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(54) **USES OF CONTROLLING PISTON VARNISH FORMATION IN AN INTERNAL COMBUSTION ENGINE**

VERWENDUNGEN ZUR KONTROLLE DER LACKBILDUNG AM KOLBEN EINES
VERBRENNUNGSMOTORS

UTILISATIONS DE LA RÉGULATION DE LA FORMATION DE VERNIS DE PISTON DANS UN
MOTEUR À COMBUSTION INTERNE

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US-A1- 2006 277 820**

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Description

[0001] This invention relates to uses of controlling piston varnish formation in a spark-ignition internal combustion engine, and in other aspects to the use of a combination of additives as a piston varnish controlling additive in a fuel composition for a spark-ignition internal combustion engine. The invention also relates to the use for controlling piston ring sticking and blow-by in an engine.

[0002] During operation of a spark-ignition internal combustion engine, blow-by gases pass from the combustion chamber over piston surfaces and into the engine sump. Fuel, lubricating oil, water vapour and combustion products may be carried with the blow-by gases and can deposit on the piston metal surfaces. High temperatures are encountered on the piston metal surfaces, which causes these components to be condensed, compacted and partially oxidised to form a varnish-like substance. The chemical composition of the fuel is therefore a factor in the rate and severity of piston varnish formation. Piston varnish builds up more in areas of low metal surface clearance (piston rubbing surface areas).

[0003] Piston varnish can reduce the performance of an engine. For instance, piston varnish can be a factor in enhanced piston ring sticking, enhanced levels of blow-by, enhanced levels of engine wear, reduced fuel economy and reduced power output.

[0004] Typically, formation of piston varnish has been controlled using additives in lubricating oils. According to the abstract of US3784474, a lubricating oil containing a hydrocarbyl-substituted amine ashless detergent, a polyoxyalkylene derivative and an alkaline earth metal reduces or prevents the formation of varnish, sludge and deposits on the inner metallic surfaces of internal combustion engines.

[0005] However, there remains a need for a fuel composition comprising components which provides suitable detergency to a spark-ignition internal combustion engine, yet controls the formation of piston varnish.

[0006] According to its paragraph [0145], US2013/000584 discloses a fuel composition comprising one or more poly(hydroxycarboxylic acid) derivatives having a terminal amine group for inhibiting the formation of varnish deposits on engine parts. The detergency of the fuel composition is not disclosed in US2013/000584.

[0007] According to its paragraph [0002], US2006/0277820 relates to a deposit control additive composition for a fuel comprising polyisobutylene amine (PIBA) having an average molecular weight of about 700 to about 1000 and a Mannich Base as synergistic components of the deposit control additive formulation.

[0008] Paragraph [0015] of US 2006/0277820 states:

"Mannich bases have been used in isolation or in combination with diamine to reduce deposits on carburettor surfaces. As disclosed in the present application, a surprising result has been achieved by using a Mannich base and Polyisobutylene amine as synergistic components of a deposit control additive formulation to drastically reduce deposits on carburettor and keep port fuel injectors and intake valves clean in gasoline fuelled spark ignition internal combustion engines."

[0009] Paragraph [0069] of US2006/0277820 relates to an Inlet Valve Deposit Test using Mercedes Benz M111 Engine as per CEC F-20-A-98 and paragraph [0070] relates to Port Fuel Injector Fouling Bench Test. The formation of piston varnish is not addressed by the disclosure in US2006/0277820.

[0010] According to its abstract, GB-A-2 010 324 relates to a dispersant additive for use in a hydrocarbon fuel, especially a fuel for a compression ignition engine, comprising a mixture of a polyalkylene amine and a Mannich base reaction product of an alkylphenol, an aldehyde and an amine. The additive provides unexpected stability in preventing thermal degradation of fuels, particularly diesel fuels.

[0011] According to its abstract, US-A-2003/029077 discloses a fuel composition comprising a hydrocarbon fuel, a combination of nitrogen-containing detergents that includes a hydrocarbyl-substituted polyamine and a Mannich reaction product, and optionally a fluidizer. Methods of operating and of controlling deposits in an internal combustion engine involve fueling the engine with the fuel composition which results in unexpectedly effective and efficient control of deposits in the fuel induction system. Therefore, there remains a need for methods and uses aspects of which reduce or at least mitigate problems, for example as identified above.

[0012] According to an aspect of the present invention there is provided the use as a piston varnish controlling additive in a fuel composition for a spark-ignition internal combustion engine or a compression-ignition gasoline internal combustion engine of:

- a. a hydrocarbyl-substituted aromatic compound; and
- b. a polyalkylene amine.

[0013] According to another aspect of the present invention there is provided the use of an additive composition comprising a combination of:

- a. a hydrocarbyl-substituted aromatic compound; and
- b. a polyalkylene amine

for improving the piston varnish control performance of a fuel composition in a spark-ignition internal combustion engine or a compression-ignition gasoline internal combustion engine.

[0014] According to a further aspect of the present invention there is provided the use as at least one of a piston ring sticking and blow-by controlling additive in a fuel composition for a spark-ignition internal combustion engine or a compression-ignition gasoline internal combustion engine of:

- a. a hydrocarbyl-substituted aromatic compound; and
- b. a polyalkylene amine.

[0015] The hydrocarbyl-substituted aromatic compound is a Mannich base additive. In embodiments, the polyalkylene amine is a polyisobutylene amine.

[0016] Aspects of the present invention address the technical problems identified and others, by the use in combination of the hydrocarbyl-substituted aromatic compound and a polyalkylene amine.

[0017] In particular it has been found that a fuel composition comprising a combination of a hydrocarbyl-substituted aromatic compound and a polyalkylene amine exhibits beneficial piston varnish formation control when used in a spark-ignition internal combustion engine. The fuel composition may also exhibit beneficial piston varnish formation control when used in a compression-ignition gasoline internal combustion engine.

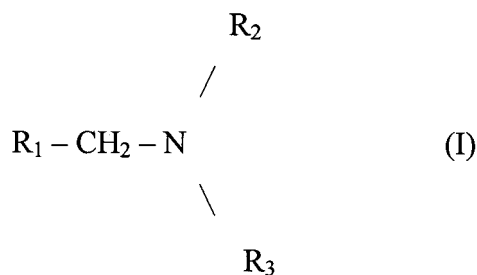
Polyalkylene Amine.

[0018] The polyalkylene amine may be a poly C₁₋₁₀-alkylene amine. For instance, the polyalkylene amine may be polyethylene amine, a polypropylene amine, a polybutylene amine, a polypentylene amine or a polyhexylene amine. In examples, the polyalkylene amine is a polybutylene amine, in particular a polyisobutylene amine.

[0019] Polyisobutylene amines are also sometimes called polyisobutylamine or PIBA. Examples of suitable polyisobutylene amines include mono-amines, di-amines and polyamines of polyisobutylene including for example, polyisobutylene that is a homopolymer of isobutylene and polyisobutylene that is a polymer of isobutylene with minor amounts (for example up to 20% by weight), of one or more other monomers including for example n-butene, propene and mixtures thereof.

[0020] Examples of suitable polyisobutylene amines include polyisobutylene amines disclosed in, and/or obtained or obtainable by methods described in, US4832702, US6140541, US6909018 and/or US7753970.

Examples of suitable polyisobutylene amines include polyisobutylene amines disclosed in, and/or obtained or obtainable by methods described in, US4832702. Thus, suitable polyisobutylene amines include compounds represented by the structural formula I:



in which R₁ is a polybutyl- or polyisobutyl group derivable or derived from isobutene and up to 20% by weight of n-butene and

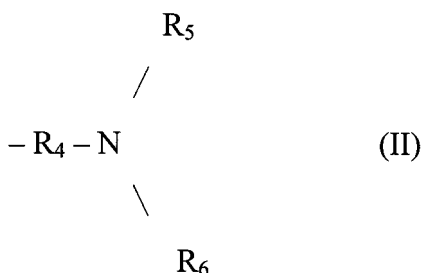
R₂ and R₃ are identical or different and are each independently:

- hydrogen;
- an aliphatic or aromatic hydrocarbyl group;
- a primary or secondary, aromatic or aliphatic aminoalkylene group or polyaminoalkylene group;
- a polyoxyalkylene group;
- a heteroaryl or heterocyclyl group; or
- together with the nitrogen atom to which they are bonded form a ring in which further hetero atoms may be present.

[0021] In at least some examples, R₂ and R₃ are identical or different and are each independently:

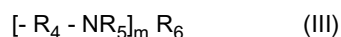
- hydrogen;

alkyl;
aryl;
hydroxyalkyl; or
an aminoalkylene group represented by the general formula (II):



wherein R_4 is alkylene and R_5 and R_6 are identical or different and are each independently: hydrogen; alkyl; aryl; hydroxyalkyl; polybutyl; or polyisobutyl; or

a polyaminoalkylene group represented by the general formula (III):



wherein the R_4 groups are the same or different and the R_5 groups are the same or different and R_4 , R_5 and R_6 have the above meaning and m is an integer from 2 to 8; or

a polyoxyalkylene group represented by the general formula (IV):



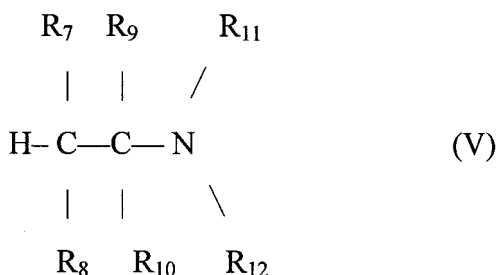
wherein the R_4 groups are the same or different and have the above meaning, X is alkyl or H and n is an integer from 1 to 30.

[0022] In at least some examples R_2 and R_3 together with the nitrogen atom to which they are bonded form a morpholinyl, pyridyl, piperidyl, pyrrolyl, pyrimidinyl, pyrrolinyl, pyrrolidinyl, pyrazinyl or pyridazinyl group.

[0023] In at least some examples R_1 is a polybutyl or polyisobutyl group containing 20 to 400 carbon atoms which is derived or derivable from isobutene and up to 20% by weight n-butene.

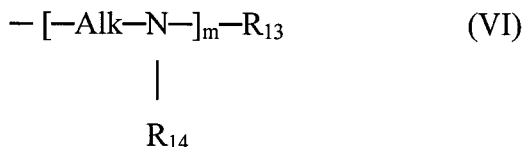
[0024] In at least some examples R_1 is a polybutyl or polyisobutyl group containing 32 to 200 carbon atoms which is derived or derivable from isobutene and up to 20% by weight n-butene and R_2 and R_3 identical or different and are each independently: hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, pentyl, hexyl, phenyl, $-CH_2-CH_2-NH_2$, $-CH_2-CH_2-CH_2-N(CH_3)_2$, or $[-CH_2-CH_2-NH]_p-CH_2-CH_2-NH_2$ where p is an integer from 1 to 7, for example 1 to 3, $-CH_2-CH_2-OH$, $[-CH_2-CH_2-O]_q-CH_2-OH$ where q is an integer from 1 to 30, or together with the nitrogen atom to which they are bonded, form a morpholinyl group.

[0025] Examples of suitable polyisobutylene amines additives also include polyisobutylene amines disclosed in, and/or obtained or obtainable by methods described in, described in US6140541 and US6909018. Thus, examples of suitable polyisobutylene amines include compounds represented by the formula (V):



wherein R_7 , R_8 , R_9 and R_{10} independently of one another, are each hydrogen or an unsubstituted or substituted, saturated or mono- or polyunsaturated aliphatic group exhibiting a number average molecular weight of up to 40000, at least one of the groups R_7 to R_{10} exhibiting a number average molecular weight of from 150 to 40000, and R_{11} and R_{12} independently of each other are each H; an alkyl group, for example a C_1 to C_{18} alkyl group; a cycloalkyl group; a hydroxyalkyl group;

an aminoalkyl group; an alkenyl group; an alkynyl group, an aryl group; an arylalkyl group; an alkylaryl group; a heteroaryl group; an alkylene-imine group represented by the formula (VI):



wherein:

Alk is a straight-chain or branched alkylene

m is an integer from 0 to 10; and

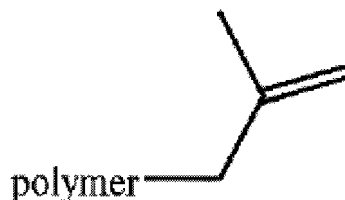
R₁₃ and R₁₄, independently of one another, are each H; an alkyl group, for example a

C₁ to C₁₈ alkyl group; a cycloalkyl group; a hydroxyalkyl group; an aminoalkyl group; an alkenyl group; an alkynyl group, an aryl group; an arylalkyl group; an alkylaryl group; a heteroaryl group or, together with the nitrogen atom to which they are bonded, form a heterocyclic structure, or

R₁₁ and R₁₂, together with the nitrogen atom to which they are bonded, form a heterocyclic structure.

[0026] In at least some examples, each of R₁₁, R₁₂, R₁₃ and R₁₄ are independently substituted by further alkyl groups carrying hydroxy or amino groups.

[0027] Examples of suitable polyisobutylene amines additives also include polyisobutylene amines disclosed in, and/or obtained or obtainable by methods described in, US7753970. Thus, examples of suitable polyisobutylene amines include polyisobutylene amines that are derived or derivable from polyisobutenes derived or derivable from isobutene or an isobutenic monomer mixture, for example a mixture of isobutene and up to 20% by weight of n-butene. Suitable polyisobutylene amines include polyisobutylene amines derived or derivable from polyisobutylene that is derived or derivable by the polymerisation of identical or different straight-chain or branched C₄ olefin monomers, which in at least some examples, are suitably randomised in the polymerisation product. Suitable polyisobutylene amines include polyisobutylene amines that are derived or derivable from highly reactive polyisobutenes. Highly reactive polyisobutenes contain a high content of terminal double bonds (also sometimes referred to alpha-olefinic double bonds and/or vinylidene double bonds), for example at least 20 %, or at least 50%, or at least 70% of the total olefinic double bonds in the polyisobutene. These are sometimes represented by the general structure:



[0028] Highly reactive polyisobutenes may be made by methods described for example in US4152499.

[0029] In at least some examples the polyisobutylene amine contains a polyisobutenic group that exhibits a number average molecular weight of from about 200 to about 10000, for example from about 500 to about 5000 or from about 700 to about 1500 or from about 800 to about 1200 or from about 850 to about 1100, for example about 1000.

[0030] In at least some examples, the polyisobutylene amine is derived from or derivable from a polyisobutene that exhibits at least one of the following properties:

(i) being derivable or derived from isobutene and up to 20% by weight of n-butene;

(ii) being derivable or derived from isobutenic mixture containing at least 70 mol. % vinylidene double bonds based on the total olefinic bonds in the polyisobutene;

(iii) containing at least 85% by weight isobutylene units;

(iv) a polydispersity in the range of from 1.05 to 7

[0031] Methods of making suitable polyisobutylene amines are described for example in US4832702, US6140541, US6909018 and/or US7753970.

[0032] In at least some examples, more than one polyalkylene amine is present/used. Where more than one polyalkylene amine is present/used, each polyalkylene amine may be a polyisobutylene amine.

[0033] In at least some examples the polyalkylene amine is present/used in the fuel composition at a concentration of actives of at least about 50 ppm, for example at a concentration of actives of at least about 70 ppm. In at least some examples the polyalkylene amine is present/used in the fuel composition at a concentration as actives of up to about 500 ppm, for example at a concentration of up to about 300 ppm. In at least some examples the polyalkylene amine is present/used in the fuel composition at a concentration of actives in the range of from about 50 ppm to about 500 ppm, such as from about 70 ppm to about 300 ppm. Concentration of actives means the concentration of the active polyalkylene amine disregarding for example, any solvent and the like. As will be clear to the skilled person, the concentration of actives expressed herein in terms of ppm is ppm by weight.

[0034] Typically, the polyalkylene amine will be present/used in the fuel composition at a concentration of actives of from about 50 ppm to about 160 ppm. In some examples, however, higher treat rates may be used. In such instances, the polyalkylene amine may be present/used in the fuel composition at a concentration of from about 160 ppm to about 500 ppm.

[0035] Where more than one polyalkylene amine is used, the total concentration of the polyalkylene amines is as described herein.

Hydrocarbyl-substituted aromatic compound.

[0036] The hydrocarbyl-substituted aromatic compound used in the fuel composition, which may be a hydrocarbyl-substituted hydroxyaromatic compound, such as a hydrocarbyl-substituted phenol compound, is a Mannich base additive. The hydrocarbyl substituent may attach at the ortho-, meta- or para- position of the phenol ring.

[0037] The hydrocarbyl substituent of the hydrocarbyl-substituted aromatic compound may exhibit a number average molecular weight of from about 700 to about 1500, such as from about 900 to about 1300.

[0038] Examples of Mannich Base additives include those obtained or obtainable by the reaction of a hydrocarbyl-substituted hydroxyaromatic compound, an amine and an aldehyde under Mannich condensation reaction conditions. Suitable reaction conditions include at least one (for example, all) of the following conditions:

- at a temperature in the range of from 40°C to 200°C;
- in the absence or presence of solvent;
- for a reaction time in the range of from 2 to 4 hours; and
- with azeotropic distillative removal of water by-product.

[0039] Examples of aldehydes suitable for the preparation of Mannich Base additives include:

- aliphatic aldehydes, including for example, formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, caprioaldehyde, heptaldehyde and stearylaldehyde;
- aromatic aldehydes including for example, benzaldehyde and salicylaldehyde; and heterocyclic aldehydes including for example, furfural aldehyde and thiophene aldehyde.

[0040] Also useful in at least some examples are formaldehyde precursors including for example paraformaldehyde and aqueous formaldehyde solutions including for example formalin.

[0041] Examples of representative hydrocarbyl substituents of the hydrocarbyl-substituted hydroxyaromatic compound include for example, polyolefin polymers for example polypropylene, polybutenes, polyisobutylene, ethylene alpha-olefin copolymers and the like. Other examples include copolymers of butylene and/or isobutylene and/or propylene and one or more mono-olefinic comonomers copolymerisable therewith (for example ethylene, 1-pentene, 1-hexene, 1-octene, 1-decene and the like) where the comonomer molecule contains at least 50% by weight of butylene and/or isobutylene and/or propylene units. In some examples the copolymers are aliphatic and in some examples contain non-aliphatic groups (for example styrene, o-methylstyrene, p-methylstyrene, divinyl benzene and the like), in any case the resulting polymers are substantially aliphatic hydrocarbon polymers.

[0042] Examples of suitable Mannich Base additives include Mannich Base additives in which the hydrocarbyl substituent of the aromatic group is or comprises polyisobutylene. Such compounds are sometimes called PIB-Mannich Base additives.

[0043] In at least some examples hydrocarbyl substituents of the hydrocarbyl-substituted hydroxyaromatic compound include polymers obtained or obtainable from pure or substantially pure 1-butene; polymers obtained or obtainable from pure or substantially pure isobutene; and polymers obtained or obtainable from mixtures of 1-butene, 2-butene and isobutene. In at least some examples the hydrocarbyl-substituted hydroxyaromatic reactant is obtained or obtainable from high reactive polyisobutene. High reactive polyisobutenes contain a high content of terminal double bonds (also sometimes referred to alpha-olefinic double bonds and/or vinylidene double bonds), for example at least 20 %, or at least 50%, or at least 70% of the total olefinic double bonds in the polyisobutene. Examples of high reactivity polybutylenes

containing relatively high proportions of polymer molecules comprising a terminal vinylidene group include those that are obtained or obtainable by methods described in US4152499 and DE2904314.

[0044] In at least some examples the hydrocarbyl substituents contain some residual unsaturation but in general they are substantially saturated.

[0045] In at least some examples the hydrocarbyl substituent is a polymer exhibiting a polydispersity of from 1 to 4, for example from 1 to 2, for example as determined by gel permeation chromatography (sometimes also referred to as GPC).

[0046] In some examples, the hydrocarbyl substituent of the hydroxyaromatic compound used to prepare the Mannich Base additive, which in some instances is or comprises polyisobutylene, may exhibit a number average molecular weight of from about 700 to about 1500, such as from about 900 to about 1300.

[0047] Examples of suitable Mannich Base additives include those disclosed in, and/or obtained or obtainable by methods described in, US5634951, US5697988, US6800103, US7597726 and/or US20090071065.

[0048] Examples of suitable Mannich Base additives include those disclosed in, and/or obtained or obtainable by methods described in, US5634951. Thus, examples of suitable Mannich Base additives include those obtainable or obtained by the reaction of (i) one mole part of at least one hydroxyaromatic compound comprising on the ring an aliphatic hydrocarbyl substituent derived from a polyolefin exhibiting a number average molecular weight in the range of 500 to 3000, (ii) from 0.8 to 1.3 mole part(s) of at least one aldehyde, and (iii) from 0.8 to 1.5 mole part(s) of at least one aliphatic polyamine comprising in the molecule one primary or secondary amino group capable of undergoing a Mannich condensation reaction with (i) and (ii), the other amino group or groups (if any) in the molecule being substantially inert towards participation in such Mannich condensation reaction, with the proviso that the mole ratio of aldehyde to amine is 1.2 or less.

[0049] Examples of suitable hydroxyaromatic compounds (i) include high molecular weight alkyl-substituted hydroxyaromatic compounds including polypropylphenol (including those formed by alkylating phenol with polypropylene), polybutylphenols (including those formed by alkylating phenol with polybutenes and/or polyisobutylene), and polybutyl-copolypropylphenols (including those formed by alkylating phenol with a copolymer of butylene and/or isobutylene and propylene). Other hydroxyaromatic compounds include for example, long chain alkylphenols for example those made by alkylating phenol with copolymers of butylene and/or isobutylene and/or propylene and one or more mono-olefinic comonomers copolymerisable therewith (including for example ethylene, 1-pentene, 1-hexene, 1-octene, 1-decene and the like), for example those in which the copolymer contains at least 50% by weight of butylene and/or isobutylene and/or propylene units. The comonomers may be aliphatic and can also contain non-aliphatic groups (for example styrene, o-methylstyrene, p-methylstyrene, divinyl benzene and the like). Suitable examples include polybutylphenols (for example, formed by alkylating phenol with polybutylene), which polybutylene includes for example, polymers made from pure or substantially pure 1-butene or isobutene and mixtures made from two, or all three of 1-butene, 2-butene and isobutene. High reactivity polybutylenes are also suitable examples for making suitable hydrocarbyl-substituted hydroxyaromatic compounds. Examples of hydrocarbyl-substituted hydroxyaromatic compounds include para-substituted hydroxyaromatic compounds. Examples of hydrocarbyl-substituted hydroxyaromatic compounds include those with one, two or more than two hydrocarbyl substituents.

[0050] Examples of suitable polyamine reactants (iii) include alkylene polyamines for example containing a single reactive primary or secondary amino group. Examples include those comprising other groups including for example hydroxyl, cyano, amido and etc. Examples of suitable polyamines include aliphatic diamines, for example, those containing one primary or secondary amino group and one tertiary amino group. Examples include N,N,N',N'-tetraalkyldialkylenetriamines; N,N,N',N'-tetraalkyltrialkylenetetramines; N,N,N',N'',N'''-pentaalkyltrialkylenetetramines; N,N-dihydroxyalkyl- α,ω -alkylenediamines; N,N,N'-trihydroxyalkyl- α,ω -alkylenediamines; tris(dialkylaminoalkyl)aminoalkylmethanes etc. including those for example, in which the alkyl groups are the same or different, including those that typically contain no more than 12 carbon atoms, for example 1 to 4 carbon atoms each e.g. methyl and/or ethyl. Examples of polyamines containing 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 reaction include for example, N-(*tert*-butyl)-1,3-propanediamine; N-neopentyl-1,3-propanediamine; N-(*tert*-butyl)-1-methyl-1,2-ethanediamine; N-(*tert*-butyl)-1-methyl-1,3-propanediamine and 3,5-di(*tert*-butyl)aminoethylpiperazine.

[0051] Examples of suitable Mannich Base additives also include those disclosed in, and/or obtained or obtainable by methods described in US5697988. Thus, examples of suitable Mannich Base additives include Mannich reaction products of (i) a high molecular weight alkyl-substituted phenol, (ii) amine and (iii) aldehyde wherein (i), (ii) and (iii) are reacted in a ratio in the range of from 1.0:0.1-10.0:0.1-10. In at least some examples the Mannich reaction products are obtained or obtainable by condensing an alkyl-substituted hydroxyaromatic compound whose alkyl-substituent has a number average molecular weight (M_n) in the range of from 600 to 14000 for example polyalkylphenol whose polyalkyl substituent is derived or derivable from 1-mono-olefin polymers exhibiting a number average molecular weight in the range of from 600 to 3000, for example in the range of from 750 to 1200; an amine containing at least one >NH group, for example an alkylene polyamine as represented by the formula: $H_2N-(A-NH)_xH$ in which A is a divalent alkylene group

containing 1 to 10 carbon atoms and x is an integer in the range of from 1 to 10; and an aldehyde, for example formaldehyde in the presence of a solvent. Suitable reaction conditions include one or more of the following:

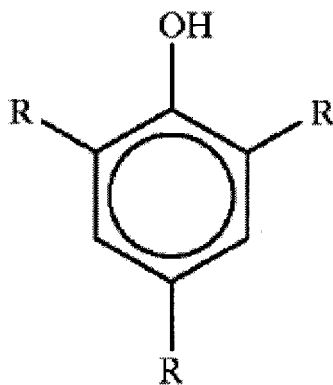
- operating at a temperature in the range of from room temperature to 95°C;
- reacting the compounds alone or in the presence of an easily removable solvent for example benzene, xylene, toluene, or solvent refined neutral oil;
- using formaldehyde (e.g. formalin) as the aldehyde;
- heating the reaction mixture at an elevated temperature (for example 120°C to 175°C) whilst for example, blowing inert stripping gas (e.g. nitrogen, carbon dioxide and the like) until dehydration is complete; and
- filtering the reaction product and diluting with solvent.

[0052] Examples of Mannich reaction products include those derived or derivable by reacting an alkylphenol, an ethylene polyamine and a formaldehyde in respective molar ratio of 1.0:0.5-2.0:1.0-3.0 wherein the alkyl group of the alkyl phenol exhibits a number average molecular weight (Mn) in the range of from 600 to 3000, for example in the range of from 740 to 1200 or in the range of from 800 to 950 or for example 900. Examples of alkyl-substituted hydroxyaromatic compounds include para-substituted mono-alkylphenols and ortho mono-alkylphenols and dialkyl phenols. Examples of amine reactants include polyamines, for example polyethylene amines. Examples of amine reactants also include mono and di-amino alkanes and their substituted analogs, for example ethylamine, dimethylamine, dimethylaminopropyl amine and diethanol amine; aromatic diamines, (e.g. phenylene diamine and diamine naphthalenes); heterocyclic amines (e.g. morpholine, pyrrole, pyrrolidine, imidazole, imidazolidine and piperidine); melamine; and their substituted analogs. Examples of amine reactants include alkylene polyamines, for example polyamines that are linear, branched or cyclic; mixtures of linear and/or branched and/or cyclic polyamines wherein each alkylene group contains from 1 to 10 carbon atoms, for example from 2 to 20 carbon atoms. Examples of polyamines include those containing from 3 to 7 nitrogen atoms.

[0053] Examples of suitable Mannich Base additives also include those disclosed in, and/or obtained or obtainable by methods described in, US6800103. Thus, examples of suitable Mannich Base additives include those obtained or obtainable by reacting a mixture of (i) at least one substituted hydroxyaromatic compound containing on the ring both (a) an aliphatic hydrocarbyl substituent derived from a polyolefin exhibiting a number average molecular weight in the range of 500 to 3000 and (b) a C₁₋₄ alkyl; (ii) at least one secondary amine; and (iii) at least one aldehyde. In at least some examples components (ii) and (iii) are pre-reacted to form an intermediate prior to addition of component (i). In at least some examples a mixture formed from components (i), (ii) and (iii) is heated at a temperature above 40°C at which Mannich condensation reaction takes place.

[0054] In at least some examples the Mannich reaction products is obtained or obtainable by reacting a di-substituted hydroxyaromatic compound in which the hydrocarbyl substituent (a) comprises polypropylene, polybutylene or an ethylene alpha-olefin copolymer exhibiting a number average molecular weight in the range of 500 to 3000 and a polydispersity in the range of 1 to 4, one or more secondary amines and at least one aldehyde. In at least some examples there is used dibutyl amine as the amine, formaldehyde or formalin as the aldehyde and a molar ratio of the substituted hydroxyaromatic compound to dibutyl amine to formaldehyde of 1 : 0.8-1.5 : 0.8-1.5 respectively, for example 1 : 0.9-1.2 : 0.9-1.2, respectively.

[0055] Examples of representative di-substituted hydroxyaromatic compounds include those represented by the general formula (VII):



(VII)

in which each R is H, C₁₋₄ alkyl or a hydrocarbyl substituent exhibiting a number average molecular weight in the range

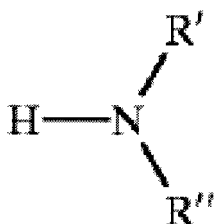
of 500 to 3000, with the proviso that one R is H, one R is a C₁₋₄ alkyl and one R is a hydrocarbyl substituent.

[0056] Examples of representative hydrocarbyl substituents of the hydrocarbyl-substituted hydroxyaromatic compound (ii) include polyolefin polymers for example polypropylene, polybutenes, polyisobutylene, ethylene alpha-olefin copolymers and the like. Other examples include copolymers of butylene and/or isobutylene and/or propylene and one or more mono-olefinic comonomers copolymerisable therewith (for example ethylene, 1-pentene, 1-hexene, 1-octene, 1-decene and the like) where the comonomer molecule contains at least 50% by weight of butylene and/or isobutylene and/or propylene units. In some examples the copolymers are aliphatic and in some examples contain non-aliphatic groups (for example styrene, o-methylstyrene, p-methylstyrene, divinyl benzene and the like), in any case the resulting polymers are substantially aliphatic hydrocarbon polymers. High reactivity polybutylenes are also suitable for making suitable hydrocarbyl-substituted hydroxyaromatic compounds.

[0057] Examples of suitable di-substituted hydroxyaromatic compounds include those obtained or obtainable by alkylating o-cresol with the high molecular weight polymers described above.

[0058] Suitably in at least some examples, the hydrocarbyl substituent is in the para-position of the disubstituted hydroxyaromatic compound and the C₁₋₄ alkyl substituent is in the ortho-position.

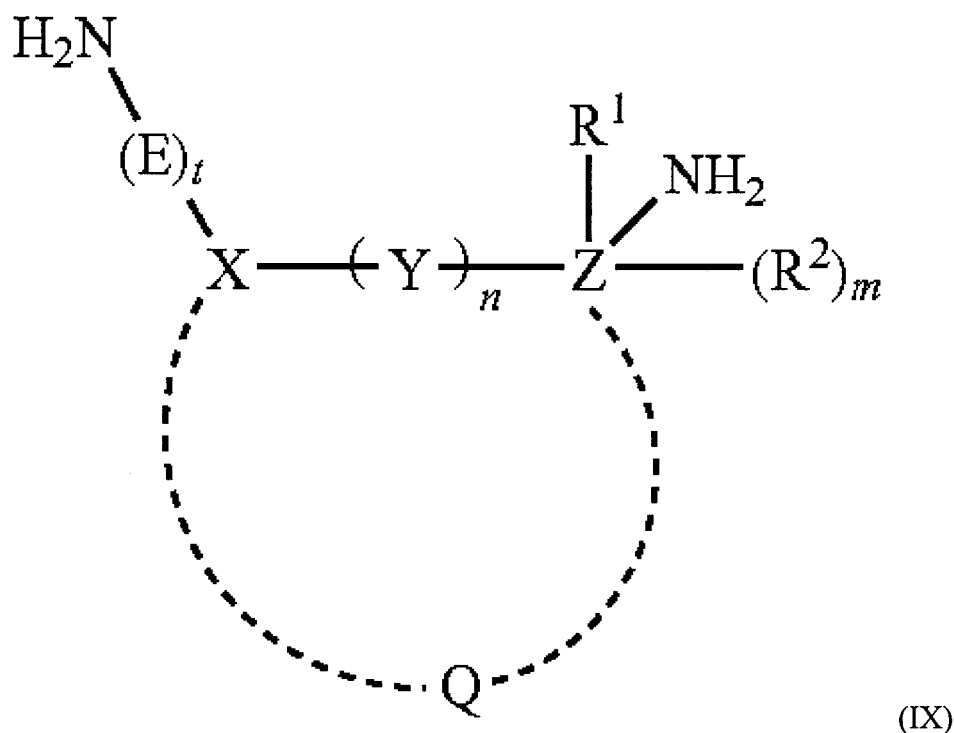
[0059] Examples of representative secondary amines (ii) include those represented by the general formula (VIII):



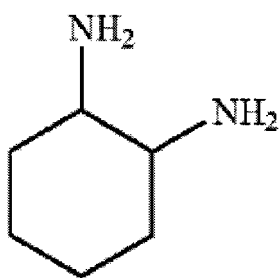
(VIII)

in which R' and R" are each independently alkyl, cycloalkyl, aryl, alkaryl or aralkyl groups containing from 1 to 30 carbon atoms, for example 1 to 18 carbon atoms or 1 to 6 carbon atoms. Examples include dimethylamine, diethylamine, dipropylamine, dibutylamine, dipentylamine and dicyclohexylamine.

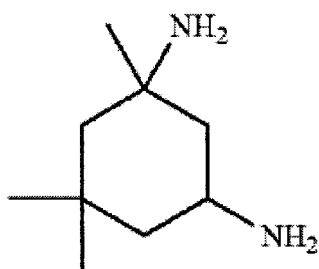
[0060] Examples of suitable Mannich Base additives also include those disclosed in, and/or obtained or obtainable by methods described in US7597726. Thus, examples of suitable Mannich Base additives include Mannich condensation reaction products of (i) a polyamine containing a sterically-hindered primary amino group, (ii) a hydrocarbyl-substituted hydroxyaromatic compound and (iii) an aldehyde. Examples of polyamines (i) containing a sterically-hindered primary amino group include (A) aliphatic cyclic polyamines containing a sterically-hindered primary amino group, (B) acyclic aliphatic polyamines containing a sterically-hindered primary amino group and combinations thereof. In at least some examples the Mannich reaction product is obtained or obtainable by reacting (1) 1,2-diaminocyclohexane, (2) polyisobutylene-substituted cresol and/or phenol, and (3) formaldehyde, for example in which the reactants (1), (2) and (3) are reacted in equimolar proportions in a Mannich reaction. In at least some examples the Mannich reaction product is dispersed in a liquid carrier fluid. In at least some examples the polyamine reactant contains an amino group that does not participate in the Mannich condensation reaction with the hydrocarbyl-substituted hydroxyaromatic reactant in addition to at least one reactive amino group in the same polyamine molecule that takes part in the Mannich reaction. Examples of reactive amino groups include primary and secondary amino groups, for example non-sterically hindered reactive primary amino groups. Examples of polyamines containing a reactive amino group and a sterically-hindered amino group include those represented by the formula (IX):



wherein X and Z each is methylene, Y is an alkylene or alkyleneamino group, n is 0 or 1, Q is an optional alkylene group suitable for forming a ring structure with X and Z, E is a hydrocarbyl group, t is 0 or 1, R¹ is a hydrocarbyl group or hydrogen provided that R¹ is hydrocarbyl if n is 1, R² is hydrogen or a hydrocarbyl group, m is 0 or 1 provided that m is 0 if Q is present. If R¹ and/or R² is hydrocarbyl, examples of such hydrocarbyl groups include C₁ to C₈ alkyl (for example methyl, ethyl, propyl, isopropyl, t-butyl and the like). Where n is 1, examples of Y include C₁ to C₈ alkylene; alkyleneamino (for example methyleneamino, (-CH₂N(H)-), dimethyleneamino (-CH₂N(H)-CH₂-), methyleneamino-ethylmethyleneamino (-CH₂N(H)-C₂H₄N(H)-CH₂-) and the like). Where t is 1, examples of E include methylene, ethylene, isopropylene and the like. Examples of Q include alkylene chains, for example C₂-C₄ alkylene chains. Examples of polyamines containing a sterically hindered primary amino group include aliphatic cyclic polyamines, including for example, polyaminocycloalkanes, for example polyaminocyclohexanes, including 1,2-diaminodicyclohexanes, 1,3-diaminodicyclohexanes and 1,4-diaminodicyclohexanes, for example as represented by the following formulae Xa, Xb and Xc:



Xa

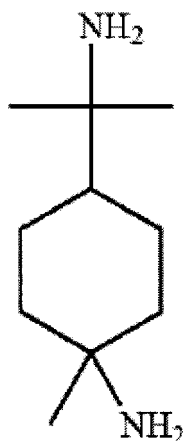


Xb

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Xc

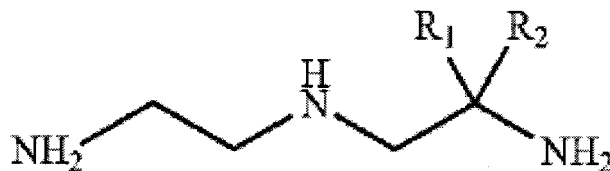
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[0061] In at least some examples in the aliphatic cyclic polyamine structure, a sterically hindering hydrocarbyl group generally is bonded to the same carbon atom from which the sterically-hindered primary amino group is bonded when the hindered/protected and reactive amino groups are present in an arrangement other than an ortho configuration relative to each other. In at least some examples (for example compound Xc), a reactive amino group is present as a moiety of an intervening substituent that is directly attached to the ring structure. In at least some examples mixtures of isomers are used. Examples of suitable acyclic aliphatic polyamine reactants include alkylene polyamines containing a primary amino group that is physically sterically-protected to prevent or at least significantly hinder its ability to participate in the Mannich condensation reaction. In at least some examples the sterically hindered primary amino group is generally attached to either a secondary or tertiary carbon atom in the polyamine compound. The acyclic aliphatic polyamine has a suitably reactive amino group (for example primary or secondary) in the same molecule for participating in the Mannich condensation reaction. In at least some examples other substituents are present, for example hydroxyl, cyano, amido and the like. Examples of acyclic aliphatic polyamines containing a sterically hindered primary amino group include those represented by formulae XIa, XIb, XIc and XId:

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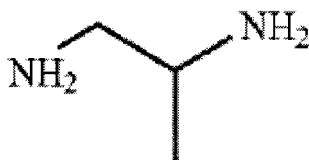


XIa

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wherein each R_1 and R_2 are a hydrocarbyl group or a hydrogen provided that at least one thereof is a hydrocarbyl group. Examples of hydrocarbyl groups include C_1 to C_8 alkyl e.g. methyl, ethyl, propyl, isopropyl and the like;

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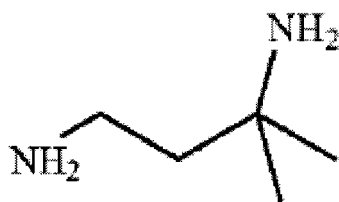
XIb

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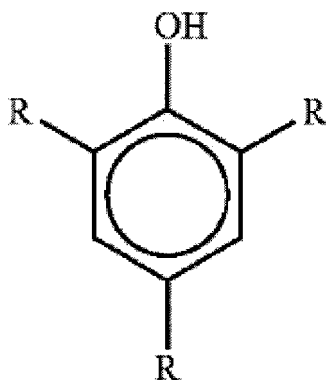
XIc

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XIId

[0062] Examples of hydrocarbyl-substituted hydroxyaromatic compounds (ii) include those represented by formula XII:



XII

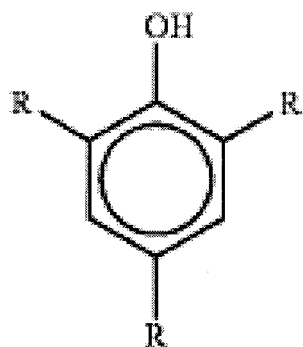
in which each R is H, C₁₋₄ alkyl or a hydrocarbyl substituent exhibiting an average molecular weight (Mw) in the range of 300 to 2000, for example 500 to 1500, for example as measured by gel permeation chromatography, with the proviso that at least one R is H and one R is a hydrocarbyl substituent as hereinbefore defined.

[0063] Examples of representative hydrocarbyl substituents of the hydrocarbyl-substituted hydroxyaromatic compound (ii) include polyolefin polymers for example polypropylene, polybutenes, polyisobutylene, ethylene alpha-olefin copolymers and the like. Other examples include copolymers of butylene and/or isobutylene and/or propylene and one or more mono-olefinic comonomers copolymerisable therewith (for example ethylene, 1-pentene, 1-hexene, 1-octene, 1-decene and the like) where the comonomer molecule contains at least 50% by weight of butylene and/or isobutylene and/or propylene units. In some examples the copolymers are aliphatic and in some examples contain non-aliphatic groups (for example styrene, o-methylstyrene, p-methylstyrene, divinyl benzene and the like), in any case the resulting polymers are substantially aliphatic hydrocarbon polymers.

[0064] In at least some examples hydrocarbyl substituents include polymers obtained or obtainable from pure or substantially pure 1-butene; polymers obtained or obtainable from pure or substantially pure isobutene; and polymer obtained or obtainable from mixtures of 1-butene, 2-butene and isobutene. In at least some examples the hydrocarbyl-substituted hydroxyaromatic reactant is obtained or obtainable from highly reactive polyisobutene.

[0065] In at least some examples a suitable di-substituted hydroxyaromatic compound is obtained or obtainable by alkylating o-cresol with a high molecular weight hydrocarbyl polymer, for example a hydrocarbyl polymer exhibiting an average molecular weight in the range of from 300 to 2000, for example by alkylating o-cresol or o-phenol with polyisobutylene exhibiting an average molecular weight in the range of from 300 to 2000, for example in the range of from 500 to 1500.

[0066] Examples of suitable Mannich Base additives also include those disclosed in, and/or obtained or obtainable by methods described in US20090071065. Thus, examples of suitable Mannich Base additives include Mannich condensation reaction products of: (i) a polyamine having primary amino groups, (ii) a hydrocarbyl-substituted hydroxyaromatic compound, and (iii) an aldehyde, where the Mannich reaction is conducted at an overall molar ratio of (i):(ii):(iii) such that, for example, the polyamine (i) is reactable with the hydrocarbyl-substituted hydroxyaromatic compound (ii) so as to obtain the substantially pure intermediate, which intermediate is reactable with the aldehyde (iii) to obtain the Mannich reaction product, for example in a one-pot reaction process. Examples of polyamine (i) include 1,2-diaminocyclohexane, 1,3-diamino propane and 1,2-diamino ethane. Examples of suitable molar ratios (i):(ii):(iii) include 1:2:3 and 1:1:2. Examples of hydrocarbyl-substituted hydroxyaromatic compounds include those represented by formula (XIII):



(XIII)

in which each R is H, C₁₋₄ alkyl, or a hydrocarbyl substituent exhibiting an average molecular weight (Mw) in the range of 300 to 2000, for example 500 to 1500, for example as determined by gel permeation chromatography, with the proviso that at least R is H and one R is a hydrocarbyl substituent as hereinbefore defined. Examples of hydrocarbyl substituents include polyolefin polymers, for example polypropylene, polybutylene, polyisobutylene and ethylene alpha-olefin copolymers and also copolymers of butylene and/or isobutylene and/or propylene and one or more mono-olefinic comonomers copolymerisable therewith (for example ethylene, 1-pentene, 1-hexene, 1-octene, 1-decene and the like) wherein the copolymer contains at least 50% by weight of butylene and/or isobutylene and/or propylene units. In at least some examples polyolefin polymer hydrocarbyl substituents contain at least 20%, for example 50%, or 70% of their olefin double bonds at a terminal position on the carbon chain as the highly reactive vinylidene isomer. Examples of hydrocarbyl substituents include those obtained or obtainable from polyisobutylene, for example polyisobutylene obtained or obtainable from pure or substantially pure 1-butene or isobutene and polymers obtained or obtainable from mixtures of two or three of 1-butene, 2-butene and isobutene. Examples of hydrocarbyl substituents include those obtained or obtainable from high reactivity polyisobutylene which have a relatively high proportion of polymer having terminal vinylidene groups, for example at least 20%, 50% or 70% of the total terminal olefinic double bonds in the polyisobutylene comprise an alkyl vinylidene isomer.

[0067] In at least some examples, more than one hydrocarbyl-substituted aromatic compound is present/used. Where more than one hydrocarbyl-substituted aromatic compound is present/used, each hydrocarbyl-substituted aromatic compound may be a Mannich base additive.

[0068] In at least some examples the hydrocarbyl-substituted aromatic compound is present/used in the fuel composition at a concentration of actives of at least about 20 ppm, for example at a concentration of actives of at least about 30 ppm. In at least some examples, the hydrocarbyl-substituted aromatic compound is present/used in the fuel composition at a concentration of actives of up to about 300 ppm, for example at a concentration of up to about 120 ppm. In at least some examples, the hydrocarbyl-substituted aromatic compound is present/used in the fuel composition at a concentration of actives in the range of from about 20 ppm to about 300 ppm, such as from about 30 ppm to about 120 ppm. Concentration of actives means the concentration of the active hydrocarbyl-substituted aromatic compound disregarding, for example, any solvent and the like.

[0069] Typically, the hydrocarbyl-substituted aromatic compound will be present/used in the fuel composition at a concentration of actives of from about 20 ppm to about 70 ppm. In some examples, however, higher treat rates may be used. In such instances, the hydrocarbyl-substituted aromatic compound may be present/used in the fuel composition at a concentration of from about 70 ppm to about 300 ppm.

[0070] Where more than one hydrocarbyl-substituted aromatic compound is present/used, the total concentration of the hydrocarbyl-substituted aromatic compounds is as described herein.

[0071] In some examples, the polyalkylene amine is present/used in the fuel composition at a concentration of actives of from about 50 ppm to about 500 ppm and the hydrocarbyl-substituted aromatic compound is present/used in the fuel composition at a concentration of actives of from about 20 ppm to about 300 ppm. Typically, the polyalkylene amine may be present/used in the fuel composition at a concentration of actives of from about 50 ppm to about 160 ppm and the hydrocarbyl-substituted aromatic compound may be present/used in the fuel composition at a concentration of actives of from about 20 ppm to about 70 ppm. However, in some examples, the polyalkylene amine may be present/used in the fuel composition at a concentration of actives of from about 160 ppm to about 500 ppm and the hydrocarbyl-substituted aromatic compound may be present/used in the fuel composition at a concentration of actives of from about 70 ppm to about 300 ppm.

[0072] In at least some examples the weight ratio of actives of the polyalkylene amine : the hydrocarbyl-substituted aromatic compound is in the range of about 10:1 to about 1:10 for example about 5:1 to about 1:5. Where more than one polyalkylene amine and/or more than one hydrocarbyl-substituted aromatic compound is present/used, the weight

ratio of actives of all of the polyalkylene amines : all of the hydrocarbyl-substituted aromatic compound is as described herein.

[0073] Typically, the polyalkylene amine, contains a polyalkylene group that exhibits a number average molecular weight of from about 700 to about 1500 (e.g. from about 800 to about 1200) and the hydrocarbyl substituent of the hydrocarbyl-substituted aromatic compound, which in some instances is or comprises polyisobutylene, exhibits a number average molecular weight of from about 700 to about 1500 (e.g. about 900 to about 1300).

Carrier fluid.

[0074] In at least some examples, a carrier fluid (sometimes also called induction aid or fluidiser) is present/used in the fuel composition, the uses and/or the methods. In at least some examples more than one carrier fluid is present/used.

[0075] In at least some examples the carrier fluid is provided with the polyalkylene amine. In at least some examples the carrier fluid is provided with the hydrocarbyl-substituted aromatic compound. In at least some examples a carrier fluid is provided with each of the polyalkylene amine and the hydrocarbyl-substituted aromatic compound, which carrier fluids may be the same or different. In at least some examples the carrier fluid is provided independently of the polyalkylene amine and the hydrocarbyl-substituted aromatic compound.

[0076] Examples of suitable carrier fluids are described for example in US2009/0071065 at paragraphs [0038] to [0053]. Thus, examples of suitable carrier fluid include liquid poly-alpha olefin oligomers, liquid polyalkene hydrocarbons (for example polypropylene, polybutenes, polyisobutene and the like), liquid hydrotreated polyalkene hydrocarbons (for example hydrotreated polypropylene, hydrotreated polybutenes, hydrotreated polyisobutene and the like), mineral oils, liquid poly(oxyalkylene) compounds, liquid alcohols, liquid polyols, liquid esters and the like.

[0077] Examples of carrier fluids include (1) a mineral oil or blend of mineral oils, for example those exhibiting a viscosity index of less than 120; (2) one or a blend of poly alpha olefins, for example those exhibiting an average molecular weight in the range of from 500 to 1500; (3) polyethers including poly(oxyalkylene) compounds, for example those exhibiting an average molecular weight in the range of from 500 to 1500; (4) one or more liquid polyalkylenes; and (5) mixtures of two or more selected from the group consisting of (1), (2), (3) and (4).

[0078] Examples of suitable mineral oil carrier fluids include paraffinic, naphthenic and asphaltic oils, for example hydrotreated oils. Examples of mineral oils exhibit a viscosity at 40 °C of less than 1600 SUS, for example 300 to 1500 SUS and/or exhibit a viscosity index of less than 100, for example in the range 30 to 60.

[0079] Examples of suitable poly alpha olefin carrier fluids include hydrotreated and unhydrotreated poly alpha olefins. Examples of poly alpha olefins include trimmers, tetramers and pentamers of alpha olefin monomers containing 6 to 12 carbon atoms.

[0080] Examples of suitable polyether carrier fluids include poly(oxyalkylene) compounds exhibiting an average molecular weight in the range of from 500 to 1500, including for example hydrocarbyl-terminated poly(oxyalkylene) monols. Examples of poly(oxyalkylene) compounds include one or a mixture of alkylpoly(oxyalkylene)monols which in its undiluted state is a gasoline-soluble liquid exhibiting a viscosity of at least 70 cSt at 40° C and at least 13 cSt at 100° C, including such monols formed by propoxylation of one or a mixture of alkanols containing at least 8 carbon atoms, for example 10 to 18 carbon atoms.

[0081] Examples of suitable poly(oxyalkylene) carrier fluids include those exhibiting a viscosity in the undiluted state of at least 60 cSt at 40° C (for example at least 70 cSt at 40° C) and at least 11 cSt at 100° C (for example at least at least 13 cSt at 100° C). Examples of suitable poly(oxyalkylene) carrier fluids include those exhibiting viscosities in their undiluted state of no more than 400 cSt at 40° C (for example no more than 300 cSt at 40° C) and no more than 50 cSt at 100° C (for example no more than 40 cSt at 100° C).

[0082] Examples of poly(oxyalkylene) compounds include poly(oxyalkylene) glycol compounds and monoether derivatives thereof, for example those that satisfy the above viscosity requirements, including those that are obtained or obtainable by reacting an alcohol or polyalcohol with an alkylene oxide, for example propylene oxide and/or butylene oxide with or without the use of ethylene oxide, for example products in which at least 80 mol. % of the oxyalkylene groups in the molecule are derived or derivable from 1,2-propylene groups.

[0083] Examples of poly(oxyalkylene) compounds include those disclosed in, and/or obtained or obtainable by methods described in, US248664, US2425845, US2425755 and US2457139.

[0084] The poly(oxyalkylene) carrier compounds should contain sufficient branched oxyalkylene units (for example methyldimethyleneoxy units and/or ethyldimethyleneoxy units) to render the poly(oxyalkylene) compound gasoline soluble.

[0085] Examples of polyalkylene carrier fluids include polypropenes, polybutenes, polyisobutenes, polyamylens, copolymers of propene and butene, copolymers of butene and isobutene, copolymers of propene and isobutene and copolymers of propene, butene and isobutene and mixtures thereof.

[0086] Examples of polyalkylene carrier fluids also include hydrotreated polypropylenes, hydrotreated polybutenes, hydrotreated polyisobutenes and the like.

[0087] Examples of polybutenes carrier fluids include those exhibiting a narrow molecular weight distribution, for example as expressed as the ratio M_w / M_n that is, (mass average molecular mass)/(the number average molecular mass), this ratio is sometimes called the polydispersity index. Examples of polybutenes carrier fluids include those exhibiting a narrow molecular weight distribution, expressed as the ratio M_w (mass average molecular mass) / M_n the number average molecular mass of 1.4 or less, for example as described in US6048373. Methods of determining mass average molecular mass include static light scattering, small angle neutron scattering, X-ray scattering, and sedimentation velocity. Number average molecular mass or weight (M_n) can be determined by gel permeation chromatography.

[0088] In at least some examples the carrier fluid is present/used in the fuel composition at a concentration of at least about 10 ppm, for example at a concentration of at least about 35 ppm. In at least some examples, the carrier fluid is present/used in the fuel composition at a concentration of up to about 500 ppm, for example at a concentration of up to about 200 ppm. In at least some examples, the carrier fluid is present/used in the fuel composition at a concentration in the range of from about 10 ppm to about 500 ppm, such as from about 35 ppm to about 200 ppm.

[0089] Where more than one carrier fluid is present/used, the total concentration of the carrier fluid is as described herein.

Fuel Composition

[0090] The fuel composition is suitable for use for example, in a spark ignition internal combustion engine. The fuel composition is preferably used in a spark-ignition internal combustion engine.

[0091] In at least some examples the fuel composition has a sulphur content of up to 50.0 ppm by weight, for example up to 10.0 ppm by weight.

[0092] Examples of suitable fuel compositions include leaded and unleaded fuel compositions.

[0093] In at least some examples the fuel composition meets the requirements of EN 228, for example as set out in BS EN 228:2012. In at least some examples the fuel composition meets the requirements of ASTM D 4814-14.

[0094] In at least some examples the fuel composition for spark-ignition internal combustion engines or for compression-ignition gasoline internal combustion engines exhibits one or more (for example all) of the following, for example, as defined according to BS EN 228:2012 :- a minimum research octane number of 95.0, a minimum motor octane number of 85.0 a maximum lead content of 5.0 mg/l, a density of 720.0 to 775.0 kg/m³, an oxidation stability of at least 360 minutes, a maximum existent gum content (solvent washed) of 5 mg/100 ml, a class 1 copper strip corrosion (3 h at 50 °C), clear and bright appearance, a maximum olefin content of 18.0 % by weight, a maximum aromatics content of 35.0 % by weight, and a maximum benzene content of 1.00 % by volume.

[0095] Examples of suitable fuel compositions include for example hydrocarbon fuels, oxygenate fuels and combinations thereof.

[0096] Hydrocarbon fuels may be derived from mineral sources and/or from renewable sources such as biomass (e.g. biomass-to-liquid sources) and/or from gas-to-liquid sources and/or from coal-to-liquid sources.

[0097] Examples of suitable oxygenate fuel components in the fuel composition include straight and/or branched chain alkyl alcohols having from 1 to 6 carbon atoms, for example methanol, ethanol, n-propanol, n-butanol, isobutanol, tert-butanol. Suitable oxygenate components in the fuel composition for spark-ignition internal combustion engines or compression-ignition gasoline internal combustion engines include ethers, for example having 5 or more carbon atoms, for example methyl tert-butyl ether and ethyl tert-butyl ether. In at least some examples the fuel composition has a maximum oxygen content of 2.7% by mass. In at least some examples fuel composition has maximum amounts of oxygenates as specified in EN 228, for example methanol: 3.0% by volume, ethanol: 5.0% by volume, iso-propanol: 10.0 % by volume, iso-butyl alcohol: 10.0 % by volume, tert-butanol: 7.0% by volume, ethers (for example having 5 or more carbon atoms): 10% by volume and other oxygenates (subject to suitable final boiling point): 10.0% by volume. In at least some examples fuel composition comprises ethanol complying with EN 15376 at a concentration of up to 15 % by volume, for example up to 10 % by volume or up to 5.0% by volume. Examples of oxygenate-containing fuel compositions include E5, E10, E15 and fuel compositions containing ethanol at higher concentrations, for example up to E85.

[0098] In at least some examples, the hydrocarbyl-substituted aromatic compound and the polyalkylene amine are incorporated into the fuel composition separately or together as components of one or more additive concentrates, one or more additive packages and/or one or more additive part packs.

[0099] In at least some examples the fuel composition and/or additive concentrates, and/or additive packages and/or additive part packs comprise at least one other fuel additive. In at least some examples the method of reducing the piston varnish forming tendency of a fuel composition comprises incorporating in one or more steps at least one other fuel additive.

[0100] In at least some examples the additives are admixed and/or incorporated as one or more additive concentrates and/or additive part packs, optionally comprising solvent or diluent.

[0101] In at least some examples, the fuel composition is prepared by admixing in one or more steps, one or more base fuels (for example hydrocarbon fuels, oxygenate fuels and combinations thereof) and components therefor, op-

tionally with one or more additives and/or part additive package concentrates. In at least some examples, the additives, additive concentrates and/or part additive package concentrates are admixed with the fuel or components therefor in one or more steps.

[0102] Examples of such other fuel additives include friction modifiers, anti-wear additives, corrosion inhibitors, de-hazers/demulsifiers, dyes, markers, odorants, octane improvers, combustion modifiers, anti-oxidants, anti-microbial agents, lubricity improvers and valve seat recession additives.

[0103] Representative suitable and more suitable independent amounts of additives (if present) in the fuel composition are given in Table 1. The concentrations expressed in Table 1 are by weight of active additive compounds that is, independent of any solvent or diluent.

[0104] In at least some examples, more than one of each type of additive is present. In at least some examples, within each type of additive, more than one class of that type of additive is present. In at least some examples more than one additive of each class of additive is present. In at least some examples additives are suitably supplied by manufacturers and/or suppliers in solvent or diluents.

Table 1

ADDITIVE TYPE	Fuel Composition	
	Suitable amount (actives), (by weight)	More suitable amount (actives), if present (by weight)
Hydrocarbyl-substituted aromatic compounds	20 - 300 ppm	30 - 120 ppm
Polyalkylene amines	50 - 500 ppm	70 - 300 ppm
Carrier fluid	10 - 500 ppm	35 - 200 ppm
Friction modifiers/anti-wear additives	10 - 200 ppm	
Corrosion inhibitors	1-20 ppm	
Octane improvers and/or combustion improvers	5 - 30000 ppm	
Anti -oxidants	0.1-20 ppm	
Dehazers/demulsifiers	0.1 - 20 ppm	
Dyes and/or markers	0.1 - 20 ppm	
Odorants	1 - 20 ppm	
Anti-microbial agents	1 - 20 ppm	
Lubricity improvers	10 - 200 ppm	
Valve seat recession additives	1 - 15000 ppm	

[0105] Examples of suitable friction modifiers and anti-wear additives include those that are ash-producing additives or ashless additives. Examples of friction modifiers and anti-wear additives include esters (for example glycerol mono-oleate) and fatty acids (for example oleic acid and stearic acid).

[0106] Examples of suitable corrosion inhibitors include ammonium salts of organic carboxylic acids, amines and heterocyclic aromatics, for example alkylamines, imidazolines and tolyltriazoles.

[0107] Examples of suitable non-metallic octane improvers include N-methyl aniline.

[0108] Examples of suitable metal-containing octane improvers include methylcyclopentadienyl manganese tricarbonyl, ferrocene and tetra-ethyl lead. Suitably, the fuel composition is free of all added metallic octane improvers including methyl cyclopentadienyl manganese tricarbonyl and other metallic octane improvers including for example, ferrocene and tetraethyl lead.

[0109] Examples of suitable anti-oxidants include phenolic anti-oxidants (for example 2,4-di-tert-butylphenol and 3,5-di-tert-butyl-4-hydroxyphenylpropionic acid) and aminic anti-oxidants (for example para-phenylenediamine, dicyclohexylamine and derivatives thereof).

[0110] Examples of suitable valve seat recession additives include inorganic salts of potassium or phosphorus.

[0111] In at least some examples the additive composition comprises solvent. Examples of suitable solvents include polyethers and aromatic and/or aliphatic hydrocarbons, for example heavy naphtha e.g. Solvesso (Trade mark), xylenes

and kerosene.

[0112] In at least some examples the additives are present in the fuel composition at a total amount in the range of 20 to 25000 ppm by weight. Therefore, the concentrations of each additive in an additive concentrate will be correspondingly higher than in the fuel composition, for example by a ratio of 1: 0.00002 to 0.025. In at least some examples the additives are used as part-packs, for example part of the additives (sometimes called refinery additives) being added at the refinery during manufacture of a fungible fuel and part of the additives (sometimes called terminal or marketing additives) being added at a terminal or distribution point.

[0113] In at least some examples the hydrocarbyl-substituted aromatic compound and the polyalkylene amine are incorporated or admixed with other components of the fuel composition as a refinery additive or as a marketing additive.

[0114] In at least some examples the hydrocarbyl-substituted aromatic compound and the polyalkylene amine are incorporated or admixed with other components of the fuel composition as a marketing additive, for example at a terminal or distribution point.

[0115] In general, there are two types of spark-ignition, internal combustion engines which are classified according to the type of system for delivering fuel to the engine combustion chambers.

[0116] Port Fuel Injection (PFI) engines are engines in which a mixture of fuel and air is injected into intake ports and then passes into combustion chambers of the engine through one or more intake valves (sometimes also called inlet valves or inlet port valves). Examples of suitable port fuel injection, spark-ignition internal combustion engines include any suitable port fuel injection, spark-ignition internal combustion engine including for example BMW 318i engine, Ford 2.3L Ranger engine and MB M111 engine.

[0117] Direct Injection (DI) engines are engines in which fuel is injected directly into combustion chambers of the engine through injectors (sometimes also called direct injectors or direct injector nozzles) and air is introduced into the combustion chambers through one or more air intake valves (sometimes also called air inlet valves or air inlet port valves). Examples of suitable direct injection spark-ignition internal combustion engines include boosted direct injection spark-ignition internal combustion engines, for example turbocharged boosted direct injection engines and supercharged boosted direct injection engines. Suitable engines include 2.0L boosted direct injection spark-ignition internal combustion engines. Suitable direct injection engines include those that have side mounted direct injectors and/or centrally mounted direct injectors.

[0118] Methods for assessing the piston varnish control performance of a fuel composition include those based upon the US industry standard test method: ASTM D-6593 (version 10), this is sometimes also called the Ford 4.6L "Sequence VG" engine test. This test is used for determining the performance of lubricants. However, the performance of fuels may be tested by using the standard reference lubricant as the lubricant, and the standard reference base fuel with the additives of interest added thereto as the fuel.

[0119] The fuel compositions used in the present invention control piston varnish formation, but it is desirable that they also exhibit good detergency in the rest of the engine. This may be determined by measuring the intake valve keep-clean performance of the fuel composition. Methods of measuring the intake valve deposit keep-clean performance of a fuel composition for use in a spark-ignition internal combustion engine include those based upon the US industry standard test method: ASTM D-6201 (version 04, 2009), this is sometimes also called the Ford 2.3L "Ranger" engine test after the engine that is used.

[0120] Further aspects of the present invention include the aspects, embodiments, instances and examples defined above but in which a Mannich Base additive is used as component a. In these aspects, the Mannich Base additive may be, but does not have to be, a hydrocarbyl-substituted aromatic compound.

[0121] The invention will now be described by way of example only with reference to the following drawing, experiment and example in which Example 1 is according to the present invention and Experiment A is not according to the present invention.

[0122] In the drawing Figure 1 represents, in graph form, the piston varnish control performance for the fuel compositions tested relative to a base fuel reference.

[0123] Intake valve deposit (IVD) keep-clean performance were assessed using the US industry standard test method: ASTM D-6201 (version 04, 2009) using a Ford 2.3 L port fuel injection spark-ignition internal combustion engine. Intake valve deposit (IVD) keep-clean performance was studied using an E10 gasoline base fuel.

[0124] Piston varnish formation was assessed using the US industry standard test method: ASTM D-6593 (version 20100628) using a Ford 4.6L port fuel injection spark-ignition internal combustion engine. The standard reference fuel in ASTM D-6593, with additives of interest added therein, was used as the fuel.

Experiment A - polyisobutylene only

[0125] The piston varnish control performance of a fuel containing PIBA additive was assessed. The amount of PIBA used in the experiment was selected to give a typical port fuel injection valve keep-clean performance.

[0126] The piston varnish control performance is shown in graph form in Figure 1 as relative % piston varnish control

performance (relative to a base fuel reference).

Example 1 - combination of Mannich Base additive and polyisobutylene amine

[0127] The piston varnish control performance of a fuel containing a combination of Mannich Base additive and PIBA additive was assessed. The amount of Mannich Base additive and PIBA used in the experiment was selected to give a typical port fuel injection valve keep-clean performance and which was comparable to that of the fuel composition used for Experiment A.

[0128] The piston varnish control performance is shown graph form in Figure 1 as relative % piston varnish control performance (relative to a base fuel reference).

[0129] The data generated in Experiment A and Example 1 are shown in Table 2.

Table 2

	Keep-clean performance (arbitrary units)	Treat rate (arbitrary units mass per volume)	Piston varnish deposit control performance (% relative to base fuel reference)*
Experiment A	10.0	20.0	106%
Example 1	9.9	18.9	115%
*a higher number indicates better control performance			

[0130] The data shown in Table 2 and in Figure 1 show that the fuel composition comprising a Mannich Base additive in combination with a polyisobutylene amine exhibits beneficial piston varnish control in a spark-ignition internal combustion engine. In particular, the data show that the fuel composition comprising a Mannich Base additive in combination with a polyisobutylene amine exhibits greater piston varnish control in a spark-ignition internal combustion engine than an un-additised fuel and a fuel containing only polyisobutylene amine. The comparison with the fuel containing polyisobutylene amine is made for example at concentrations of additives providing comparable detergency performance, when measured using a Ford 2.3 L port fuel injection spark-ignition internal combustion engine according to the industry standard test method: ASTM D-6201.

[0131] These data illustrate a method of controlling piston varnish formation in a spark-ignition internal combustion engine which method comprises supplying to the engine a fuel composition which comprises a combination of:

- a. a hydrocarbyl-substituted aromatic compound; and
- b. a polyalkylene amine.

[0132] The data also illustrate the use as a piston varnish controlling additive in a fuel composition for a spark-ignition internal combustion engine of:

- a. a hydrocarbyl-substituted aromatic compound; and
- b. a polyalkylene amine.

[0133] The data also illustrate a method of reducing the piston varnish forming tendency of a fuel composition for use in a spark-ignition internal combustion engine which method comprises incorporating into the fuel composition in one or more steps:

- a. a hydrocarbyl-substituted aromatic compound; and
- b. a polyalkylene amine

to produce a fuel composition which comprises said additives in combination and which on use in a spark-ignition internal combustion engine produces less piston varnish than the piston varnish formed when using in said engine the fuel composition without said combination of additives.

[0134] The data also illustrate that the piston varnish control performance of a fuel composition comprising a combination of a hydrocarbyl-substituted aromatic compound and a polyalkylene amine is improved relative to that of a fuel composition which comprises a polyalkylene amine, but does not comprise a hydrocarbyl-substituted aromatic compound. The piston varnish control performance of a fuel composition comprising a combination of a hydrocarbyl-substituted

aromatic compound and a polyalkylene amine may also be improved relative to that of a fuel composition which comprises a hydrocarbyl-substituted aromatic compound, but does not comprise a polyalkylene amine. Accordingly, in some examples, an additive composition comprising a combination of:

- a. a hydrocarbyl-substituted aromatic compound; and
- b. a polyalkylene amine

is used for improving the piston varnish control performance of a fuel composition in a spark-ignition internal combustion engine.

Claims

1. The use as a piston varnish controlling additive in a fuel composition for a spark-ignition internal combustion engine of:

- a. a hydrocarbyl-substituted aromatic compound; and
- b. a polyalkylene amine,

wherein the hydrocarbyl-substituted aromatic compound is a Mannich Base additive.

2. The use of an additive composition comprising a combination of:

- a. a hydrocarbyl-substituted aromatic compound; and
- b. a polyalkylene amine,

wherein the hydrocarbyl-substituted aromatic compound is a Mannich Base additive, for improving the piston varnish control performance of a fuel composition in a spark-ignition internal combustion engine.

3. The use of Claim 1 or Claim 2, wherein the polyalkylene amine is a polyisobutylene amine.

4. The use of any of Claims 1 to 3, wherein the hydrocarbyl-substituted aromatic compound is present in the fuel composition at a concentration of actives of from 20 ppm to 300 ppm.

5. The use of any of Claims 1 to 4, wherein the hydrocarbyl substituent of the aromatic compound exhibits a number average molecular weight of from 700 to 1500.

6. The use of any of Claims 1 to 5, wherein the hydrocarbyl substituent of the aromatic compound is or comprises polyisobutylene.

7. The use of any of Claims 1 to 6, wherein the polyalkylene amine is present in the fuel composition at a concentration of actives of from 50 ppm to 500 ppm.

8. The use of any of Claims 1 to 7, wherein the polyalkylene amine contains a polyalkylene group that exhibits a number average molecular weight of from 700 to 1500.

9. The use of any of Claims 1 to 8, wherein the weight ratio of actives of the polyalkylene amine : the hydrocarbyl-substituted aromatic compound in the fuel composition is in the range of from 5:1 to 1:5.

10. The use as at least one of a piston ring sticking and blow-by controlling additive in a fuel composition for a spark-ignition internal combustion engine of:

- a. a hydrocarbyl-substituted aromatic compound; and
- b. a polyalkylene amine,

wherein the hydrocarbyl-substituted aromatic compound is a Mannich Base additive.

Patentansprüche

1. Verwendung:

- a. einer Hydrocarbyl-substituierten aromatischen Verbindung und
- b. eines Polyalkylenamins

als ein Kolbenlack-Steueradditiv in einer Kraftstoffzusammensetzung für einen Verbrennungsmotor mit Fremdzündung,

wobei die Hydrocarbyl-substituierte aromatische Verbindung ein Mannich-Basen-Additiv ist.

2. Verwendung einer Additivzusammensetzung, umfassend eine Kombination aus:

- a. einer Hydrocarbyl-substituierten aromatischen Verbindung und
- b. einem Polyalkylenamin,

wobei die Hydrocarbyl-substituierte aromatische Verbindung ein Mannich-Basen-Additiv ist, zur Verbesserung der Kolbenlack-Steuerleistung einer Kraftstoffzusammensetzung in einem Verbrennungsmotor mit Fremdzündung.

3. Verwendung nach Anspruch 1 oder Anspruch 2, wobei das Polyalkylenamin ein Polyisobutylenamin ist.

4. Verwendung nach einem der Ansprüche 1 bis 3, wobei die Hydrocarbyl-substituierte aromatische Verbindung in der Kraftstoffzusammensetzung bei einer Wirkstoffkonzentration von 20 ppm bis 300 ppm vorliegt.

5. Verwendung nach einem der Ansprüche 1 bis 4, wobei der Hydrocarbylsubstituent der aromatischen Verbindung ein zahlenmittleres Molekulargewicht von 700 bis 1500 aufweist.

6. Verwendung nach einem der Ansprüche 1 bis 5, wobei der Hydrocarbylsubstituent der aromatischen Verbindung Polyisobutylen ist oder umfasst.

7. Verwendung nach einem der Ansprüche 1 bis 6, wobei das Polyalkylenamin in der Kraftstoffzusammensetzung bei einer Wirkstoffkonzentration von 50 ppm bis 500 ppm vorliegt.

8. Verwendung nach einem der Ansprüche 1 bis 7, wobei das Polyalkylenamin eine Polyalkylengruppe enthält, die ein zahlenmittleres Molekulargewicht von 700 bis 1500 aufweist.

9. Verwendung nach einem der Ansprüche 1 bis 8, wobei das Wirkstoffgewichtsverhältnis des Polyalkylenamins : der Hydrocarbyl-substituierten aromatischen Verbindung in der Kraftstoffzusammensetzung im Bereich von 5 : 1 bis 1 : 5 liegt.

10. Verwendung:

- a. einer Hydrocarbyl-substituierten aromatischen Verbindung und
- b. eines Polyalkylenamins

als zumindest eines von einem Kolbenring-Haft- und -Vorbeiström-Steueradditiv in einer Kraftstoffzusammensetzung für einen Verbrennungsmotor mit Fremdzündung,

wobei die Hydrocarbyl-substituierte aromatische Verbindung ein Mannich-Basen-Additiv ist.

Revendications

1. Utilisation en tant qu'additif de régulation de vernis de piston dans une composition de carburant pour un moteur à combustion interne à allumage commandé de :

- a. un composé aromatique substitué par un groupe hydrocarbyle ; et
- b. une polyalkylène-amine,

dans laquelle le composé aromatique substitué par un groupe hydrocarbyle est un additif de type base de Mannich.

2. Utilisation d'une composition d'additif comprenant une combinaison de :

- a. un composé aromatique substitué par un groupe hydrocarbyle ; et
b. une polyalkylène-amine,

dans laquelle le composé aromatique substitué par un groupe hydrocarbyle est un additif de type base de Mannich, pour améliorer la performance de régulation de vernis de piston d'une composition de carburant dans un moteur à combustion interne à allumage commandé.

3. Utilisation selon la revendication 1 ou la revendication 2, dans laquelle la polyalkylène-amine est une polyisobutylène-amine.

4. Utilisation selon l'une quelconque des revendications 1 à 3, dans laquelle le composé aromatique substitué par un groupe hydrocarbyle est présent dans la composition de carburant à une concentration d'ingrédients actifs de 20 ppm à 300 ppm.

5. Utilisation selon l'une quelconque des revendications 1 à 4, dans laquelle le substituant hydrocarbyle du composé aromatique présente un poids moléculaire moyen en nombre de 700 à 1 500.

6. Utilisation selon l'une quelconque des revendications 1 à 5, dans laquelle le substituant hydrocarbyle du composé aromatique est ou comprend du polyisobutylène.

7. Utilisation selon l'une quelconque des revendications 1 à 6, dans laquelle la polyalkylène-amine est présente dans la composition de carburant à une concentration d'ingrédients actifs de 50 ppm à 500 ppm.

8. Utilisation selon l'une quelconque des revendications 1 à 7, dans laquelle la polyalkylène-amine contient un groupe polyalkylène qui présente un poids moléculaire moyen en nombre de 700 à 1 500.

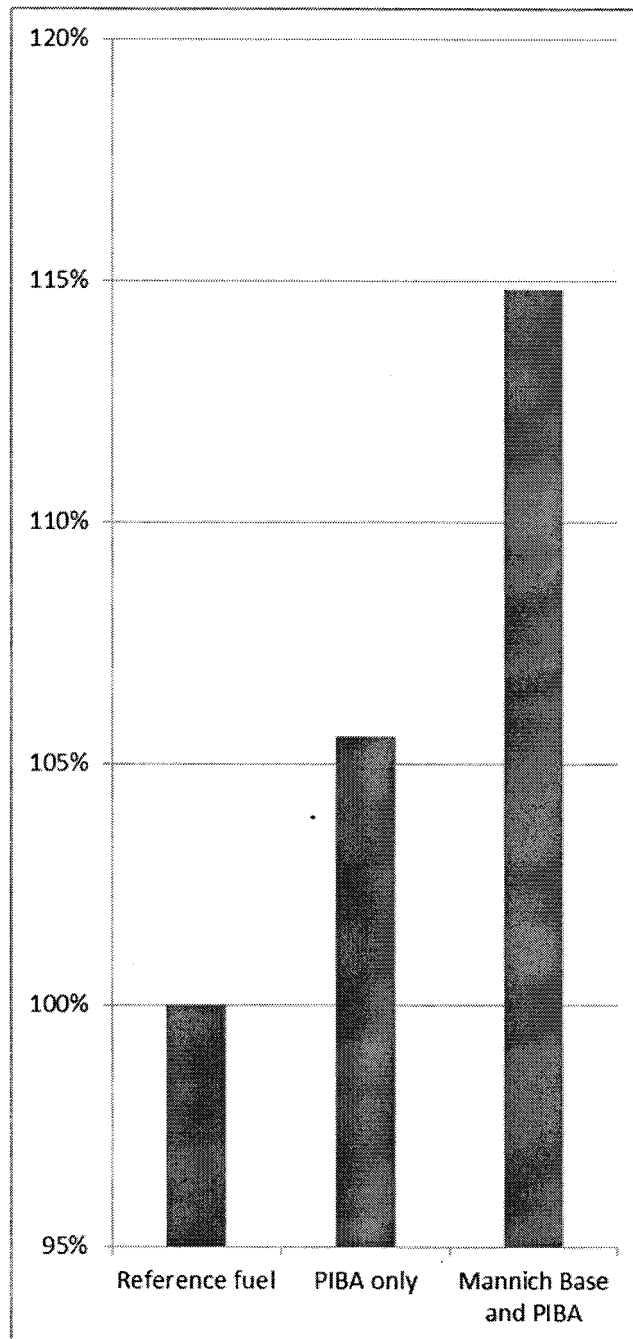
9. Utilisation selon l'une quelconque des revendications 1 à 8, dans laquelle le rapport pondéral des ingrédients actifs de la polyalkylène-amine/le composé aromatique substitué par un groupe hydrocarbyle dans la composition de carburant est dans la plage de 5/1 à 1/5.

10. Utilisation en tant qu'au moins l'un d'un additif de régulation de blocage des segments de piston et de fuite des gaz dans une composition de carburant pour un moteur à combustion interne à allumage commandé de :

- a. un composé aromatique substitué par un groupe hydrocarbyle ; et
b. une polyalkylène-amine,

dans laquelle le composé aromatique substitué par un groupe hydrocarbyle est un additif de type base de Mannich.

Figure 1



REFERENCES CITED IN THE DESCRIPTION

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