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(54) **ORTHO-ALKYLPHENOL DERIVED
MANNICH DETERGENT COMPOSITION
AND CONCENTRATE, FUEL AND METHOD
THEREOF**

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(57) **ABSTRACT**

A detergent composition comprises a Mannich reaction product of a hydrocarbyl-substituted ortho-alkyl substituted phenol (1) or a mixture of the phenol (1) and a hydrocarbyl-substituted phenol (2), an aldehyde, and an amine where the phenol (1) is present in the mixture at about 50 mole % or higher. Concentrate and fuel compositions include the detergent composition. A method of controlling deposits in an internal combustion engine comprises operating the engine with the fuel composition which results in unexpectedly superior detergent performance.

**ORTHO-ALKYLPHENOL DERIVED MANNICH
DETERGENT COMPOSITION AND
CONCENTRATE, FUEL AND METHOD THEREOF**

**CROSS-REFERENCE TO RELATED
APPLICATIONS**

[0001] This application claims priority from U.S. Provisional Application Nos. 60/288,930 and 60/288,931 filed May 4, 2001.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] This invention involves a detergent composition, concentrate and fuel compositions that include the detergent composition, and a method that includes the fuel composition in controlling engine deposits in internal combustion engines.

[0004] 2. Description of the Related Art

[0005] Hydrocarbon fuels generally contain numerous deposit-forming substances. When used in internal combustion engines, deposits tend to form on and around constricted areas of the engine in contact with the fuel. In diesel engines deposits tend to accumulate in the fuel injection system, thereby hampering good performance of the engine. In automobile engines deposits can build up on engine intake valves leading to progressive restriction of gaseous fuel mixture flow into the combustion chamber and also to valve sticking. It is common practice therefore to incorporate a detergent composition into a hydrocarbon fuel for the purpose of controlling engine deposits by inhibiting their formation and facilitating their removal, thereby maintaining or improving engine performance.

[0006] U.S. Pat. Nos. 5,634,951 (Colucci et al., filed Jun. 7, 1996) and 5,725,612 (Malfer et al., filed Apr. 10, 1997) disclose Mannich condensation products which are effective detergents for use in spark ignition fuels and that are formed from a) a hydrocarbyl substituted hydroxyaromatic compound or a hydroxyaromatic compound having both a hydrocarbyl and a C₁₋₄ alkyl substituent, b) an aldehyde and c) an aliphatic polyamine having one and only one primary or secondary amino group capable of participating in the Mannich condensation reaction.

[0007] International Publication No. WO0125294 discloses a method to prepare Mannich adducts useful as detergent additives in fuel compositions where the Mannich adduct is derived from an amine having at least one secondary amino group but no primary amino group or from an adduct of formaldehyde and an amine having at least one primary or secondary amino group.

[0008] U.S. Pat. No. 6,179,885 filed Jun. 22, 1999 (McAtee) discloses Mannich compounds useful as detergents in fuels which are derived from hydroxy containing aromatic compounds, an aldehyde or ketone, and a mixture of water and an amine where the hydroxy containing aromatic compound can be substituted with about 1 to 4 hydrocarbyl groups and the hydrocarbyl groups can be derived from polyisobutylenes having a number average molecular weight of 200 to 5,000.

[0009] U.S. Pat. Nos. 6,048,373 (Malfer et al., filed Nov. 30, 1998) and 5,697,988 (Malfer et al., filed Jun. 7, 1996)

disclose Mannich compounds useful as detergents in fuel compositions which are derived from alkyl-substituted hydroxyaromatic compounds, an aldehyde, and an amine where the alkyl-substituted hydroxyaromatic compound can be an alkyl-substituted derivative of cresol, xyleneol, hydroxydiphenyl, benzylphenol or phenethylphenol.

[0010] It has now been found that the detergent composition of the present invention, comprising a Mannich reaction product derived from a hydrocarbyl-substituted phenol having an ortho-alkyl substituent, unexpectedly provides significantly better detergency performance in a hydrocarbon fuel compared to a conventional Mannich reaction product derived from a hydrocarbyl-substituted phenol.

SUMMARY OF THE INVENTION

[0011] It is an object of the present invention to control deposits in an internal combustion engine and thus maintain or improve engine performance.

[0012] Another object of the invention is to control deposits in a gasoline engine.

[0013] A further object of this invention is to control deposits in a diesel engine.

[0014] The objects, advantages and embodiments of the present invention are in part described in the specification and in part are obvious from the specification or from the practice of this invention. Therefore, it is understood that the invention is claimed as described or obvious as falls within the scope of the appended claims.

[0015] To achieve the foregoing objects in accordance with the invention as described and claimed herein, a detergent composition of this invention useful in hydrocarbon fuels comprises a Mannich reaction product prepared by adding an aldehyde to a mixture of a phenol (1) having a hydrocarbyl substituent and an ortho-alkyl substituent; and at least one amine selected from the group consisting of a primary monoamine, and a polyamine having at least two amino groups capable of undergoing a Mannich reaction wherein at least one of the amino groups is a primary amino group; and reacting the aldehyde; the phenol (1); and the at least one amine to form the Mannich reaction product.

[0016] In a further embodiment of this invention the Mannich reaction product of the above described detergent composition is derived from a mixture of the phenol (1) and a phenol (2) having a hydrocarbyl substituent where the phenol (1) is present in the mixture at about 50 mole % or higher.

[0017] An additional embodiment of this invention is a concentrate composition comprising a solvent and the detergent composition of the present invention where the Mannich reaction product is derived from the phenol (1).

[0018] Another embodiment of the present invention is a concentrate composition comprising a solvent and the detergent composition of the present invention where the Mannich reaction product is derived from a mixture of the phenol (1) and the phenol (2).

[0019] In another instance of the present invention a fuel composition comprises a hydrocarbon fuel and the detergent composition of the present invention where the Mannich reaction product is derived from the phenol (1).

[0020] In yet another instance of the present invention a fuel composition comprises a hydrocarbon fuel and the detergent composition of the present invention where the Mannich reaction product is derived from a mixture of the phenol (1) and the phenol (2).

[0021] In yet a further embodiment of this invention a method for controlling deposits in an internal combustion engine comprises operating the engine with the fuel composition of the present invention that contains the detergent composition where the Mannich reaction product is derived from a mixture of the phenol (1) and the phenol (2).

DETAILED DESCRIPTION OF THE INVENTION

[0022] A detergent composition of the present invention useful in hydrocarbon fuels comprises a Mannich reaction product prepared by adding an aldehyde to a mixture of a phenol (1) having a hydrocarbyl substituent and an ortho-alkyl substituent; and at least one amine selected from the group consisting of a primary monoamine, and a polyamine having at least two amino groups capable of undergoing a Mannich reaction wherein at least one of the amino groups is a primary amino group; and reacting the aldehyde; the phenol (1); and the at least one amine to form the Mannich reaction product. In another embodiment of this invention the Mannich reaction product of the detergent composition is derived from a mixture of the phenol (1) and a phenol (2) having a hydrocarbyl substituent where the phenol (1) is present in the mixture at about 50 mole % or higher, preferably at about 70 mole % or higher, and more preferably at about 80 mole % or higher.

[0023] The hydrocarbyl substituent of the phenol (1) and the phenol (2) can have a number average molecular weight (Mn) of 200 to 5,000 or 200 to 750, preferably of 300 to 3,000 or 350 to 700, and more preferably of 400 to 1,500 or 450 to 650. The hydrocarbyl substituent is a univalent radical of carbon atoms that is predominantly hydrocarbon in nature but can have nonhydrocarbon substituent groups and can contain heteroatoms. The hydrocarbyl substituent can be derived from a polyolefin. The polyolefin can be a homopolymer from one olefin or a copolymer from two or more olefins. The polyolefin can be prepared from olefin monomers of 2 to about 10 carbon atoms to include ethylene, propylene, isomers of butene, isomers of decene and mixtures of two or more thereof. Examples of polyolefins are polyethylenes, polypropylenes, polybutenes and copolymers of ethylene and propylene. A preferred polyolefin is a polyisobutene (PIB) derived from a refinery stream having a butene isomer content of about 35 to 75% by weight and an isobutene content of about 30 to 60% by weight. A more preferred polyolefin is a polyisobutene having at least 70% of the olefinic double bonds at a terminal position on the carbon chain as the vinylidene type. Polyisobutenes having a high vinylidene content are highly reactive and are commercially available such as the Glissopal® series marketed by BASF.

[0024] The ortho-alkyl substituent of the phenol (1) can be an alkyl group of 1 to about 10 carbon atoms.

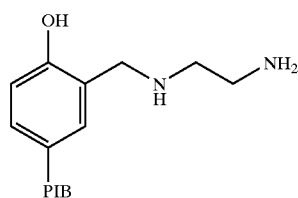
[0025] The hydrocarbyl-substituted ortho-alkyl substituted phenol (1) can be prepared by methods well known in the art including alkylation of an ortho-alkyl substituted phenol with a polyolefin using an acidic catalyst as detailed

in the examples hereinbelow. Examples of commercially available ortho-alkylphenols which are useful in this invention include o-cresol, xlenols having an ortho methyl group, o-ethylphenol, o-propylphenol, o-isopropylphenol, o-butylphenol and 2-t-butylphenol.

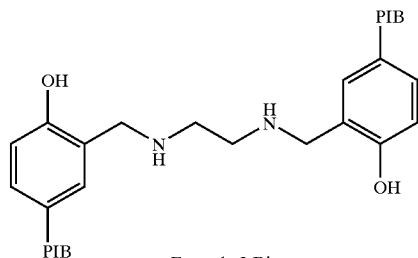
[0026] The aldehyde used to prepare the Mannich reaction product of the present invention can be an aldehyde having 1 to about 6 carbon atoms. In one embodiment formaldehyde can be used in one of its reagent forms such as paraformaldehyde and formalin. In another instance the aldehyde can have 2 to about 6 carbon atoms to include acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde and hexanal.

[0027] The amine used to prepare the Mannich reaction product of this invention is capable of undergoing a Mannich reaction and in one embodiment where the aldehyde includes formaldehyde can be selected from the group consisting of a primary monoamine, and a polyamine having at least two amino groups capable of undergoing a Mannich reaction where at least one of the amino groups is a primary amino group. Primary monoamines can have 1 to about 22 carbon atoms and include amines such as ammonia, propylamine, and butylamine. Primary monoamines also include alkanolamines having a single amino group and one or more hydroxy groups such as ethanolamine and 1-amino-2-propanol. The polyamine can be an alkylenediamine to include amines such as ethylenediamine, N-methylethylenediamine, propylenediamine, and N-methylpropylenediamine. The polyamine can be a polyalkylenepolyamine such as diethylenetriamine. The polyamine can be an alkanolamine having one or more hydroxy groups and at least two amino groups as described above such as 2-(2-aminoethylamino)ethanol. In another embodiment where the aldehyde has 2 to about 6 carbon atoms the amine used to prepare the Mannich reaction product of this invention can be selected from the group consisting of a primary monoamine, a secondary monoamine, and a polyamine having at least two amino groups capable of undergoing a Mannich reaction. The secondary mono-amine can have 2 to about 22 carbon atoms and includes dimethylamine, diethylamine, dipropylamine and dibutylamine as well as alkanolamines having a single amino group and one or more hydroxy groups such as 2-(methylamino)-ethanol and diethanolamine; also included under polyamines in addition to those described above are N,N'-dimethylethylenediamine and N,N'-dimethylpropylene-diamine.

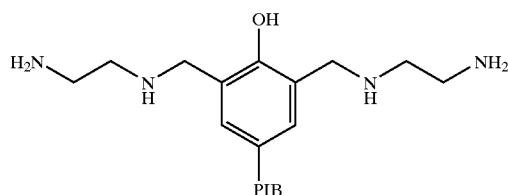
[0028] The Mannich reaction product of this invention can be prepared by methods well known in the art, and can also be prepared by processes as detailed in the examples hereinbelow which form a part of this invention. The reaction of a hydrocarbyl-substituted phenol with an aldehyde and an amine such as ethylenediamine can result in several product components being formed. For example, when a PIB-substituted phenol is reacted with formaldehyde and ethylenediamine, about three product components can be formed. The PIB phenol can undergo a single Mannich condensation with formaldehyde and the amine to form a "Mono" product component as depicted by Formula 1 below.



Formula 1 Mono



Formula 2 Bis



Formula 3 Diamine

[0029] If this Mono product component has another reactive amine site, it can condense with a second PIB phenol and formaldehyde to form a “Bis” product component as depicted by Formula 2. Alternately, the Mono product component can undergo a second condensation with formaldehyde and the amine to form a “Diamine” product component as depicted in Formula 3. Generally, all three product components will be formed in a Mannich reaction although it is possible to increase the formation of more of one of these product components by modifying the reaction conditions such as sequence of addition, dilution level, solvent selection and the molar ratio of the reactants. The Mannich reaction product of this invention is derived from a hydrocarbyl-substituted ortho-alkyl substituted phenol (1), such as a PIB-substituted ortho-cresol, so that Mono and Bis product components are formed while the Diamine product component is not formed since the phenol (1) reactant has only one ortho site available for a Mannich condensation reaction. In another aspect of this invention the Mannich reaction product is derived from a mixture of the phenol (1) and a hydrocarbyl-substituted phenol (2), such as a PIB-substituted phenol, so that the Diamine product component is formed in only a limited amount depending on the amount of the phenol (2) present in the mixture. The mole ratio of reactants in the present invention can be about 1-2 of phenol (1) or of mixture of phenol (1) and phenol (2):1-2 of aldehyde:1 of amine with a preferred ratio being about 1:1:1. In one embodiment of the present invention where the aldehyde includes formaldehyde the Mannich reaction product can be prepared by adding the aldehyde to a mixture of the phenol (1) or of the phenol (1) and the phenol (2); and the at least one amine; and reacting the aldehyde; the phenol (1) or the phenol (1) and phenol (2); and the at least one

amine to form the Mannich reaction product. The temperature of the mixture of the phenol or phenols and the amine to which the aldehyde is added will generally be elevated to a temperature at which the Mannich reaction can occur such as about 50-160° C., preferably about 70-140° C., more preferably about 100-130° C. Alternatively, the at least one amine can be added to a mixture of the phenol or phenols and the aldehyde. In another embodiment of the present invention where the aldehyde has 2 to about 6 carbon atoms the Mannich reaction product can be prepared as described above or by any other of the well known methods for preparation.

[0030] The examples and corresponding engine evaluations presented below illustrate the superior detergency performance of the Mono and Bis product components of this invention relative to conventional Mannich reaction products and the Diamine product component.

[0031] An additive package or concentrate composition of the present invention comprises the detergent composition as described above, a solvent and optionally a carrier fluid. The detergent composition is preferably present in a fuel composition as an additive package or concentrate composition. The additive package can be present in the fuel composition at about 50 to 5,000 ppm, preferably at about 125 to 3,000 ppm, and more preferably at about 200 to 900 ppm. The detergent composition is generally present in the additive package at about 5 to 40% by weight. Suitable carrier fluids include alkylphenols, optionally alkoxyated; esters of carboxylic acids with alcohols, polyols and glycol ethers to include vegetable oils and where the acids can be saturated or unsaturated; phthalate esters; trimellitate esters; alkoxyated alcohols or polyols; polyalkylene glycols; polyetheramines such as cynaoethylated and hydrogenated alkoxyated alcohols or polyalkylene glycols; amine alkoxyates and mineral oils. Suitable solvents may include most known aromatic or aliphatic hydrocarbons, glycol ethers, alcohols and mixtures thereof that result in a fluid, homogeneous composition.

[0032] A fuel composition of the present invention comprises a hydrocarbon fuel and the detergent composition as described above comprising a Mannich reaction product derived from a hydrocarbyl-substituted ortho-alkyl substituted phenol (1) where the ortho-alkyl substituent has 1 to 10 carbon atoms. In another embodiment of the invention a fuel composition comprises a hydrocarbon fuel and the above described detergent composition where the Mannich reaction product is derived from a mixture of the phenol (1) and the phenol (2) where the phenol (1) is present in the mixture at 50 mole % or higher. The invention in a still further aspect is a fuel composition comprising a hydrocarbon fuel and the above-described additive package or concentrate composition containing the detergent composition of the present invention. The detergent composition can be present in the fuel composition from 10 to 1,000 ppm, preferably from 30 to 500 ppm, and more preferably from 50 to 250 ppm.

[0033] The hydrocarbon fuel of the present invention may suitably comprise a hydrocarbon fraction boiling in the gasoline range or a hydrocarbon fraction boiling in the diesel range.

[0034] Gasolines suitable for use in spark ignition engines, e.g. automobile engines, generally boil in the range from 30 to 230° C. Such gasolines may comprise mixtures of satu-

rated, olefinic and aromatic hydrocarbons. They may be derived from straight-run gasoline, synthetically produced aromatic hydrocarbon mixtures, thermally or catalytically cracked hydrocarbon feedstocks, hydrocracked petroleum fractions or catalytically reformed hydrocarbons. The octane number of the base fuel is not critical and will generally be above 65. In the gasoline, hydrocarbons may be replaced in part by alcohols, ethers, ketones or esters, typically in an amount up to 20% by weight.

[0035] Alternatively, as the liquid hydrocarbon fuel there may be used any fuel suitable for operating spark compression engines, such as those which may be found in road vehicles, ships and the like. Generally, such a diesel fuel will boil in the range from about 140° C. to about 400° C. (at atmospheric pressure), particularly in the range from about 150 to 390° C., especially from about 175 to 370° C. Such fuels may be obtained directly from crude oil (straight-run) or from a catalytically or thermally cracked product or a hydrotreated product, or from a mixture of the aforesaid. Alternatively there may be used a biofuel, for example, rape seed methyl ester. The cetane number will typically be in the range from 25 to 60. The hydrocarbon fuel can also be a mixture of a diesel fuel and a biofuel.

[0036] The fuel composition contains the detergent composition of this invention in an amount sufficient to provide detergency. Typically in a gasoline fuel this amount will be in the range from 10 to 1000 ppm w/w based on the total weight of the composition. Typically in a diesel fuel this amount will be in the range from 20 to 500 ppm w/w based on the total weight of the composition.

[0037] The fuel composition and concentrate composition may suitably be prepared by blending the various components until the mixture is homogeneous.

[0038] The fuel composition and concentrate composition in addition to the detergent composition may contain known additives. The nature of the additives will depend to some extent on the end-use of the fuel composition. Diesel fuel compositions may contain nitrates or nitrites as a cetane improver and copolymers of ethylene and vinyl esters, e.g. vinyl acetate, as a cold flow improver. Gasoline fuel compositions may contain a lead compound as an anti-knock additive, an antioxidant, e.g. 2,6-di-tert-butyl phenol, an anti-knock compound other than a lead compound such as cyclopentadienyl manganese tricarbonyl compounds, and an additional detergent, for example, a PIB-substituted polyamine, a polyetheramine such as cyanoethylated and hydrogenated alkoxyated alcohols, and mixtures thereof. Other additives that can be present in the fuel and concentrate compositions include corrosion inhibitors such as alk-enylsuccinic acids, anti-static agents, biocidal additives, smoke suppressants, antifoam agents such as silicone fluids, lubricity additives such as tall oil fatty acid, and demulsifiers such as alkoxyated alkylphenols. These additives may be blended directly into the fuel composition or may be incorporated by way of a concentrate composition.

[0039] The method of the present invention of controlling deposits in an internal combustion engine comprises operating the engine with the fuel composition of the present invention as described above. The internal combustion engine in one instance is a gasoline engine and in another instance is a diesel engine.

[0040] The invention will now be further illustrated in the following examples and corresponding performance evalu-

ations in engine testing which demonstrate the superior performance of the invention in controlling engine deposits.

EXAMPLE 1

Preparation of 1000 Mn Polyisobutene-Substituted Phenol

[0041] 203.2 g (2.16 mol) of phenol was melted at 40° C. and added to boron trifluoride etherate (73.5 ml, 0.60 mol) in a 5 litre round bottomed flask. Glissopal® 1000 (1090 g, 1.09 mol), a "highly reactive" polyisobutene (PIB) (Mn=1000), was dissolved in hexane (1863 ml) and the solution added to the flask containing the phenol via a pressure equalising dropping funnel, at a rate sufficient to maintain the temperature of the reaction mixture at 22-27° C. This took three hours. The solution was stirred for a further 16 hours at room temperature before ammonia (400 ml of 30% w/w aqueous, 2.88 mol) was added. The solution turned a deep blue colour. 1000 ml of water was added and the mixture stirred, after which it was separated in a five litre separating funnel and the aqueous layer extracted with 4x500 ml hexane. The organic layers were combined and dried over MgSO₄ overnight, then filtered through a 12 mm Celite pad. The solvent was removed from the filtrate at 80° C./23"Hg on a rotary evaporator.

EXAMPLE 2

Preparation of 1000 Mn Polyisobutene-Substituted o-Cresol

[0042] 233.3 g (2.16 mol) of o-Cresol was melted at 40° C. and added to boron trifluoride etherate (73.5 ml, 0.60 mol) in a 5 litre round bottomed flask. Glissopal® 1000 (1090 g, 1.09 mol), a "highly reactive" polyisobutene (PIB) (Mw=1000), was dissolved in hexane (1863 ml) and the solution added to the flask containing the o-Cresol via a pressure equalising dropping funnel, at a rate sufficient to maintain the temperature of the reaction mixture at 22-27° C. This took three hours. The solution was stirred for a further 16 hours at room temperature before ammonia (400 ml of 30% w/w aqueous, 2.88 mol) was added. The solution turned a deep blue colour. 1000 ml of water was added and the mixture stirred, after which it was separated in a five litre separating funnel and the aqueous layer extracted with 4x500 ml hexane. The organic layers were combined and dried over MgSO₄ overnight, then filtered through a 12 mm Celite pad. The solvent was removed from the filtrate at 80° C./23" Hg on a rotary evaporator.

EXAMPLE 3

Preparation of 550 Mn Polyisobutene-Substituted o-Cresol

[0043] 233.3 g (2.16 mol) of o-Cresol was melted at 40° C. and added to boron trifluoride etherate (73.5 ml, 0.60 mol) in a 5 litre round bottomed flask. Glissopal® 550 (594 g, 1.09 mol), a "highly reactive" polyisobutene (PIB) (Mn=550), was dissolved in hexane (1024 ml) and the solution added to the flask containing the phenol via a pressure equalising dropping funnel, at a rate sufficient to maintain the temperature of the reaction mixture at 22-27° C. This took three hours. The solution was stirred for a further 16 hours at room temperature before ammonia (400 ml of 30%

w/w aqueous, 2.88 mol) was added. The solution turned a deep blue colour. 1000 ml of water was added and the mixture stirred, after which it was separated in a five litre separating funnel and the aqueous layer extracted with 4x500 ml hexane. The organic layers were combined and dried over MgSO_4 overnight, then filtered through a 12 mm Celite pad. The solvent was removed from the filtrate at 80° C./23"Hg on a rotary evaporator.

EXAMPLE 4

Comparative

Preparation of Conventional Adduct of 1000 Mn Polyisobutene-Substituted Phenol and Ethylenediamine

[0044] The polyisobutene-substituted phenol of Example 1 (300 g, 0.295 mol), ethylenediamine, (EDA) (19.47 g, 0.325 mol) and toluene (100 g, solvent) were charged to a round-bottomed flask and heated rapidly to 100° C., formaldehyde solution 37% by wt. (27.5 g, 0.339 mol) was then added over 15 minutes via a pressure equalising dropping funnel. The reaction was heated to 130° C. for two hours and 5.5 ml of aqueous distillate collected. The reaction was then refluxed at 130° C. for 2.5 hours prior to vacuum distillation at 27"Hg vacuum and 130° C. Analysis revealed 1.20% nitrogen, alkalinity value of 48 mgKOH/g.

EXAMPLE 5

Preparation of Mainly Mono Adduct of 1000 Mn Polyisobutene-Substituted o-Cresol and Ethylenediamine

[0045] Ethylenediamine (7.1 g, 0.118 mol), formaldehyde solution 37% wt. (10.5 g, 0.130 mol) and 2-Ethylhexanol (225 g, solvent) were charged to a round-bottomed flask and heated rapidly to 100° C. The polyisobutene-substituted o-Cresol from Example 2 (112.2 g, 0.101 mol) was dissolved in 2-ethylhexanol (450 g, solvent) and added to the reaction via a pressure equalising dropping funnel over a two hour period. The reaction was heated to 130° C. over two hours and 9.1 ml of aqueous distillate was collected. The reaction was then refluxed at 130° C. for 2.5 hours prior to vacuum distillation at 27"Hg vacuum and 130° C. The product of reaction was washed with 2x100 ml of hot water to remove any unreacted residual amine. Analysis revealed 1.209% nitrogen, alkalinity value of 8.84 mgKOH/g.

EXAMPLE 6

Preparation of Mainly Bis Adduct of 1000 Mn Polyisobutene-Substituted o-Cresol and Ethylenediamine

[0046] The reaction product from Example 5 (100 g, 0.085 mol), the reaction product from Example 2 (70.55 g, 0.067 mol) and 2-ethylhexanol (110 g, solvent) were charged to a round-bottomed flask and heated rapidly to 100° C. Formaldehyde solution 37% wt. (4.02 g, 0.134 mol) was added to the reaction over 15 minutes via a pressure equalising dropping funnel. The reaction was heated to 130° C. over two hours. The reaction was then refluxed at 130° C. for 2.5 hours prior to vacuum distillation at 27"Hg vacuum and 130° C. The product of reaction was washed with 2x100 ml

of hot water to remove any unreacted residual amine. Analysis revealed 0.65% nitrogen.

EXAMPLE 7

Comparative

Preparation of Mainly Diamine Adduct of 1000 Mn Polyisobutene-Substituted Phenol and Ethylenediamine

[0047] The reaction product from Example 1 (200 g, 0.183 mol), ethylenediamine (23.93 g, 0.399 mole) and 2-Ethylhexanol (90 g, solvent) were charged to a round-bottomed flask and heated rapidly to 100° C. Formaldehyde solution 37% wt. (34.4 g, 0.424 mol) was added to the reaction over 15 minutes via a pressure equalising dropping funnel. The reaction was heated to 130° C. over two hours. The reaction was then refluxed at 130° C. for 2.5 hours prior to vacuum distillation at 27"Hg vacuum and 130° C. 35 ml of aqueous distillate was collected. The product of reaction was washed with 2x100 ml of hot water to remove any unreacted residual amine. Analysis revealed 1.53% nitrogen, alkalinity value of 81.8 mgKOH/g.

EXAMPLE 8

Preparation of Adduct of 1000 Mn Polyisobutene-Substituted o-Cresol and Ethylenediamine

[0048] The polyisobutene-substituted o-Cresol from Example 2 (845 g, 0.761 mol), ethylenediamine, (50.23 g, 0.837 mol) and a highly aromatic type solvent (638 g) were charged to a round-bottomed flask and heated rapidly to 100° C. Formaldehyde solution 37% by wt. (74.04 g, 0.913 mol) was then added over 15 minutes via a pressure equalising dropping funnel. The reaction was heated to 130° C. for 2 hours and 78 ml of aqueous distillate was collected. The reaction was then refluxed at 130° C. for 2.5 hours prior to vacuum distillation at 27"Hg vacuum and 130° C. Analysis revealed 1.04% nitrogen, alkalinity value of 36.7 mgKOH/g.

EXAMPLE 9

Preparation of Adduct of 550 Mn Polyisobutene-Substituted o-Cresol and Ethylenediamine

[0049] The polyisobutene-substituted o-Cresol from Example 3 (900 g, 1.370 mol), ethylenediamine (90.41 g, 1.507 mol) and a highly aromatic type solvent (545 g) were charged to a round-bottomed flask and heated rapidly to 100° C. Formaldehyde solution 37% by wt. (127.7 g, 1.575 mol) was then added over 15 minutes via a pressure equalising dropping funnel. The reaction was heated to 130° C. for 2 hours and 107 ml of aqueous distillate was collected. The reaction was then refluxed at 130° C. for 2.5 hours prior to vacuum distillation at 27"Hg vacuum and 130° C. Analysis revealed 1.71% nitrogen, alkalinity value of 71.5 mgKOH/g.

EXAMPLE 10

Preparation of Mono Adduct of 1000 Mn Polyisobutene-Substituted o-Cresol and a Methyl hindered Ethylenediamine

[0050] The polyisobutene-substituted o-Cresol of Example 2 (250 g, 0.228 mol), N,N,N' -trimethylethylenedi-

amine (25 g, 0.245 mol), and toluene (100 g, solvent) were charged to a round-bottomed flask and heated rapidly to 100°C. Formaldehyde solution 37% by wt. (22.0 g, 0.271 mol) was then added over 15 minutes via a pressure equalising dropping funnel. The reaction was heated to 130°C. for 2 hours and 19.0 ml of aqueous distillate collected: the reaction was then refluxed at 130°C. for 2.5 hours prior to vacuum distillation at 27"Hg vacuum and 130°C. where 256 g of organic distillate was collected. The product of reaction was washed with 2×100 ml of hot water to remove any unreacted residual amine. The product was then re-dissolved into 150 gms of to give 65% by wt active solution. Analysis revealed 1.88% nitrogen, alkalinity value of 67.7 mgKOH/g.

EXAMPLE 11

Preparation of Bis Adduct of 1000 Mn Polyisobutene-Substituted o-Cresol and a Methyl Hindered Ethylenediamine

[0051] The polyisobutene-substituted o-Cresol of Example 2 (300 g, 0.274 mol), N,N'-dimethylethylenediamine (12.4 g, 0.141 mol), and toluene (300 g, solvent) were charged to a round-bottomed flask and heated rapidly to 100°C. Formaldehyde solution 37% by wt. (26.3 g, 0.324 mol) was then added over 15 minutes via a pressure equalising dropping funnel. The reaction was heated to 130°C. for 2 hours, the reaction was then refluxed at 130°C. for 2.5 hours prior to vacuum distillation at 27"Hg vacuum and 130°C. The product of reaction was washed with 2×100 ml of hot water to remove any unreacted residual amine. The product was then re-dissolved in toluene sufficient to give a 65% by wt active solution. Analysis revealed 0.73% nitrogen, alkalinity value of 28.5 mgKOH/g.

EXAMPLE 12

Comparative

Preparation of Diamine Adduct of 1000 Mn Polyisobutene-Substituted Phenol and a Methyl Hindered Ethylenediamine

[0052] The polyisobutene-substituted phenol of Example 1 (300 g, 0.274 mol), N,N,N'-dimethylethylenediamine (61.0 g, 0.598 mol), and toluene (300 g, solvent) were charged to a round-bottomed flask and heated rapidly to 100°C. Formaldehyde solution 37% by wt. (53.0 g, 0.654 mol) was then added over 15 minutes via a pressure equalising dropping funnel. The reaction was heated to 130°C. for 2 hours, the reaction was then refluxed at 130°C. for 2.5 hours prior to vacuum distillation at 27"Hg vacuum and 130°C. The product of reaction was washed with 2×100 ml of hot water to remove any unreacted residual amine. The product was then re-dissolved in toluene sufficient to give a 65% by wt active solution. Analysis revealed 2.55% nitrogen, alkalinity value of 96.4 mgKOH/g.

EXAMPLE 13

Preparation of a Mono Adduct of 550 Mn Polyisobutene-Substituted o-Cresol and Dimethylamine

[0053] The polyisobutene-substituted o-Cresol of Example 3 (350 g, 0.533 mol), dimethylamine at 40% in water (69.65 g, 0.633 mol), and toluene (114 g, solvent) were charged to a round-bottomed flask and heated rapidly

to 100°C. Formaldehyde solution 37% by wt solution in water (53.67 g, 0.662 mol) was then added over 20 minutes via a pressure equalising dropping funnel. The reaction was heated to 130°C. as azeo distillation allowed, the reaction was then refluxed at 130°C. for 2.5 hours prior to vacuum distillation at 27"Hg vacuum and 130°C. where 110 g of toluene was removed. Analysis revealed 1.6% nitrogen, alkalinity value of 71.4 mgKOH/g.

Engine Tests

[0054] A. 40 hr Honda Generator Test

[0055] Mannich reaction products from the preceding examples were evaluated for deposit control in a Honda 2 cylinder generator at a treat rate of 70 ppm on an active chemicals basis in BP-15 fuel. In this test a lower deposit is better with values below 10 considered excellent.

TABLE 1

EXAMPLE	DEPOSITS (avg. mg)
No additive	107
4 Conventional	25.5
5 Mono	2.5
6 Bis	8.0
7 Diamine	125

[0056] In Table 1 both the Mono and Bis Mannichs of Examples 5 and 6 gave excellent performance compared to the conventional Mannich of Example 4. The Diamine Mannich of Example 7 was worse than the base fuel having no additive. The absence or reduction of a Diamine Mannich type component in the Mono and Bis Mannichs of Examples 5 and 6 is responsible for their improved performance over the conventional Mannich of Example 4.

TABLE 2

EXAMPLE	DEPOSITS (avg. mg)
No additive	73.1
4 Conventional	26.9
10 Mono, Hindered Amine	3.8
11 Bis, Hindered Amine	6.5
12 Diamine, Hindered Amine	51.5

[0057] In Table 2 the Mono and Bis Mannichs prepared from hindered amine in Examples 10 and 11 also provide excellent performance compared to the conventional Mannich of Example 4. The Diamine Mannich prepared from a hindered amine in Example 12 gave poor performance although better than the base fuel having no additive. These results further demonstrate the performance advantage of this invention when the Diamine component is eliminated from or reduced in a Mannich reaction product.

TABLE 3

EXAMPLE	DEPOSITS (avg. mg)
No additive	114.3
4 Conventional	65
	(avg of three)
13 Mono, 550 Mn, Monoamine	7.9

[0058] In Table 3 the Mono Mannich of Example 13 from 550 Mn PIB ortho-cresol and a monoamine gave excellent

performance compared to conventional Mannich of Example 4 further demonstrating the performance advantage of the present invention.

[0059] B. MB M102 CEC Inlet Valve Deposit Test

[0060] Several Mannich reaction products prepared in the examples above were evaluated as detergency additives in fuels according to a standard engine test, following method CEC F-05 A-93 on a Mercedes Benz M 102.982 engine. The fuel employed was unleaded CEC DF-12 batch 2. The compounds tested were incorporated in an additive package with the following formulation:

Branched tridecanol/propylene oxide (1:24 mol ratio) carrier	28.375% by weight
Aromatic solvent	38.105% by weight
Additive of Examples 4, 8, 9	33.520% by weight

[0061] Measurements were made of the inlet valve deposits (IVD), and the valves were also given a visual rating. In this test a visual rating of 9.5 or greater is considered to be a good result.

TABLE 4

EXAMPLE	Treat Rate ppm m/m	DEPOSITS (mg)	VISUAL RATING
no additive package	0	494	7.14
4 (1000 phenol)	735	8	9.86
4 (1000 phenol)	600	38	9.65
8 (1000 mw cresol)	600	3	9.88
9 (550 mw cresol)	600	7	9.71

[0062] The results show that Mannichs such as those from polyisobutene-substituted o-Cresol and ethylene-diamine (Examples 8 and 9) have improved IVD control ability in comparison to conventional Mannichs such as those from polyisobutene-substituted phenol and ethylenediamine (Example 4) because Examples 8 and 9 do not contain Diamine type structures. The results also indicate that 550 Mn polyiso-butene o-Cresol derivatives have equal performance to the 1000 Mn polyisobutylene o-Cresol derivatives in this test.

1. A detergent composition useful in hydrocarbon fuels, comprising:

a Mannich reaction product prepared by adding an aldehyde to a mixture of a phenol (1) having a hydrocarbyl substituent and an ortho-alkyl substituent; a phenol (2) having a hydrocarbyl substituent wherein the phenol (1) is present at about 50 mole % or higher in a combination of the phenol (1) and the phenol (2); and at least one amine selected from the group consisting of a primary monoamine, and a polyamine having at least two amino groups capable of undergoing a Mannich reaction wherein at least one of the amino groups is a primary amino group; and reacting the aldehyde; the phenol (1); the phenol (2); and the at least one amine to form the Mannich reaction product.

2. A concentrate composition, comprising:

a solvent; and

the detergent composition of claim 1.

3. A fuel composition, comprising.

a hydrocarbon fuel; and

the detergent composition of claim 1.

4. The detergent composition of claim 1; wherein the phenol (1) is present at about 70 mole % or higher in the combination of the phenol (1) and the phenol (2).

5. The detergent composition of claim 4; wherein the phenol (1) is present at about 80 mole % or higher in the combination of the phenol (1) and the phenol (2).

6. The detergent composition of claim 4; wherein the ortho-alkyl substituent of the phenol (1) has 1 to about 10 carbon atoms.

7. The detergent composition of claim 6; wherein the ortho-alkyl substituent of the phenol (1) has 1 carbon atom.

8. The detergent composition of claim 4; wherein the hydrocarbyl substituent of the phenol (1) and the phenol (2) is derived from a polyolefin having a number average molecular weight of 200 to 5,000.

9. The detergent composition of claim 8; wherein the hydrocarbyl substituent has a number average molecular weight of 200 to 750.

10. The detergent composition of claim 8; wherein the polyolefin is a polyisobutene.

11. The detergent composition of claim 10; wherein the polyisobutene has a vinylidene content of at least 70%.

12. The detergent composition of claim 4; wherein the aldehyde is formaldehyde.

13. The detergent composition of claim 12; wherein the amine is propylamine, butylamine, ethylenediamine, N-methylethylenediamine, propylenediamine, N-methylpropylenediamine, diethylenetriamine, ethanolamine, or 2-(2-aminoethyl-amino)ethanol.

14. The detergent composition of 4; wherein the aldehyde has 2 to about 6 carbon atoms; and the at least one amine is selected from the group consisting of a primary monoamine, a secondary monoamine, and a polyamine having at least two amino groups capable of undergoing a Mannich reaction.

15. A concentrate composition, comprising:

a solvent; and

the detergent composition of claim 4.

16. The concentrate composition of claim 15, further comprising:

a carrier fluid.

17. A fuel composition, comprising:

a hydrocarbon fuel; and

the concentrate composition of claim 16.

18. A fuel composition, comprising:

a hydrocarbon fuel; and

the detergent composition of claim 4.

19. The fuel composition of claim 18; wherein the hydrocarbon fuel is a gasoline, a diesel fuel, a biofuel, or a mixture of a diesel fuel and a biofuel.

20. A method for controlling deposits in an internal combustion engine, comprising:

operating the engine with the fuel composition of claim 18.

21. The method of claim 20; wherein the engine is a gasoline engine or a diesel engine.