on cresol, catechol, hydroxydiphenyl, benzylphenol, naphthol, and/or tolylnaphthol are less preferred as they only have one active ortho site on the aromatic ring having substituents already bonded to at least one ortho position on the aromatic ring.

**[00036]** In another approach, representative aldehydes for use in the preparation of Mannich detergents herein include the aliphatic aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, caproaldehyde, heptaldehyde, 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,

or aqueous formaldehyde solutions such as formalin. Most preferred is formaldehyde or formalin.

**[00037]** In yet another approach, representative amine reactants for the Mannich detergents herein include, but are not limited to, alkylene polyamines having at least one suitably reactive primary or secondary amino group in the molecule. Other substituents such as hydroxyl, cyano, amido, etc., can be present in the polyamine. In a preferred embodiment, the alkylene polyamine is a polyethylene polyamine. Suitable alkylene polyamine reactants include ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, and mixtures of such amines having nitrogen contents corresponding to alkylene polyamines of the formula  $H_2N-(A-NH-)_nH$ , where A is divalent ethylene or propylene and n is an integer of from 1 to 10, preferably 1 to 4. The alkylene polyamines may be obtained by the reaction of ammonia and dihalo alkanes, such as dichloro alkanes.

**[00038]** The amine may preferably be an aliphatic diamine having one primary or secondary amino group and at least one tertiary amino group in the molecule. Examples of suitable polyamines include N, N, N'', N'''- tetraalkyldialkylenetriamines (two terminal tertiary amino groups and one central secondary amino group), N, N, N', N''- tetraalkyltrialkylenetetramines (one terminal tertiary amino group, two internal tertiary amino groups and one terminal primary amino group), N, N, N', N'', N'''- pentaalkyltrialkylenetetramines (one terminal tertiary amino group, two internal tertiary amino groups and one terminal secondary amino group), N, N-dihydroxyalkyl-  $\alpha$ ,  $\omega$ -alkylenediamines (one terminal tertiary amino group and one terminal primary amino group), N, N, N'-trihydroxyalkyl-  $\alpha$ ,  $\omega$ -alkylenediamines (one terminal tertiary amino group and one terminal secondary amino group), tris (dialkylaminoalkyl) aminoalkylmethanes (three terminal tertiary amino groups and one terminal primary amino group), and similar compounds, wherein the alkyl groups are the same or different and typically contain no more than about 12 carbon atoms each, and which preferably contain from 1 to 4 carbon atoms each. Most preferably these alkyl groups are methyl and/or ethyl groups. Preferred polyamine reactants are N, N-dialkyl- $\alpha$ ,  $\omega$ -alkylenediamine, such as those having from 3 to about 6 carbon atoms in the alkylene group and from 1 to about 12 carbon atoms in each of the alkyl groups, which most preferably are the same but which can be different. Most preferred is N, N-dimethyl-1, 3-propanediamine and N-methyl piperazine.

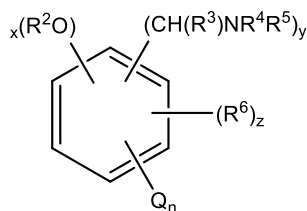
**[00039]** Examples of polyamines having one reactive primary or secondary amino group that can participate in the Mannich condensation reaction, and at least one sterically hindered amino group that cannot participate directly in the Mannich condensation reaction

to any appreciable extent include N- (tert-butyl)-1, 3propanediamine, N-neopentyl-1, 3-propanediamine, N-(tert-butyl)-1-methyl-1, 2ethanediamine, N- (tert-butyl)-1-methyl-1, 3-propanediamine, and 3,5-di (tertbutyl) aminoethylpiperazine.

**[00040]** As regards the preparation of such Mannich products, alkylation of the hydroxyaromatic compound may be performed in the presence of an alkylating catalyst at a temperature in the range of about 0°C to about 200°C, preferably about 0 to about 100°C. Acidic catalysts may be used to promote Friedel Crafts alkylation. Possible catalysts for use in this regard include sulphuric acid, BF<sub>3</sub>, aluminum phenoxide, methanesulphonic acid, cationic exchange resin, acidic clays and modified zeolites. The preferred configuration of the alkyl-substituted hydroxyaromatic compound is that of a para-substituted mono-alkylphenol.

**[00041]** The condensation reaction among the alkylphenol, the specified amine(s), and the aldehyde may be conducted at a temperature in the range of about 40°C to about 200°C. The reaction can be conducted in bulk (no diluent or solvent) or in a solvent or diluent. Water is evolved and can be removed by azeotropic distillation during the course of the reaction. In some embodiments, the Mannich reaction products are formed by reacting a molar ratio of the hydrocarbyl-substituted hydroxyaromatic compound (preferably, the PIB-substituted phenol) to the amine (preferably, dimethylaminopropylamine) to formaldehyde of 1 to 0.9-2.0 to 1.5-3.0 and, more preferably, 1 to 1-2 to 2-3, and even more preferably, 1 to 1-2 to 2, and most preferably, 1 to 2 to 2. Notably, a molar ratio of 1:1:1 does not provide sufficient emission particulate reduction in the context of GDI engines.

**[00042]** In other approaches or embodiments, the present disclosure also provides a Mannich detergent product comprising a compound which includes the noted PIB substituent of a Mannich reaction product having a structure of Formula I below:



(Formula I)

wherein

each R<sup>2</sup> is independently H or, together with the R<sup>4</sup> or R<sup>5</sup> moiety in an adjacent –CH(R<sup>3</sup>)NR<sup>4</sup>R<sup>5</sup> group, is a divalent –CH(R<sup>3</sup>)– group;

x is 1, 2 or 3;

each R<sup>3</sup> is independently H or hydrocarbyl comprising 1 to 10 carbon atoms;

each  $R^4$  and  $R^5$  is independently H, hydrocarbyl comprising 1 to 3000 carbon atoms which may be interrupted by one or more O, S and/or  $NR^3$  moieties, or together with  $R^2$  forms a divalent  $-CH(R^3)-$  group as defined above;

y is 1, 2 or 3;

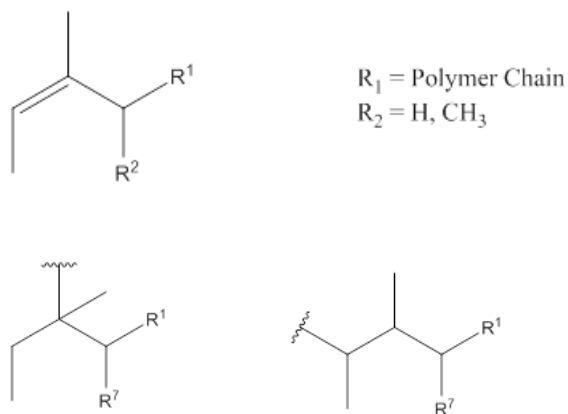
each  $R^6$  is independently hydrocarbyl comprising 1 to 3000 carbon atoms which may be interrupted by one or more O, S and/or  $NR^3$  moieties;

z is 0, 1 or 2;

n is 1, 2 or 3; and

Q is a PIB group, a conventional PIB group, and/or a HR-PIB group as described herein;

wherein in at least 50 % of the compounds of formula (I), said PIB group is bonded to the central benzene ring such that it has the structure:



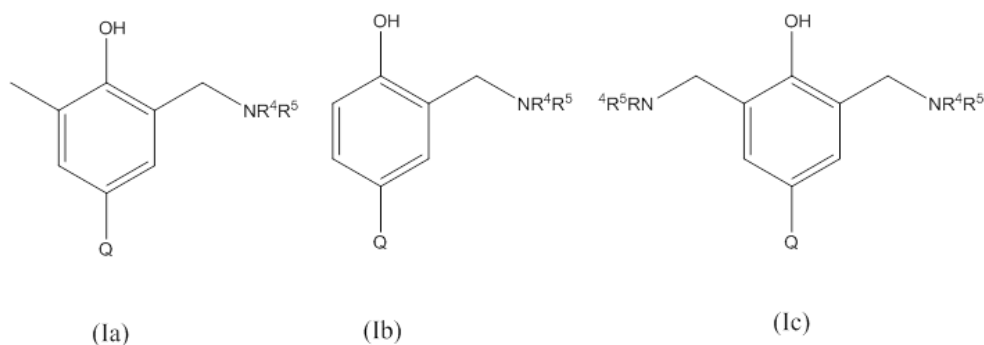
wherein

$R^1$ , together with the moiety  $-CH_2-C(CH_3)(CH_2CH_3)-$  through which it is attached to the central benzene ring, represents the PIB group.

Preferably in formula (I):

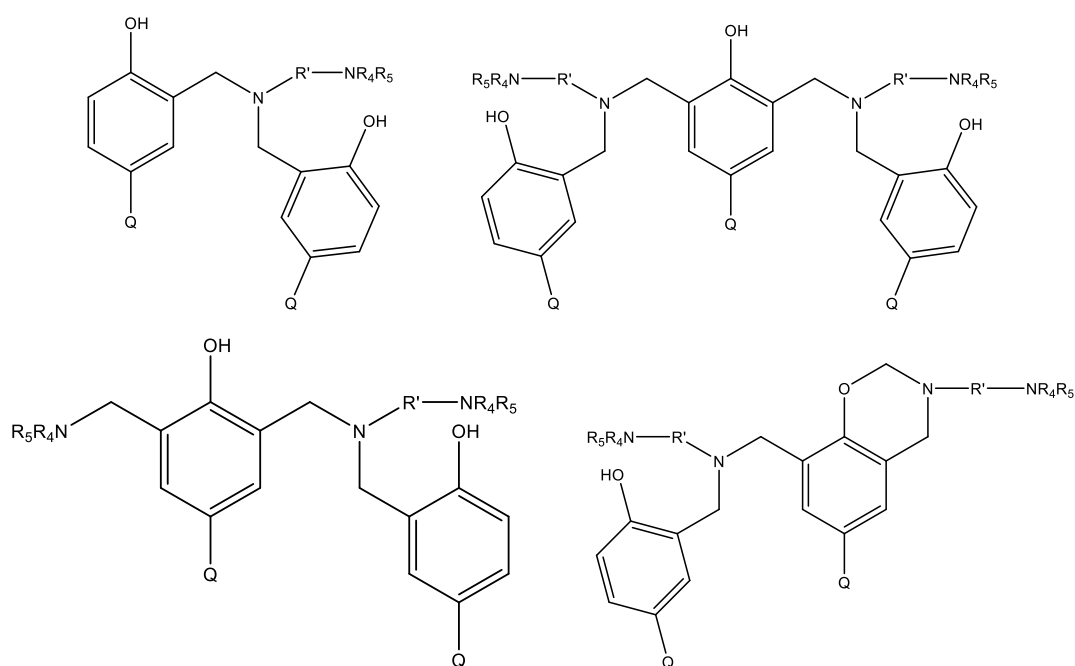
- any Q groups are para to an  $-OR^2$  group,
- any  $-CH(R^3)NR^4R^5$  groups are ortho to at least one  $-OR^2$  group,
- $R^6$  (if present) is ortho to at least one  $-OR^2$  group, and/or
- $R^7$  is  $-H$  or  $-CH_3$ .

**[00043]** In other approaches or embodiments, particularly preferred examples of the Mannich reaction products herein are compounds having the structures of Formula (Ia), (Ib), and/or (Ic) below with a preferred example for the  $-NR^4R^5$  group of these structure being  $-NH(CH_2)_3N(CH_3)_2$  and Q as defined above:

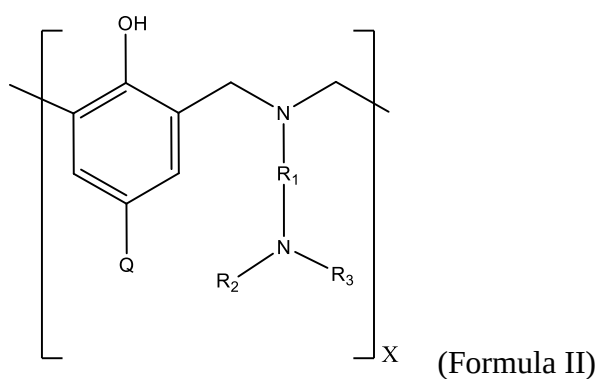


Mannich detergents and methods of preparing such detergents suitable for the present disclosure are also described in US 2018/0223017, which is incorporated herein by reference.

**[00044]** In yet other approaches or embodiments, additional examples of exemplary compounds of the Mannich reaction products herein include one or more of the following oligomer structures (with the following compounds or oligomers having Q as defined above and the  $-NR^4R^5$  group being either  $-N(CH_3)_2$  or  $-NH(CH_2)_3N(CH_3)_2$  and R' being C1 to C4 and preferably C3):



**[00045]** In yet other approaches, a generic oligomer structure of the Mannich reaction products herein has the exemplary structure of Formula II below with X being an integer selected from 2 to 10 or an integer to form an oligomer molecular weight of about 300 to about 2000 g/mol:



wherein Q is defined above and R<sub>1</sub> of Formula II above is a C1 to C10 group (preferably, a C1 to C4 group, and more preferably a C3 group), and R<sub>2</sub> and R<sub>3</sub> of Formula II above are, independently, C1 to C4 alkyl groups, and preferably C1 groups.

**[00046]** In approaches or embodiments, the present disclosure also provides the use of any embodiment of the Mannich detergent products as defined herein in a fuel (or alternatively a lubricant) to achieve particulate emission reductions. Preferably, any embodiment of the Mannich detergent products herein is used as a detergent in gasoline fuel combusted in a direct injection gasoline (DIG) engine to achieve the particulate emission reductions. As shown in the Examples below, particulate emission reductions are measured as set forth in EP 3 775 112 B1 (e.g., Example 3 and paragraphs 298 to 303 thereof), which is incorporated herein by reference in its entirety. In other embodiments, the present disclosure also provides the use of Mannich detergents as described herein having a substituent PIB group enriched in tri-PIB (e.g. PIB in which at least 50, 60, 70, 80, 90 or 95 mol% of the PIB macromolecules have a tri-substituted alkene group) to achieve particulate emission reductions in GDI engines (as measured pursuant to EP 3 775 112 B1).

**[00047]** In yet other embodiments, the present disclosure also provides the use of Mannich detergents as described herein and formed by reacting a molar ratio of the hydrocarbyl-substituted hydroxyaromatic compound (preferably, the PIB-substituted phenol) to the amine (preferably, dimethylaminopropylamine) to formaldehyde of 1 to 0.9-2.0 to 1.5-3.0 and, more preferably, 1 to 1-2 to 2-3, and even more preferably, 1 to 1-2 to 2, and most preferably, 1 to 2 to 2 in order to achieve particulate emission reductions in GDI engines (as measured pursuant to EP 3 775 112 B1).

**[00048]** In yet other embodiments, the present disclosure also provides the use of Mannich detergents as shown by any formula or oligomer of this disclosure in order to achieve particulate emission reductions in GDI engines (as measured pursuant to EP 3 775 112 B1).

**[00049]** The present disclosure also provides a method of reducing particulate emissions of a GDI engine, which method includes adding to the engine (e.g., via a gasoline fuel or via a lubricant) any embodiment of the PIB-substituted Mannich detergent(s) as defined herein. Preferably, the method includes reducing particulate emissions in the GDI engine, and more particularly, where the method includes fuelling the GDI engine with gasoline including any embodiment of the PIB-substituted Mannich detergent(s) as defined herein and combusting the gasoline including the PIB-substituted Mannich detergent as defined herein to achieve particulate emission reductions as measured via EP 3 775 112 B1 (e.g., Example 3 and paragraphs 298 to 303 thereof).

**[00050]** The present disclosure also provides an additive composition comprising any embodiment of the Mannich detergent product as defined herein and a carrier fluid. The additive composition is preferably for use in adding the product to a fuel or lubricant composition. Thus, the present disclosure also provides a fuel and/or a lubricant comprising any embodiment of the disclosure. In a preferred embodiment, the disclosure provides gasoline including any embodiment of the Mannich detergent product of the disclosure.

**[00051]** In other approaches or embodiment, the size of the PIB group of the detergent products of the present disclosure is not particularly limited. However, preferably it has a number average molecular weight of at least 400, such as at least 500, at least 600, at least 700, at least 800, or at least 900. It preferably has a number average molecular weight of no more than 5000, such as no more than 4000, or 3000, or 2000, or 1500, or 1200. Number average molecular is determined as described below.

**[00052]** In preferred embodiments where the detergent products of the present disclosure are added to gasoline fuel, they may be added in an amount of from about 1 to about 5000 ppm by weight, especially from about 5 to about 3000 ppm by weight, in particular from about 10 to about 1000 ppm by weight. In other embodiments, the detergent products are added to a gasoline fuel in amount of about 5 to about 500 ppm, about 10 to about 400 ppm, about 20 to about 300 ppm, about 30 to about 200 ppm, or about 40 to about 100 ppm.

**[00053]** In one approach or embodiment, emission particulate reductions (as measured using the procedures of EP 3 775 112 as described herein) using the Mannich detergents as described herein may obtain emission particulate reductions of at least about 90 percent, at least about 92 percent, at least about 94 percent, at least about 96 percent, or at least about 98 percent as compared to a base fuel without the Mannich detergents herein. In other approaches, compositions and methods of combusting a gasoline fuel in GDI engines using the Mannich detergents as described herein may also result in no more than about 100,000

particles per cubic centimeter when tested according to the procedures of EP 3 775 112, no more than about 80,000 particles per cubic centimeter, no more than about 60,000 particles per cubic centimeter, no more than about 50,000 particles per cubic centimeter, no more than 40,000 particles per cubic centimeter, or no more than 30,000 particles per cubic centimeter. As a comparison, a base fuel devoid of the Mannich detergents (or other detergent additives) commonly has more than 3,000,000 particles per cubic centimeter when evaluated according to the methods of EP 3 775 112.

**[00054]** In some embodiments, the select Mannich detergents have a structure of formula (II) shown above and also features (i) a molar ratio of the hydrocarbyl-substituted hydroxyaromatic compound (e.g., a hydrocarbyl-substituted phenol) to amine (e.g., dimethylaminopropylamine) to formaldehyde of 1 to 0.9-2.0 to 1.5-3.0 and, more preferably, 1 to 1-2 to 2-3, and even more preferably, 1 to 1-2 to 2, and most preferably, 1 to 2 to 2. These detergents may further feature that Q in formula (II) is conventional PIB or HR-PIB.

**[00055]** In other embodiments, the select Mannich detergents have a structure of formula (II) shown above, wherein Q is a conventional PIB. These Mannich detergents may further feature (i) a molar ratio of the hydrocarbyl-substituted hydroxyaromatic compound (e.g., a hydrocarbyl-substituted phenol) to amine (e.g., dimethylaminopropylamine) to formaldehyde of 1 to 0.9-2.0 to 1.5-3.0 and, more preferably, 1 to 1-2 to 2-3, and even more preferably, 1 to 1-2 to 2, and most preferably, 1 to 2 to 2.

**[00056]** In other embodiments, the select Mannich detergents have a structure of formula (II) shown above, wherein Q is a HR-PIB. These Mannich detergents may further feature (i) a molar ratio of the hydrocarbyl-substituted hydroxyaromatic compound (e.g., a hydrocarbyl-substituted phenol) to amine (e.g., dimethylaminopropylamine) to formaldehyde of 1 to 0.9-2.0 to 1.5-3.0 and, more preferably, 1 to 1-2 to 2-3, and even more preferably, 1 to 1-2 to 2, and most preferably, 1 to 2 to 2.

**[00057]** In other embodiments, the select Mannich detergents are Mannich which contains a substituent of conventional PIB. These Mannich detergents may further feature (i) a molar ratio of the hydrocarbyl-substituted hydroxyaromatic compound (e.g., a hydrocarbyl-substituted phenol) to amine (e.g., dimethylaminopropylamine) to formaldehyde of 1 to 0.9-2.0 to 1.5-3.0 and, more preferably, 1 to 1-2 to 2-3, and even more preferably, 1 to 1-2 to 2, and most preferably, 1 to 2 to 2.

**[00058]** In other embodiments, the select Mannich detergents are Mannich which contains a substituent of HR-PIB. These Mannich detergents may further feature (i) a molar ratio of the hydrocarbyl-substituted hydroxyaromatic compound (e.g., a hydrocarbyl-substituted

phenol) to amine (e.g., dimethylaminopropylamine) to formaldehyde of 1 to 0.9-2.0 to 1.5-3.0 and, more preferably, 1 to 1-2 to 2-3, and even more preferably, 1 to 1-2 to 2, and most preferably, 1 to 2 to 2.

**[00059]** Optionally, other components and additives, if desired, may be included in the compositions, gasoline fuel, or methods of the present disclosure and, if used, would be added in amounts customary for this purpose. One or more optional compounds may be present in the fuel additives, fuels, or methods of the disclosed embodiments herein as needed for a particular application and/or fuel type. For example, the fuel additive or fuels may contain conventional quantities of cetane improvers, octane improvers, corrosion inhibitors, cold flow improvers (CFPP additive), pour point depressants, solvents, demulsifiers, lubricity additives, friction modifiers, amine stabilizers, combustion improvers, detergents, dispersants, antioxidants, heat stabilizers, conductivity improvers, metal deactivators, marker dyes, organic nitrate ignition accelerators, cyclomatic manganese tricarbonyl compounds, carrier fluids, and the like. In some aspects, the compositions described herein may contain about 10 weight percent or less, or in other aspects, about 5 weight percent or less, based on the total weight of the additive concentrate, of one or more of the above optional additives. Similarly, the fuels may contain suitable amounts of conventional fuel blending components such as methanol, ethanol, dialkyl ethers, 2-ethylhexanol, and the like.

**[00060]** For instance, other commercially available detergents may be used in combination with the reaction products described herein. Such detergents include but are not limited to succinimides, other Mannich base detergents, PIB amine detergents, quaternary ammonium detergents, bis-aminotriazole detergents as generally described in U.S. patent application Ser. No. 13/450,638, and a reaction product of a hydrocarbyl substituted dicarboxylic acid, or anhydride and an aminoguanidine, wherein the reaction product has less than one equivalent of amino triazole group per molecule as generally described in U.S. patent application Ser. Nos. 13/240,233 and 13/454,697.

**[00061]** In other aspects of the disclosed embodiments, organic nitrate ignition accelerators that include aliphatic or cycloaliphatic nitrates in which the aliphatic or cycloaliphatic group is saturated, and that contain up to about 12 carbons may be used. Examples of organic nitrate ignition accelerators that may be used are methyl nitrate, ethyl nitrate, propyl nitrate, isopropyl nitrate, allyl nitrate, butyl nitrate, isobutyl nitrate, sec-butyl nitrate, tert-butyl nitrate, amyl nitrate, isoamyl nitrate, 2-amyl nitrate, 3-amyl nitrate, hexyl nitrate, heptyl nitrate, 2-heptyl nitrate, octyl nitrate, isooctyl nitrate, 2-ethylhexyl nitrate,

nonyl nitrate, decyl nitrate, undecyl nitrate, dodecyl nitrate, cyclopentyl nitrate, cyclohexyl nitrate, methylcyclohexyl nitrate, cyclododecyl nitrate, 2-ethoxyethyl nitrate, 2-(2-ethoxyethoxy)ethyl nitrate, tetrahydrofuranyl nitrate, and the like. Mixtures of such materials may also be used.

**[00062]** Examples of suitable optional metal deactivators useful in the compositions of the present application are disclosed in U.S. Pat. No. 4,482,357, the disclosure of which is herein incorporated by reference in its entirety. Such metal deactivators include, for example, salicylidene-o-aminophenol, disalicylidene ethylenediamine, disalicylidene propylenediamine, and N,N'-disalicylidene-1,2-diaminopropane.

**[00063]** Suitable optional cyclomatic manganese tricarbonyl compounds which may be employed in the compositions of the present application include, for example, cyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese tricarbonyl, indenyl manganese tricarbonyl, and ethylcyclopentadienyl manganese tricarbonyl. Yet other examples of suitable cyclomatic manganese tricarbonyl compounds are disclosed in U.S. Pat. No. 5,575,823 and U.S. Pat. No. 3,015,668 both of which disclosures are herein incorporated by reference in their entirety.

**[00064]** The additives of the present application and optional additives used in formulating the fuels of this disclosure may be blended into the base fuel individually or in various sub-combinations. In some embodiments, the additive components of the present application may be blended into the fuel concurrently using an additive concentrate, as this takes advantage of the mutual compatibility and convenience afforded by the combination of ingredients when in the form of an additive concentrate. Also, use of a concentrate may reduce blending time and lessen the possibility of blending errors.

**[00065]** As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having a predominantly hydrocarbon character. Each hydrocarbyl group is independently selected from hydrocarbon substituents, and substituted hydrocarbon substituents containing one or more of halo groups, hydroxyl groups, alkoxy groups, mercapto groups, nitro groups, nitroso groups, amino groups, pyridyl groups, furyl groups, imidazolyl groups, oxygen and nitrogen, and wherein no more than two non-hydrocarbon substituents are present for every ten carbon atoms in the hydrocarbyl group.

**[00066]** As used herein, the term "percent by weight" or "wt%", unless expressly stated otherwise, means the percentage the recited component represents to the weight of the entire composition. All percent numbers herein, unless specified otherwise, is weight percent.

**[00067]** The term "alkyl" as employed herein refers to straight, branched, cyclic, and/or substituted saturated chain moieties from about 1 to about 200 carbon atoms. The term "alkenyl" as employed herein refers to straight, branched, cyclic, and/or substituted unsaturated chain moieties from about 3 to about 30 carbon atoms. The term "aryl" as employed herein refers to single and multi-ring aromatic compounds that may include alkyl, alkenyl, alkylaryl, amino, hydroxyl, alkoxy, halo substituents, and/or heteroatoms including, but not limited to, nitrogen, and oxygen.

**[00068]** As used herein, molecular weight is determined by gel permeation chromatography (GPC) using commercially available polystyrene standards (with a Mp of about 162 to about 14,000 as the calibration reference). The molecular weight ( $M_n$ ) for any embodiment herein may be determined with a gel permeation chromatography (GPC) instrument obtained from Waters or the like instrument and the data processed with Waters Empower Software or the like software. The GPC instrument may be equipped with a Waters Separations Module and Waters Refractive Index detector (or the like optional equipment). The GPC operating conditions may include a guard column, 4 Agilent PLgel columns (length of 300x7.5 mm, particle size of 5  $\mu$ , and pore size ranging from 100-10000 Å) with the column temperature at about 40°C. Un-stabilized HPLC grade tetrahydrofuran (THF) may be used as solvent, at a flow rate of 0.38 mL/min. The GPC instrument may be calibrated with commercially available polystyrene (PS) standards having a narrow molecular weight distribution ranging from 500 – 380,000 g/mol. The calibration curve can be extrapolated for samples having a mass less than 500 g/mol. Samples and PS standards can be dissolved in THF and prepared at concentration of 0.1-0.5 weight percent and used without filtration. GPC measurements are also described in US 5,266,223, which is incorporated herein by reference. The GPC method additionally provides molecular weight distribution information; see, for example, W. W. Yau, J. J. Kirkland and D. D. Bly, "Modern Size Exclusion Liquid Chromatography", John Wiley and Sons, New York, 1979, also incorporated herein by reference.

**[00069]** As used herein and unless the context suggests otherwise, a major amount refers to greater than 50 weight percent (greater than 60 weight percent, greater than 70 weight percent, greater than 80 weight percent or greater than 90 weight percent), and a minor

amount refers to less than 50 weight percent (less than 40 weight percent, less than 30 weight percent, less than 20 weight percent, or less than 10 weight percent).

**[00070]** It is to be understood that throughout the present disclosure, the terms "comprises," "includes," "contains," etc. are considered open-ended and include any element, step, or ingredient not explicitly listed. The phrase "consists essentially of" is meant to include any expressly listed element, step, or ingredient and any additional elements, steps, or ingredients that do not materially affect the basic and novel aspects of the invention. The present disclosure also contemplates that any composition described using the terms, "comprises," "includes," "contains," is also to be interpreted as including a disclosure of the same composition "consisting essentially of" or "consisting of" the specifically listed components thereof.

### EXAMPLES

**[00071]** The following examples are illustrative of exemplary embodiments of the disclosure. In these examples as well as elsewhere in this application, all ratios, parts, and percentages are by weight unless otherwise indicated. It is intended that these examples are being presented for the purpose of illustration only and are not intended to limit the scope of the invention disclosed herein. Any reference to a standardized test method, unless apparent from the context of its use in the specification, claims, or these Examples, refers to the version of the test method publically available at the time of this disclosure. Particulate reductions of the Examples were evaluated as described in EP 3 775 112 B1 and, in particular, Example 3 of EP 3 775 112 B1.

**[00072]** EXAMPLE 1

**[00073]** Conventional PIB-Mannich detergents were prepared for use in gasoline fuels for GDI engines. The analysis of purified PIB-phenols that were taken forward for use in preparing the Mannich detergent products is set out in Table 1 below.

**[00074]** Table 1

| Property            | Method              | Conventional PIB |
|---------------------|---------------------|------------------|
| <b>Residual PIB</b> | HPLC                | None Detected    |
| <b>Phenol</b>       | GC                  | None Detected    |
| <b>Mn</b>           | <sup>13</sup> C NMR | 960              |
| <b>Mn</b>           | Titration           | 961              |
| <b>%OH</b>          | Titration           | 1.77             |
| <b>mgKOH/g</b>      | Titration           | 58.4             |

**[00075]** The conventional PIB-phenol noted above was then subjected to a Mannich reaction under the same conditions as follows: A solution of 72.22 g of conventional (LR) PIB phenol with a hydroxyl number of 58.4 mgKOH/g (corresponding to 75.2 mmol phenol OH groups) in xylene (108 mL) was added to a 500 mL four neck round bottom flask equipped with a Dean-Stark trap and a reflux condenser. 4.56 g (152.0 mmol) of paraformaldehyde was added to the reaction vessel and heated to 90°C. After 15 minutes at 90°C, 15.53 g (152.0 mmol) of N,N-dimethyl-1,3-propanediamine was added by addition funnel in under 8 minutes in order to maintain an internal reaction temperature of 90-95°C. Upon complete addition, the reaction temperature was raised to 148°C and held at this temperature for 2h while water was continuously collected in the Dean-Stark trap. After two hours, the reaction was stopped and the reaction residue was concentrated to dryness on a rotary evaporator at 145°C and 1 mbar yielding 81.0 g of the Mannich product as an amber oil.

**[00076]** The preparation of PIB-Phenol using Conventional PIB is as follows: 430.00g (0.464 mol) conventional PIB was added to an addition funnel. The PIB was about 900 molecular weight and contained < 10% alpha-vinylidene double bonds. 78.66g (0.835 mol) phenol was dissolved in 50g heptane at 40°C under nitrogen in a 4-neck 2000 mL round bottomed flask. 13.18g BF<sub>3</sub>OEt<sub>2</sub> (0.092mol) was added to the phenol / heptane mixture. The PIB was added to the reaction flask over the course of 70 minutes. The reaction was stirred at 40-42°C for an additional 2 hours at which point it was quenched with ammonia gas. The reaction was diluted with heptane and filtered. Solvent was removed by rotary distillation and excess phenol was removed by vacuum distillation at 130°C and 0.5 mmHg; 409 g (86% yield excluding transfer loss). The nominal molecular weight was 1284 as determined by Quantitative Carbon-NMR Integration, which corresponds to 1.32% OH.

**[00077]** Purification of Conventional-PIB-Phenol is as follows: 311 g of PIB-Phenol from the crude reaction (1.32 % OH) was dissolved in an equal volume of heptane and loaded onto a column containing 2 kg of silica gel. The column was eluted with 3 L of heptane to remove unreacted PIB. Subsequently 3 L of a 20% Ethyl Acetate/Heptane mixture was used to remove the active PIB-Phenol. The resulting solution was concentrated on a rotary evaporator at between 50 and 60 °C under vacuum. The final % OH was 1.90, thus indicating significant enrichment of the PIB-Phenol. The nominal molecular weight was 897 as determined by Quantitative Carbon-NMR integration.

**[00078]** EXAMPLE 2

**[00079]** HR PIB-Mannich detergents were prepared in a similar manner as described in Example 1 above (using HR PIB instead).

**[00080]** EXAMPLE 3

**[00081]** The Mannich reaction products prepared Examples 1 and 2 were combusted in a base fuel and particulate emissions were evaluated according to the procedures of Example 3 from EP 3 775 112 B1. More particularly, the vehicle test was carried out on a chassis dynamometer test cell, with a 2014 BMW mini Cooper S having a B48 direct injection spark ignition engine, with a turbocharger and an engine displacement of 1998 cubic centimeters. The vehicle was operated at a constant engine speed of 3500 rpm for 24 hours. The chassis dynamometer was controlled with the US Government EPA-specified test vehicle coefficients to properly simulate driving the test vehicle on the open road. The particulate emissions were directly measured by a Cambustion DMS500 Mark II instrument, connected directly to the mini Cooper tailpipe. The Cambustion DMS500 Mark II counted the particulate emissions regularly over the 24 hour test period, to ensure the emissions were known throughout the test. The instrument returned a particulate number (PN) in units of N per cubic centimeter. To arrive at the PN value for each tested fuel composition, the PN for the 24<sup>th</sup> hour was calculated by averaging the emissions measured at the end of each 20-minute interval of the final hour. Particulate emissions were also evaluated of the base fuel (without additives). Results are provided in Table 2 below.

**[00082]** Table 2: Emission Testing

| Fuel           | Detergent                     | Detergent, ppm | 24 hour Particle Number Result (#/cm <sup>3</sup> ) | % Improvement to Base Fuel |
|----------------|-------------------------------|----------------|-----------------------------------------------------|----------------------------|
| Gasoline Fuel  | N/A                           | N/A            | 3,256,007                                           | -                          |
| Gasoline Fuel  | Inventive Mannich (Example 1) | 90             | 28,615                                              | 99.1%                      |
| Gasoline Fuel* | Inventive Mannich (Example 1) | 90             | 43,286                                              | 98.6%                      |

\*using new injectors in GDI engine.

**[00083]** 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 antioxidant” includes two or more different antioxidants. 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

**[00084]** 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.

**[00085]** It is to be understood that each component, compound, substituent or parameter disclosed herein is to be interpreted as being disclosed for use alone or in combination with one or more of each and every other component, compound, substituent or parameter disclosed herein.

**[00086]** It is further understood that each range disclosed herein is to be interpreted as a disclosure of each specific value within the disclosed range that has the same number of significant digits. Thus, for example, a range from 1 to 4 is to be interpreted as an express disclosure of the values 1, 2, 3 and 4 as well as any range of such values.

**[00087]** It is further understood that each lower limit of each range disclosed herein is to be interpreted as disclosed in combination with each upper limit of each range and each specific value within each range disclosed herein for the same component, compounds, substituent or parameter. Thus, this disclosure is to be interpreted as a disclosure of all ranges derived by combining each lower limit of each range with each upper limit of each range or with each specific value within each range, or by combining each upper limit of each range with each specific value within each range. That is, it is also further understood that any range between the endpoint values within the broad range is also disclosed herein. Thus, a range from 1 to 4 also means a range from 1 to 3, 1 to 2, 2 to 4, 2 to 3, and so forth.

**[00088]** Furthermore, specific amounts/values of a component, compound, substituent or parameter disclosed in the description or an example is to be interpreted as a disclosure of either a lower or an upper limit of a range and thus can be combined with any other lower or upper limit of a range or specific amount/value for the same component, compound,

substituent or parameter disclosed elsewhere in the application to form a range for that component, compound, substituent or parameter.

What is claimed is

1. A method of reducing particulate emission in a gasoline direct injection engine, the method comprising:

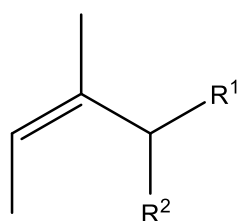
combusting in the engine a gasoline composition including a Mannich detergent as an additive, wherein the Mannich detergent is produced by the reaction of hydrocarbyl-substituted phenol, an amine, and formaldehyde at a molar ratio of 1 : 1-2 : 2-3; and

wherein the Mannich detergent is present in the gasoline composition at a concentration of about 40 to about 100 ppm.

2. The method of claim 1, wherein the molar ratio of the hydrocarbyl-substituted phenol, amine, and formaldehyde is 1 : 1-2 : 2, and preferably wherein the molar ratio of the hydrocarbyl-substituted phenol, amine, and formaldehyde is 1 : 2 : 2.

3. The method of claim 1, wherein the hydrocarbyl substituent is derived from polyisobutylene and wherein at least 50 mol percent of polyisobutylene macromolecules have a tri-substituted alkene group, or wherein the hydrocarbyl substituent is derived from polyisobutylene and wherein at least 50 mol percent of polyisobutylene macromolecules have a tri-substituted alkene group and a tetra-substituted alkene group.

4. The method of claim 3, wherein the polyisobutylene having a tri-substituted alkene group has the following stereochemistry:



wherein

R<sup>1</sup> is a polymer chain

R<sup>2</sup> is -H or -CH<sub>3</sub>.

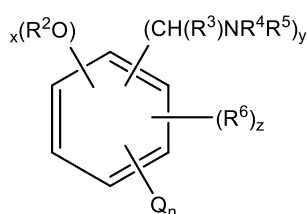
5. The method of claim 4, wherein the polyisobutylene has less than 50 mol percent of terminal double bonds.

6. The method of claim 3, wherein the polyisobutylene includes one or more of a  $\beta$ -olefin isomer structure, a  $\beta$ -olefin structure, or a tetra-substituted olefin structure.

7. The method of claim 1, wherein the hydrocarbyl substituent is derived from polyisobutylene having a number average molecular weight of about 400 to about 1500.

8. The method of claim 7, wherein at least 50 mol percent of polyisobutylene macromolecules have a tri-substituted alkene group, or wherein at least 50 mol percent of polyisobutylene macromolecules have a tri-substituted alkene group and a tetra-substituted alkene group.

9. The method of claim 1, wherein the Mannich detergent is a compound having a structure of Formula I:



(Formula I)

wherein

each  $R^2$  is independently H or, together with the  $R^4$  or  $R^5$  moiety in an adjacent  $-CH(R^3)NR^4R^5$  group, is a divalent  $-CH(R^3)-$  group;

$x$  is an integer of 1, 2 or 3;

each  $R^3$  is independently H or hydrocarbyl comprising 1 to 10 carbon atoms;

each  $R^4$  and  $R^5$  is independently H, hydrocarbyl comprising 1 to 3000 carbon atoms which may be interrupted by one or more O, S and/or  $NR^3$  moieties, or together with  $R^2$  forms a divalent  $-CH(R^3)-$  group as defined above;

$y$  is an integer of 1, 2 or 3;

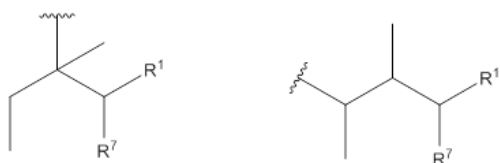
each  $R^6$  is independently hydrocarbyl comprising 1 to 3000 carbon atoms which may be interrupted by one or more O, S and/or  $NR^3$  moieties;

$z$  is an integer of 0, 1 or 2;

$n$  is an integer of 1, 2 or 3; and

$Q$  is the hydrocarbyl substituent.

10. The method of claim 9, wherein, in at least 50 % of the compounds of formula (I), said Q group is bonded to the central benzene ring such that it has the structure:



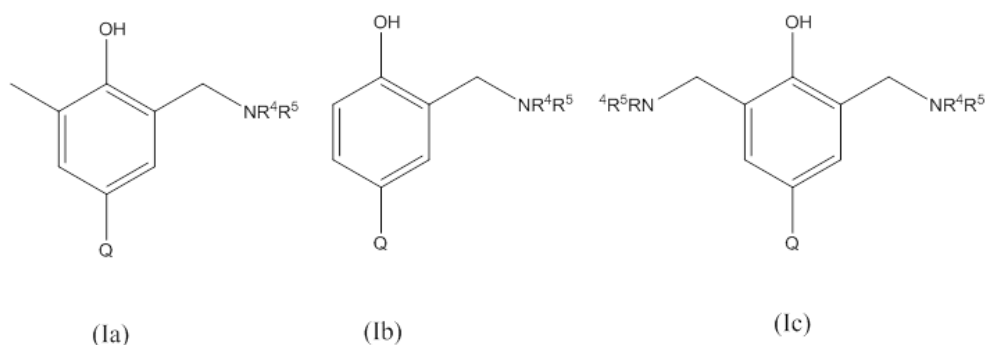
wherein

$R^1$  is a polymer chain, and together with the moiety  $-\text{CH}_2-\text{C}(\text{CH}_3)(\text{CH}_2\text{CH}_3)-$  through which it is attached to the central benzene ring, represents the Q group; and

$R^7$  is  $-\text{H}$  or  $-\text{CH}_3$ .

11. The method of claim 9, wherein (1) any Q groups are para to an  $-\text{OR}^2$  group, (2) any  $-\text{CH}(\text{R}^3)\text{NR}^4\text{R}^5$  groups are ortho to at least one  $-\text{OR}^2$  group, and/or (3)  $-\text{R}^6$  (if present) is ortho to at least one  $-\text{OR}^2$  group; and/or wherein the hydrocarbyl substituent Q is derived from polyisobutylene and wherein at least 50 mol percent of polyisobutylene macromolecules have a tri-substituted alkene group, or wherein the hydrocarbyl substituent Q is derived from polyisobutylene and wherein at least 50 mol percent of polyisobutylene macromolecules have a tri-substituted alkene group and a tetra-substituted alkene group.

12. The method of claim 9, wherein the Mannich detergent is a compound having a structure of Formula (Ia), (Ib), and/or (Ic):



13. The method of claim 12, wherein the  $-\text{NR}^4\text{R}^5$  group of Formula (Ia), (Ib), and/or (Ic) is  $-\text{NH}(\text{CH}_2)_3\text{N}(\text{CH}_3)_2$ .

14. The method of claim 12, wherein the hydrocarbyl substituent Q is derived from polyisobutylene and wherein at least 50 mol percent of polyisobutylene macromolecules have a tri-substituted alkene group, or wherein the hydrocarbyl substituent

is derived from polyisobutylene and wherein at least 50 mol percent of polyisobutylene macromolecules have a tri-substituted alkene group and a tetra-substituted alkene group.

15. The method of claim 1, wherein the amine is an alkylene polyamine, and preferably wherein the alkylene polyamine is ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, or mixtures of alkylene polyamines of the formula  $H_2N-(A-NH)_nH$  where A is divalent ethylene or propylene and n is an integer of from 1 to 10.