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(54) Fuel compositions and additives therefor

Kraftstoffzusammensetzungen, und Zusätze dafür

Compositions de combustible, et additifs

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EP 0 647 700 B1

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Description

[0001] This invention relates to fuel additive compositions that can be used for control of intake valve deposits without significantly affecting octane requirement increase in the engine.

[0002] Over the years considerable work has been devoted to additives for controlling (preventing or reducing) deposit formation in the fuel induction systems of spark-ignition internal combustion engines. In particular, additives that can effectively control intake valve deposits represent the focal point of considerable research activities in the field and despite these efforts, further improvements are desired. Among relatively recent efforts along these lines is U.S. 5,242,469 and published Canadian patent application 2,089,833.

[0003] The additive systems described in U.S. 5,242,469 comprise an ester and at least one dispersant component chosen from certain monosuccinimides, bis(succinimides), polyolefin polyamines, and benzylamine derivatives. The benzylamine derivatives appear to be Mannich-type detergents*. These additive combinations may further contain a polyoxyalkylene glycol or derivative thereof having a molecular weight of 500-5000, preferably 1000-3000. Also, a specified type of lubricating oil fraction may be included in the additive mixture. The polyoxyalkylene glycol derivatives referred to in the text of the patent include the ethers, esters and ether aminoacid esters of the polyoxyalkylene glycol.

[0004] Canadian patent application 2,089,833 bearing a publication date of August 21, 1993 describes a similar additive system. In particular, the gasoline is to contain (a) from 75 to 450 ppmw of a specified group of Mannich base detergents in combination with (b) from 75 to 175 ppmw of an oil-soluble poly(oxyalkylene) alcohol, glycol or polyol or mono or di ether thereof, wherein the weight ratio of (a) to (b) in the mixture is at least 0.43.

[0005] It has now been discovered that oil-soluble poly(oxyalkylene) alcohols, glycols or polyols or mono or di ethers thereof do not yield equivalent results on intake valve cleanliness when used in conjunction with a Mannich base detergent, and that for reasons not presently understood, the viscosity properties of the poly(oxyalkylene) component appear to have a profound effect on the intake valve cleanliness performance of the overall composition.

[0006] Accordingly, in one of its embodiments, this invention provides, a fuel-soluble additive composition which comprises

a) a gasoline-soluble Mannich reaction product of

(i) a high molecular weight alkyl-substituted phenol wherein the alkyl group has a number average molecular weight of from 600 to 3000,
(ii) amine and (iii) aldehyde;

b) a gasoline-soluble poly(oxyalkylene) compound having a viscosity in its undiluted state of at least 70 cSt at 40°C and at least 13 cSt at 100°C; and

c) one or more poly- α -olefins collectively having viscosities at 40°C and 100°C that are not more than approximately 25% higher than the respective viscosities of said poly(oxyalkylene) compound at 40°C and 100°C,

wherein the proportions of a) to b) are such that there are from 0.2 to 5 parts by weight of active Mannich base in a) per part by weight of b).

[0007] The composition contains one or more liquid poly- α -olefins which, whether a single poly- α -olefin or a mixture of different poly- α -olefins, has a viscosity that is not substantially in excess of the viscosity of the poly(oxyalkylene) compound.

[0008] Typically the proportions of a) to b) in the compositions of this invention are such that there are from 0.2 to 5 parts by weight of a) per part by weight of b), preferably from 0.5 to 3 parts by weight of a) per part by weight of b), and more preferably from 0.8 to 2 parts by weight of a) per part by weight of b), with the weight of a) being on an "active ingredient basis". By this is meant that component a) will usually be supplied in admixture on a weight basis with a minor amount of a hydrocarbon diluent and a minor amount of unreacted polyolefin used in making the alkylated phenol from which the Mannich detergent is produced. Thus the foregoing proportions of a) to b) are based on the content of Mannich base detergent in component a) excluding the weight of any diluent or solvent and any unreacted polyolefin which may be associated therewith in the form in which it is supplied. Component b) will normally be supplied in undiluted form, and in such case its weight can be used directly in calculating the ratio of a) to b). But if the poly(oxyalkylene) compound is being blended with a) when the poly(oxyalkylene) compound is in admixture with a solvent or diluent, the weight of b) should be based on the weight of the poly(oxyalkylene) compound itself and should likewise exclude the weight of any such solvent or diluent associated therewith.

* According to the patent the hydroxybenzyl amine derivatives are made by alkylating a hydroxybenzyl amine which in turn presumably would be formed by a Mannich reaction among phenol, formaldehyde and polyamine. The resultant product should be similar, if not identical, to a product made in the more usual sequence of alkylating the phenol and then conducting the Mannich reaction with the resultant alkylated phenol, formaldehyde and a polyamine

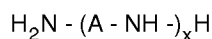
[0009] It will be understood that any such ancillary solvent or diluent, whether hydrocarbon or otherwise, must not adversely affect the intake valve deposit control performance of the above additive composition in any material way. Thus as long as they do not exert such adverse effect, ethers, esters or other inert solvents or diluents may be present in the additive composition.

5 [0010] As component c) the compositions of the invention include one or more poly- α -olefins which collectively have viscosities at 40°C and 100°C that are not substantially in excess of the viscosity of the poly(oxyalkylene) compound. More particularly, these collective poly- α -olefin viscosities are not more than approximately 25 percent higher than the corresponding 40°C and 100°C viscosities of the poly(oxyalkylene) compound being used. Not only does this ensure that the intake valve deposit control effectiveness of the composition will not be adversely affected in any material way, but it keeps the cost of the additive composition to a minimum.

10 [0011] In another embodiment, this invention provides a method for reducing intake valve deposits in gasoline engines. The method comprises fueling and operating said engines with the fuel composition of the present invention.

15 [0012] As noted above, the Mannich reaction product component of this invention typically contains a significant portion of hydrocarbonaceous ingredients which are inactive in the sense that they do not possess polarity or surface activity and therefore do not serve as detergents. For example, subsequent to the manufacture of the Mannich reaction product, hydrocarbon solvent is typically added to dilute the product to facilitate handling and blending. Thus, the Mannich product as received typically contains 40 to 55 wt.% of the active Mannich base ingredient, the balance being solvent or diluent, and unreacted materials from the synthesis steps, such as polyolefin polymer. A generally used dilution solvent is a mixture of aromatic hydrocarbons such as o-, p-, and m-xylene, mesitylene, and higher boiling aromatics such as Aromatic 150 (commercially available from Chemtech).

20 [0013] The Mannich reaction products of this invention are obtained by condensing an alkylphenol whose alkyl substituent, for example alkyl derived from 1-monoolefin polymer, has a number average molecular weight of from 600 to 3000, preferably 750 to 1200, more preferably 800 to 1200, and most preferably 800 to 950; an amine having at least one >NH group, preferably an alkylene polyamine of the formula



25 where A is a divalent alkylene radical having 1 to 10 carbon atoms and x is an integer from 1 to 10; and an aldehyde, preferably formaldehyde or a formaldehyde precursor, in the presence of a solvent. Commercial grades of alkylene polyamines often contain mixtures of linear, branched and cyclic species.

30 [0014] High molecular weight Mannich reaction products useful as additives in the fuel additive compositions of this invention are preferably prepared according to conventional methods employed for the preparation of Mannich condensation products, using the above-named reactants in the respective molar ratios of (i) high molecular weight alkyl-substituted hydroxyaromatic compound, (ii) amine, and (iii) aldehyde of 1.0 : 0.1-10 : 1-10. For example it is common to charge about 1 to 3 moles of polyamine and about 1.2 to 4 moles of aldehyde per mole of (i).

35 [0015] Preferred Mannich reaction product additives employed in this invention are derived from high molecular weight Mannich condensation products, formed by reacting an alkylphenol, an ethylene polyamine, and a formaldehyde affording reactants in the respective molar ratio of 1.0 : 0.5-2.0 : 1.0-3.0, wherein the alkyl group of the alkylphenol has a number average molecular weight (Mn) of from 600 to 3,000, and more preferably from 750 to 1,200.

40 [0016] Representative of the high molecular weight alkyl-substituted hydroxyaromatic compounds are polypropylphenol (formed by alkylating phenol with polypropylene), polybutylphenol (formed by alkylating phenol with polybutenes or polyisobutylene), and other similar long-chain alkylphenols. Polypropylphenol is the most preferred reactant. Polyalkylphenols may be obtained by the alkylation, in the presence of an alkylating catalyst such as BF₃, of phenol with high molecular weight polypropylene, polybutylene and other polyalkylene compounds to give alkyl substituents on the benzene ring of phenol having a number average molecular weight (Mn) of from 600 to 14,000.

45 [0017] The alkyl substituents on the hydroxyaromatic compounds may be derived from high molecular weight polypropylenes, polybutenes, and other polymers of mono-olefins, principally 1-mono-olefins. Also useful are copolymers of mono-olefins with monomers copolymerizable therewith wherein the copolymer molecule contains at least 90% by weight, of mono-olefin units. Specific examples are copolymers of butenes (butene-1, butene-2, and isobutylene) with monomers copolymerizable therewith wherein the copolymer molecule contains at least 90% by weight of propylene and butene units, respectively. The monomers copolymerizable with propylene or butenes include monomers containing a small proportion of unreactive polar groups such as chloro, bromo, keto, ether, aldehyde, which do appreciably lower the oil-solubility of the polymer. The comonomers polymerized with propylene or such butenes may be aliphatic and can also contain non-aliphatic groups, e.g., styrene, methylstyrene, p-dimethylstyrene, divinyl benzene, for example. From the foregoing limitation placed on the monomer copolymerized with propylene or the butenes, it is clear that the resulting polymers and copolymers are substantially aliphatic hydrocarbon polymers. Thus, the resulting alkylated phenols contain substantially alkyl hydrocarbon substituents having a number average molecular weight (Mn) of from

600 to 3000.

[0018] In addition to the foregoing high molecular weight hydroxyaromatic compounds, other phenolic compounds which may be used include, high molecular weight alkyl-substituted derivatives of resorcinol, hydroquinone, cresol, catechol, xyleneol, hydroxydi-phenyl, benzylphenol, phenethylphenol, naphthol, tolylnaphthol, among others. Preferred for the preparation of such preferred Mannich condensation products are the polyalkylphenol reactants, e.g., polypropylphenol and polybutylphenol whose alkyl group has a number average molecular weight of 600-3000, the more preferred alkyl groups having a number average molecular weight of 740-1200, while the most preferred type of alkyl groups is a polypropyl group having a number average molecular weight of 900-950.

[0019] The preferred configuration of the alkyl-substituted hydroxyaromatic compound is that of a para-substituted mono-alkylphenol. However, any alkylphenol readily reactive in the Mannich condensation reaction may be employed. Thus, Mannich products made from alkylphenols having only one ring alkyl substituent, or two ring alkyl substituents are suitable for use in this invention.

[0020] Representative amine reactants are alkylene polyamines, principally polyethylene polyamines. Other representative organic compounds containing at least one HN< group suitable for use in the preparation of the Mannich reaction products are well known and include the mono and di-amino alkanes and their substituted analogs, e.g., ethylamine, dimethylamine, dimethylaminopropyl amine, and diethanol amine; aromatic diamines, e.g., phenylene diamine, diamino naphthalenes; heterocyclic amines, e.g., morpholine, pyrrole, pyrrolidine, imidazole, imidazolidine, and piperidine; melamine and their substituted analogs.

[0021] The alkylene polyamine reactants which are useful with this invention include polyamines which are linear, branched or cyclic; or a mixture of linear, branched and/or cyclic polyamines wherein each alkylene group contains from 1 to 10 carbon atoms. A preferred polyamine is a polyamine containing from 2 to 10 nitrogen atoms per molecule or a mixture of polyamines containing an average of from 2 to 10 nitrogen atoms per molecule such as ethylenediamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, hexaethylene heptamine, heptaethylene octamine, octaethylene nonamine, nonaethylene decamine, and mixtures of such amines. Corresponding propylene polyamines such as propylene diamine, and dipropylene triamine, tripropylene tetramine, tetrapropylene pentamine, pentapropylene hexamine are also suitable reactants. A particularly preferred polyamine is a polyamine or mixture of polyamines having from 3 to 7 nitrogen atoms with diethylene triamine or a combination or mixture of ethylene polyamines whose physical and chemical properties approximate that of diethylene triamine being the most preferred. In selecting an appropriate polyamine, consideration should be given to the compatibility of the resulting detergent/dispersant with the gasoline fuel mixture with which it is mixed.

[0022] Ordinarily the most highly preferred polyamine, diethylene triamine, will comprise a commercially available mixture having the general overall physical and/or chemical composition approximating that of pure diethylene triamine but which can contain minor amounts of branched-chain and cyclic species as well as some other linear polyethylene polyamines such as triethylene tetramine and tetraethylene pentamine. For best results, such mixtures should contain at least 50% and preferably at least 70% by weight of the linear polyethylene polyamines of which at least 50 mole % is diethylene triamine. In one embodiment the amine is selected from diethylene triamine and triethylene tetramine or mixtures thereof.

[0023] Representative aldehydes for use in the preparation of high molecular weight Mannich products include the aliphatic aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, caproaldehyde, heptaldehyde, stearaldehyde. Aromatic aldehydes which may be used include benzaldehyde and salicylaldehyde. Illustrative heterocyclic aldehydes for use herein are furfural and thiophene aldehyde, for example. Also useful are formaldehyde-producing reagents such as paraformaldehyde, or aqueous formaldehyde solutions such as formalin. Most preferred is formaldehyde or formalin.

[0024] Important considerations insofar as the present invention is concerned, are to insure that the alkylphenol having an alkyl substituent with the desired number average molecular weight be reacted with the preferred polyethylene polyamine and aldehyde compounds and that the reactants be employed in proportions such that the resultant Mannich reaction product contains the requisite proportions of the chemically combined reactants, all as specified herein. When utilizing this combination of features, the resultant compositions of this invention not only possess exceptional effectiveness in controlling or reducing the amount of induction system deposits formed during engine operation but which permit adequate demulsification performance.

[0025] A key feature of this invention is that the Mannich reaction products are used in combination with one or more poly(oxyalkylene) compounds having the requisite viscosity parameters referred to hereinabove.

[0026] The poly(oxyalkylene) compounds suitable for use in the practice of this invention comprise one or more gasoline-soluble poly(oxyalkylene) alcohols, glycols or polyols or mono or diethers thereof, with the proviso that such compounds have in their undiluted state a viscosity of at least 70 centistokes (cSt) at 40°C and at least 13 cSt at 100°C. Such compounds can be represented by the following formula



wherein R_1 is a hydrogen atom, or hydroxy, alkyl, cycloalkyl, aryl, alkaryl, aralkyl, alkoxy, cycloalkoxy, or amino group having in the range of 1-200 carbon atoms, R_2 is an alkylene group having 2-10 carbon atoms (preferably 2-5 carbon atoms), R_3 is a hydrogen atom or alkyl, cycloalkyl, aryl, alkaryl, aralkyl, or hydrocarbylamino group having 1-200 carbon atoms, and n is an integer in the range from 1 to 500 (and preferably in the range of from 3 to 120) representing the number of repeating alkyleneoxy groups, all with the proviso that the product in its undiluted state is a gasoline-soluble liquid having a viscosity of at least 70 centistokes (cSt) at 40°C and at least 13 cSt at 100°C.

[0027] Generally speaking, the poly(oxyalkylene) compounds used in the practice of this invention will have viscosities of no more than 400 cSt at 40°C and no more than 50 cSt at 100°C. Preferably, the viscosities of the poly(oxyalkylene) compounds used will not exceed 300 cSt at 40°C and 40 cSt at 100°C. The most preferred poly(oxyalkylene) compounds will have viscosities of no more than 200 cSt at 40°C, and no more than 30 cSt at 100°C.

[0028] Preferred poly(oxyalkylene) compounds are poly(oxyalkylene) glycol compounds and monoether derivatives thereof that satisfy the above viscosity requirements and that are comprised of repeating units formed by reacting an alcohol or polyalcohol with an alkylene oxide, such as propylene oxide and/or butylene oxide with or without use of ethylene oxide, and especially products in which at least 80 mole % of the oxyalkylene groups in the molecule are derived from 1,2-propylene oxide. Details concerning preparation of such poly(oxyalkylene) compounds are referred to, for example, in Kirk-Othmer, Encyclopedia of Chemical Technology, Third Edition, Volume 18, pages 633-645 (Copyright 1982 by John Wiley & Sons), and in references cited therein. U.S. Patent Nos. 2,425,755; 2,425,845; 2,448,664; and 2,457,139 also describe such procedures.

[0029] Preferred poly(oxyalkylene) compounds can be represented by the formula



wherein R_4 is a hydrogen atom, or a hydrocarbyl group having up to 18 carbon atoms, and more preferably an alkyl group having up to 10-12 carbon atoms; R_5 is an alkylene group of 2-5 carbon atoms which thus can be an ethylene group (i.e., dimethylene) group, but which preferably is a propylene (i.e., methyldimethylene) group, or butylene (i.e., ethyldimethylene) group; R_6 is a hydrogen atom, or a hydrocarbyl group having up to 18 carbon atoms, and more preferably an alkyl group having up to 10-12 carbon atoms; and p is a integer that yields a product having the viscosity parameters given above. Commercially available products are often composed of mixtures in which the individual species of the mixture have different numerical values for p , and thus in the case of such mixtures the value of p for the overall product represents an average value. The alkylene groups R_5 can all be the same or they can be different and if different, can be arranged either randomly or in prearranged blocks or sequences. Particularly preferred are the poly(oxyalkylene) alcohols and glycols in which from 70 to 100% and especially 80 to 100% of the alkylene groups are propylene groups (methyldimethylene groups) derived from use 1,2-propylene oxide in the alkoxylation reaction usually employed in the production of such products. In these particularly preferred poly(oxyalkylene) alcohols, glycols and diethers, if less than 100% of the alkylene groups are propylene groups, the remainder are either ethylene or butylene groups, or both, proportioned to yield a liquid gasoline-soluble product having the requisite viscosity properties specified above. Monools derived by propoxylation of alkanols (R_4 in Formula (II) is alkyl, R_5 is methyldimethylene groups, R_6 is a hydrogen atom, and p is as defined above) are most preferred. Such compounds can also be thought of as monoethers of poly(oxyalkylene) glycols.

[0030] Other poly(oxyalkylene) glycols and ethers which may be employed can be represented by the formula



wherein R_7 and R_{11} can be the same or different and each is independently a hydrogen atom or a hydrocarbyl group, preferably an alkyl group of up to 18 carbon atoms, and more preferably of up to 10-12 carbon atoms; R_8 and R_{10} can be the same or different and are alkylene groups of 2-5 carbon atoms each, which thus can be ethylene groups (i.e., dimethylene groups), but which preferably comprise or consist of propylene (i.e., methyldimethylene) groups, and/or butylene (i.e., ethyldimethylene) groups; R_9 is a divalent hydrocarbylene group derived from the initiator, and thus can be a group such as a phenylene group or an alkylene group which is preferably an ethylene (i.e., dimethylene) group, a propylene (i.e., methyldimethylene) group, or a butylene (i.e., ethyldimethylene) group, and q and r are independently integers that yield a product having the viscosity parameters given above. Commercially available products are often composed of mixtures in which the individual species of the mixture have different numerical values for q and

different numerical values for r, and thus in the case of such mixtures the values of q and r for the overall product represent average values. As noted, the alkylene groups can all be the same or they can be different and if different, can be arranged either randomly or in blocks or sequences.

5 [0031] The poly(oxyalkylene) compounds used pursuant to this invention will contain a sufficient number of branched oxyalkylene units (e.g., methyltrimethyleneoxy units and/or ethyltrimethyleneoxy units) to render the poly(oxyalkylene) compound gasoline soluble.

10 [0032] The most preferred poly(oxyalkylene) glycol derivative compound useful in the compositions and methods of this invention is known commercially as EMKAROX AF22 available from ICI Chemicals & Polymers Ltd. This compound has a pour point of about -42°C, a density of about 0.980 g/ml at 20°C, an open cup flash point of about 230°C, a viscosity of about 90 cSt (typically in the range of 87 to 98 cSt) at 40°C and about 17 cSt (typically in the range of 15 to 19 cSt) at 100°C, an average molecular weight of about 1700, a viscosity index of about 200, and a volatility as determined by the Volatility Determination Method described hereinafter of less than about 50%. The number average molecular weight of the poly(oxyalkylene) compounds of this invention is preferably in the range of from about 200 to about 5000, more preferably from 500 to 3000, and most preferably from 1500 to 2500.

15 [0033] The hydrocarbon component c) of the fuel compositions of this invention is a poly- α -olefin. The poly- α -olefins (PAO) useful in compositions and methods of this invention can be fully hydrogenated (hydrotreated), partially hydrogenated, or unhydrogenated poly- α -olefins. These materials are poly- α -olefins oligomers, primarily trimers, tetramers, and pentamers of alpha-olefin monomers containing from 6 to 12, generally 8 to 12 and most preferably about 10 carbon atoms. Preferred for use in the compositions of the present invention are poly- α -olefins having a viscosity (measured at 100°C) of at least 8 centistokes, and most preferably about 10 centistokes at 100°C. The volatility of the poly- α -olefin is also of significance and may be determined by the Volatility Determination Method described below.

20 [0034] To determine the volatility of a substance the following Volatility Determination Method is used. The substance, e.g., a poly- α -olefin (110-135 grams) is placed in a three-neck, 250 mL round-bottomed flask having a threaded port for a thermometer. Such a flask is available from Ace Glass (Catalog No. 6954-72 with 20/40 fittings). Through the center nozzle of the flask is inserted a stirrer rod having a Teflon blade, 19 mm wide x 60 mm long (Ace Glass catalog No. 8085-07). The substance (e.g., poly- α -olefin) is heated in an oil bath to 300°C for 1 hour while stirring the substance in the flask at a rate of 150 rpm. During the heating and stirring, the free space above the substance in the flask is swept with 7.5 L/hr of inert gas (e.g., nitrogen, argon, etc.). The volatility of the substance poly- α -olefin thus determined is expressed in terms of the weight percent of material lost based on the total initial weight of material tested. Utilizing the foregoing procedure, it is particularly preferred to select poly- α -olefins for use in the additive formulations of this invention that have a volatility of less than about 50%, more preferably less than about 25%.

25 [0035] In an embodiment of the invention, the alkyl group of the alkyl-substituted phenol (i) has a number average molecular weight of from 800 to 1200, the amine is a polyamine, the aldehyde is formaldehyde or a formaldehyde precursor, and the poly(oxyalkylene) compound has a viscosity of from 87 to 98 cSt at 40°C and of from 15 to 19 cSt at 100°C, and an average molecular weight of 1700.

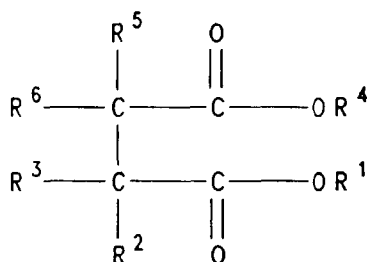
30 [0036] While not required for the purposes of this invention, it is preferred that the fuel compositions of this invention include other conventional additives such as antioxidants, demulsifiers, corrosion inhibitors, aromatic solvents, for example. Accordingly, components for use in the formulations of this invention will now be described.

35 [0037] Antioxidant. Various compounds known for use as oxidation inhibitors can be utilized in the practice of this invention. These include phenolic antioxidants, amine antioxidants, sulfurized phenolic compounds, and organic phosphites, among others. For best results, the antioxidant should be composed predominantly or entirely of either (1) a hindered phenol antioxidant such as 2-tert-butylphenol, 2,6-di-tert-butylphenol, 2,4,6-tri-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 4,4'-methylenebis(2,6-di-tert-butylphenol), and mixed methylene bridged polyalkyl phenols, or (2) an aromatic amine antioxidant such as the cycloalkyl-di-lower alkyl amines, and phenylenediamines, or a combination of one or more such phenolic antioxidants with one or more such amine antioxidants. Particularly preferred for use in the practice of this invention are tertiary butyl phenols, such as 2,6-di-tert-butylphenol, 2,4,6-tri-tert-butylphenol, o-tert-butylphenol, and mixtures thereof.

40 [0038] Demulsifier. A wide variety of demulsifiers are available for use in the practice of this invention, including, for example, poly(oxyalkylene) glycols, oxyalkylated phenolic resins, for example. Particularly preferred are mixtures of poly(oxyalkylene) glycols and oxyalkylated alkylphenolic resins, such as are available commercially from Petrolite Corporation under the TOLAD trademark. One such proprietary product, identified as TOLAD 9308, is understood to be a mixture of these components dissolved in a solvent composed of heavy aromatic naphtha and isopropanol. This product has been found efficacious for use in the compositions of this invention. However, other known demulsifiers can be used such as TOLAD 286.

45 [0039] Corrosion Inhibitor. Here again, a variety of materials are available for use as corrosion inhibitors in the practice of this invention. Thus, use can be made of dimer and trimer acids, such as are produced from tall oil fatty acids, oleic acid or linoleic acid, for example. Another useful type of corrosion inhibitor for use in the practice of this invention are the alkenyl succinic acid and alkenyl succinic anhydride corrosion inhibitors such as, for example, tetrapropenylsuccinic

acid, tetrapropenylsuccinic anhydride, tetradecenylsuccinic acid, tetradecenylsuccinic anhydride, hexadecenylsuccinic acid, hexadecenylsuccinic anhydride, for example. Also useful are the half esters of alkenyl succinic acids having 8 to 24 carbon atoms in the alkenyl group with alcohols such as the polyglycols. Also useful are the aminosuccinic acids or derivatives thereof represented by the formula:



wherein each of R², R³, R⁵ and R⁶ is, independently, a hydrogen atom or a hydrocarbyl group containing 1 to 30 carbon atoms, and wherein each of R¹ and R⁴ is, independently, a hydrogen atom, a hydrocarbyl group containing 1 to 30 carbon atoms, or an acyl group containing from 1 to 30 carbon atoms.

[0040] The groups R¹, R², R³, R⁴, R⁵, and R⁶ when in the form of hydrocarbyl groups, can be, for example, alkyl, cycloalkyl or aromatic containing groups. Preferably R¹, R², R³, R⁴ and R⁵ are hydrogen or the same or different straight-chain or branched-chain hydrocarbon radicals containing 1-20 carbon atoms. Most preferably, R¹, R², R³, R⁴, and R⁵ are hydrogen atoms. R⁶ when in the form of a hydrocarbyl group is preferably a straight-chain or branched-chain saturated hydrocarbon radical.

[0041] Most preferred is a tetraalkenyl succinic acid of the above formula wherein R¹, R², R³, R⁴ and R⁵ are hydrogen and R⁶ is a tetrapropenyl group.

[0042] Aromatic Hydrocarbon Solvent A wide variety of aromatic hydrocarbon solvents can be used with this invention such as benzene, and alkyl substituted benzene or mixtures thereof. Particularly useful are mixtures of o-, p-, and m-xylenes and mesitylene and higher boiling aromatics such as Aromatic 150 which is available from Chemtech. However, other mixtures of aromatic hydrocarbon solvents may also be used.

[0043] The relative proportions of the various ingredients used in the additive concentrates and fuels of this invention can be varied within reasonable limits. However, for best results, the additive concentrate should contain, on an active ingredient basis, from 20 to 35 parts by weight (preferably from 25 to 30 parts by weight) of Mannich reaction product; up to 50 parts by weight (preferably from 20 to 40 parts by weight) of poly(oxyalkylene) component; up to 40 parts by weight (preferably from 0 to 30 parts by weight) of hydrotreated or unhydrotreated poly- α -olefin; 0 to 5 parts by weight (preferably, from 1 to 3 parts by weight) of antioxidant; from 0 to 10 parts by weight (preferably, from 0.1 to 3 parts by weight) of demulsifier; from 25 to 80 parts by weight (preferably 30 to 75 parts by weight) of aromatic hydrocarbon solvent (including any diluent or solvent present in the Mannich detergent as received); and from 0 to 5 parts by weight (preferably, from 0.025 to 1.0 parts by weight) of corrosion inhibitor per each one hundred parts by weight of fuel additive composition. The composition of the invention generally comprises, per 100 parts by weight of the composition, 1 to 5 parts by weight of gasoline-soluble antioxidant, 0.1 to 3 parts by weight of gasoline-soluble demulsifier, and 0.025 to 1.0 part by weight of gasoline-soluble corrosion inhibitor.

[0044] The above additive compositions of this invention are preferably employed in hydrocarbon mixtures in the gasoline boiling range or hydrocarbon/oxygenate mixtures, or oxygenates, but are also suitable for use in middle distillate fuels, notably, diesel fuels and fuels for gas turbine engines. The nature of such fuels is so well known to those skilled in the art as to require no further comment. By oxygenates is meant alkanols and ethers such as methanol, ethanol, propanol, methyl-tert-butyl ether, ethyl-tert-butyl ether, tert-amyl-methyl ether, for example, or combinations thereof. It will of course be understood that the base fuels may contain other commonly used ingredients such as cold starting aids, dyes, metal deactivators, lubricity additives, octane improvers, cetane improvers, emission control additives, antioxidants, metallic combustion improvers, for example. Cyclopentadienyl manganese tricarbonyl compounds such as methylcyclopentadienyl manganese tricarbonyl are preferred because of their outstanding ability to reduce tailpipe emissions such as NOX and smog forming precursors and to significantly improve the octane quality of gasolines, both of the conventional variety and of the newer "reformulated" types.

[0045] When formulating the fuel compositions of this invention, the additives are employed in amounts sufficient to reduce or inhibit deposit formation on intake valves. Deposits on fuel injectors may also be reduced or at least controlled. Generally speaking, the finished additized fuel will contain, by weight and on an active ingredient basis, no more than (and usually less than) about 5000 parts of the combination of components a) and b) per million parts of gasoline, and

preferably, up to (and more preferably less than) about 3000 parts of the combination of components a) and b) per million parts of gasoline. On an active ingredient basis, the total amount of components a) and b), proportioned as above, in the finished fuels of this invention, is preferably no more than about 2000 ppm (by weight), and most preferably in the range of 200 to 1000 ppm (by weight). An additive comprising a Mannich reaction product, a poly(oxyalkylene) compound, and at least one liquid hydrocarbon such as one or more low boiling aromatic hydrocarbons, a poly- α -olefin oligomer and/or a mineral oil of suitable viscosity will be employed in unleaded gasoline in minor amounts such that the gasoline portion of the fuel (including oxygenates such as ethers or alcohol blending agents) is the major component, usually amounting to over 95% by weight. The other components which are preferably used in conjunction with the fuel additive composition can be blended into the fuel individually or in various subcombinations. However, it is definitely preferable to blend all of the components concurrently using an additive concentrate of this invention as this takes advantage of the mutual compatibility afforded by the combination of ingredients when in the form of an additive concentrate, and reduces the possibility of blending errors.

[0046] In order to illustrate the advantages of this invention, the following examples are given. In these examples, the concentrations of additives are typically referred to in terms of pounds per thousand barrels (ptb). One pound per thousand barrels of additive in a gasoline of typical specific gravity is generally equivalent to 3.8 to 4.0 parts per million (ppm) on a weight basis. In addition, the amount of the Mannich dispersant is given on an "as received basis". Since the Mannich dispersant contained approximately 40% by weight of active Mannich Reaction Product (the balance being hydrocarbon diluent and unreacted polyolefin), the actual quantity of active Mannich detergent is approximately 40% of the values reported in the examples.

Reference Example 1

[0047] The vital importance of the viscosity properties of component b) in providing the exhaust valve deposit control performance achievable by the practice of this invention was demonstrated by a series of series of engine tests. For each run, a 1991 Oldsmobile Cutlass equipped with a General Motors 2.3L QUAD 4 engine was operated on an chassis dynamometer for the equivalent of 8047 km (5,000 miles) and the amount of engine deposits was determined. The engine was operated on a driving cycle representative of 10% city, 20% suburban and 70% highway driving. Average speed was equivalent to 72.4 km/hr (45 miles per hour) with the engine accumulating 1448 km/day (900 miles per day). Before each test was begun, the intake manifold and cylinder head were cleaned and inspected, the fuel injectors were checked for proper flow and spray pattern. Following each cleaning and inspection, the engine was rebuilt with new intake valves and the crankcase oil was changed. The base fuel was a clear (i.e., unadditized) regular unleaded gasoline. The crankcase oil used in the test runs was an SAE 5W-30 SG API-quality oil.

[0048] In this series of engine tests various poly(oxyalkylene) compounds of differing viscosities were mixed in the same proportions with separate portions of the same Mannich base detergent, viz., a reaction product of (i) a 900 number average molecular weight polypropyl-substituted phenol, (ii) formalin, and (iii) diethylene triamine (a Mannich base detergent commercially available from Ethyl Petroleum Additives, Inc. as HiTEC® 4997 additive.) Each additive mixture also contained Super High Flash Naphtha, a liquid hydrocarbon product having a flash point of about 40°C (about 100°F) and consisting of essentially 100% of aromatic hydrocarbons. These three additives were formulated into additive concentrates in which the weight ratio of component a) (using the weight on an as received basis): component b) : aromatic hydrocarbon diluent was 70:35:100. The additive concentrates were then blended into separate quantities of the same base fuel and the resultant fuel compositions were then evaluated in the above engine test. A control run was also carried out in which the clear (i.e., unadditized) base fuel was used in the test.

[0049] Six different poly(oxyalkylene) products from different commercial manufacturers were used in these tests. Two met the viscosity requirements of this invention, the other four did not.

[0050] The two poly(oxyalkylene) products meeting the viscosity parameters of this invention were:

A - EMKAROX AF22 (ICI Chemicals & Polymers Ltd.), apparently a poly(oxypropylene) monool with a molecular weight of about 1700 with a viscosity typically in the range of 87 to 98 cSt at 40°C and typically in the range of 15 cSt at 100°C. The sample used had a viscosity of 96 cSt at 40°C and 17 cSt at 100°C.

B - DFA36 (ICI Chemicals & Polymers Ltd.), a proprietary experimental poly(oxyalkylene) product obtained under a non-analysis agreement, for which the manufacturer specified a viscosity of 73 cSt at 40°C and 13.5 cSt at 100°C. Other properties given were Appearance, Clear by Method C&P Appendix 2-1; Water Content, 0.055% by Method C&P/CO/pm/584; Color (Hazen), 10 by Method C&P/CO/pm/579; Density, 0.9725 g/mL by Method C&P/CO/pm/561; Pour Point, -34°C by Method NFT60105; and Flash Point, 228°C by Method C&P/CO/pm/578.

[0051] The four poly(oxyalkylene) products not meeting the viscosity parameters of this invention were:

C - An experimental proprietary poly(oxyalkylene) monool having a viscosity of 63 cSt at 40°C and 8 cSt at 100°C.

EP 0 647 700 B1

Properties specified by the manufacturer were Approximate Molecular Weight, 1000; Mw/Mn, 1.79; OH Number (meq KOH/g), 86; and Viscosity, 120 cP at 25°C.

D - A commercially available polyoxypropylene glycol butyl ether having a viscosity of 57 cSt at 40°C and 11 cSt at 100°C. Typical properties specified by the manufacturer were Average Molecular Weight, 1150; Average Freezing Point, -40°C; Flash Point (PMCC), >400°F (>204.4°C); Refractive Index, 1.446 at 25°C; Specific Gravity, 0.9888 at 25°C; and Viscosity Index, 177.

E - A proprietary experimental poly(oxyalkylene) product obtained under a non-analysis agreement, but identified by the manufacturer to be an alkylphenol propoxylate. It has a viscosity of 67 to 70 cSt at 40°C and 10 cSt at 100°C.

F - A proprietary experimental poly(oxyalkylene) product obtained under a non-analysis agreement having a viscosity of 44 to 45 cSt at 40°C and 8.4 to 8.6 cSt at 100°C. Other properties given were Appearance, Clear by Method C&P Appendix 2-1; Water Content, 0.07% by Method C&P/CO/pm/584; Color (Hazen), 15 by Method C&P/CO/pm/579; Density, 0.9586 g/mL by Method C&P/CO/pm/561; Pour Point, -39°C by Method NFT60105; and Flash Point, 220°C by Method C&P/CO/pm/578.

[0052] The intake valve deposit performance of this series of tests is summarized in Table 1. The fuels designated A through F contained the poly(oxyalkylene) compounds identified above as A through F, respectively. Fuels A through F each contained component a) at a concentration of 70 pounds per thousand barrels (equivalent to approximately 0.027 wt%), the respective poly(oxyalkylene) compound at a concentration of 35 pounds per thousand barrels (equivalent to approximately 0.013 wt%), and the aromatic hydrocarbon solvent (which in effect became part of the gasoline) at a concentration of 100 pounds per thousand barrels (equivalent to approximately 0.04 wt%).

Table 1

Fuel	40°C Viscosity, cSt	100°C Viscosity, cSt	Intake Valve Deposits, mg
A	96	17	36.3*
B	73	13.5	74.2
C	63	8	221.5
D	57	11	143.4
E	67-70	10	142.6
F	44-45	8.4-8.6	105.3
Control	--	--	128.0

* Average of two runs.

[0053] In addition, the total combustion chamber deposits formed when using fuels A and B was almost 3% less than the total combustion chamber deposits formed in the runs using fuels C, D, E and F.

Example 1

[0054] Another group of tests was conducted in a 1991, General Motors 2.3L QUAD 4 engine operated as described in Reference Example 1. Once again the base fuel was an unadditized regular unleaded gasoline, and the fuel detergent used was the reaction product of (i) a 900 number average molecular weight polypropyl-substituted phenol, (ii) formalin, and (iii) diethylene triamine. In this group of tests some of the test fuels contained, in addition to the combination of the detergent and a poly(oxyalkylene) compound, a poly- α -olefin oligomer (a 10 cSt unhydrotreated poly- α -olefin of 1-decene, hereinafter referred to as PAO) or an antioxidant (HiTEC® 4733 additive (commercially available from Ethyl Petroleum Additives, Inc.). HiTEC® 4733 additive is a mixture of tert-butyl phenols containing about 10 wt.% 2-tert-butyl phenol, about 75 wt.% 2,6-di-tert-butyl phenol, about 2 wt.% 2,4-di-tert-butyl phenol, and about 13 wt.% 2,4,6-tri-tert-butyl phenol.

[0055] The poly(oxyalkylene) compounds used both satisfied the requirements of this invention, one of them being the poly(oxyalkylene) product identified as A in Example 1. The other product, G, is P1200 (Dow Chemical Company), a commercially available polyoxypropylene glycol having a typical viscosity of about 90 cSt at 40°C and about 13.5 cSt at 100°C. Typical properties as given by the manufacturer were Average Molecular Weight, 1200; Average Pour Point, -40°C; Flash Point (PMCC), 345°F (174°C); Refractive Index, 1.448 at 25°C; Specific Gravity, 1.007 at 25°C; and Viscosity Index, 161.

[0056] Table 2 gives the compositions of additives in the fuel for each run (where ptb is pounds per thousand barrels) as well as the average of the intake valve (IVD) and combustion chamber deposits (CCD) for each cylinder. The com-

EP 0 647 700 B1

bustion chamber deposits are a combination of the piston top deposits and the cylinder head deposits. Runs 1 and 2 give base line results for the unadditized fuel, and fuel containing Mannich detergent and PAO only. Runs 5 and 7 are of the invention and illustrate the reduction in deposits that can be achieved by additive formulations in accordance with the present invention.

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Table 2

Run No.	HiTEC® 4997, ptb	HiTEC® 4733, ptb	Prod. A, ptb	Prod. G, ptb	PAO, ptb	Avg. dep., mg
1	--	--	--	--	--	905
2	80	4	--	--	40	877
3	80	--	--	40	--	962
4	80	4	--	40	--	736
5	80	--	--	20	20	864
6	80	4	40	--	--	846
7	80	--	20	--	20	805
8	80	--	40	--	--	746

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Example 2

[0057] In another series of runs, a stationary 1985, Ford 2.3L, 4 cylinder, single spark plug engine was run for 200 hours under various loads utilizing Union Oil fuel and containing the additives indicated in Table 3. The transient test cycle consisted of 2 minutes at 1,400 rpm and under a load of 18 inches of Hg intake manifold vacuum, 5 minutes at 2,000 rpm and a of 0.4 bar (12 inches of Hg) intake manifold vacuum, and 3 minutes at 2,500 rpm at 10 inches Hg intake manifold vacuum. The engine coolant temperature was maintained at about 74°C and the combustion air was controlled at a temperature of 32°C and a humidity of 80 grains of moisture per pound of dry air. The test is primarily an intake valve deposit test, but measurements of combustion chamber deposits and octane requirement increase can be made. In Table 3 octane requirement increase is the difference in octane requirement of the engine as measured at 0 and 200 hours. The crankcase oil used in the test runs was an SAE 5W-30 SG API-quality oil. New intake valves and valve stem seals were installed after each test run, and new exhaust valves were installed every fourth test run. Prior to and subsequent to each test run, the intake valves, ports, manifolds, and throttle blade were weighed and/or rated. Runs 10, 11, and 12, are given for comparative purposes and represent the baseline case of fuel without additive. Runs 10, 11, 12, and 13 were run with a different lot of the same fuel as runs 14, 15, 16, and 17. Results of the tests indicate a significant reduction in intake valve deposits (IVD) with surprisingly little change in ORI or combustion chamber deposits. The poly(oxyalkylene) compound used pursuant to the invention was the same as product A of Reference Example 1. The fuel in Run 16 contained 4 ptb of sulfurized 2,6-di-tert-butylphenol as antioxidant and the fuel in run 17 had 4 ptb of nonyl phenol sulfide as antioxidant. No antioxidant was added to the other fuels of this series.

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Table 3

Run No.	HiTEC® 4997 (ptb)	Product A (ptb)	PAO (ptb)	IVD (mg)	CCD (mg)	ORI
10	--	--	--	721.0	1587	10
11	--	--	--	519.8	1668	8
12	--	--	--	577	1855	8-10
13	90	45	--	28.3	2210	11
14	90	45	--	43.1	1481	10
15	90	22.5	22.5	41.6	1655	11
16	90	45	--	37.8	1745	11
17	90	45	--	28.0	1740	9

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Example 3

[0058] This series of runs is similar to the runs of Example 1. In this series of runs, a 1985, 2.3L, 4 cylinder Ford

EP 0 647 700 B1

engine containing a single spark plug was run for 112 hours, operating between a 3-minute "power" cycle (37 HP) at 2,800 rpm and a 1-minute "idle" cycle (0-4 HP) at 2,000 rpm. The engine coolant temperature was maintained at about 74°C and the combustion air was not temperature and humidity controlled. The octane requirement increase is the difference in octane requirement as measured at 0 and 112 hours. The crankcase oil used in the test runs was an SAE 10W-40 SG API-quality oil. New intake valves and valve stem seals were installed after each test run, and new exhaust valves were installed every fourth test run. Prior to and subsequent to each test run, the intake valves, ports, manifolds, and throttle blade were weighed and/or rated. Table 4 illustrates the advantages of fuel additives of this invention. The poly(oxyalkylene) compound used pursuant to the invention was the same as product A of Reference Example 1.

Table 4

Run No.	HiTEC® 4997 (ptb)	Product A (ptb)	PAO (ptb)	IVD (mg)	CCD (mg)	ORI
18	90	45	--	19.8	1348	7
19	90	45	--	14.1	1469	8
20	90	22.5	22.5	22.5	1282	10
21	90	45	--	29.6	1273	8
22	90	45	--	24.9	1193	10

Example 4

[0059] This series of runs is similar to the runs of Example 3. In this series, a 1993, dual spark plug, 4 cylinder 2.3 L Ford engine was run for 100 hours, operating between a 3-minute "power" cycle at 2,800 rpm and a 1-minute "idle" cycle at 2,000 rpm. The combustion air was controlled at a temperature of 32°C and a humidity of 80 grains of moisture per pound of dry air. Runs 23-27 were run at an engine coolant temperature of 91°C and Runs 28 and 29 were run at an engine coolant temperature of 74°C. The octane requirement increase is the difference in octane requirement as measured at 0 and 100 hours. The crankcase oil used in the test runs was an SAE 5W-30 SG API-quality oil. Prior to and subsequent to each test run, the intake valves, ports, manifolds, and throttle blade were weighed and/or rated. New spark plugs, intake valves and valve guide seals were installed every test run. New exhaust valves were installed every fourth test run. Table 5 illustrates the advantages of fuel additives of this invention. The fuels in Runs 26 and 27 contained 4 ptb of sulfurized 2,6-di-tert-butylphenol as antioxidant. No antioxidant was added to the other fuels of this series.

Table 5

Run No.	HiTEC® 4997 (ptb)	Product A (ptb)	PAO (ptb)	IVD (mg)	CCD (mg)	ORI
23	--	--	--	261.0	647	6
24	90	45	--	41.6	961	5
25	90	22.5	22.5	29.5	1283	5
26	90	45	--	31.2	1183	6
27	90	22.5	22.5	37.3	1258	6
28	--	--	--	338.0	719	8
29	90	45	--	29.5	1283	5

[0060] As used herein the term "fuel soluble" means that the additive under discussion has sufficient solubility in the particular gasoline fuel composition in which it is being used to dissolve at 20°C to the extent of at least the minimum concentration required to achieve control of intake valve deposits in an internal combustion engine operated on the resulting fuel. Preferably, and in almost all cases, the additive should (and will) have a substantially greater gasoline solubility than this. However, the term does not require that the additive be soluble in all proportions in the gasoline fuel composition.

Claims

1. A fuel additive composition for control of intake valve deposits comprising
 - 5 a) a gasoline-soluble Mannich reaction product of (i) a high molecular weight alkyl-substituted phenol wherein the alkyl group has a number average molecular weight of from 600 to 3000, (ii) amine and (iii) aldehyde;
 - b) a gasoline-soluble poly(oxyalkylene) compound having a viscosity in its undiluted state of at least 70 cSt at 40°C and at least 13 cSt at 100°C; and
 - 10 c) one or more poly- α -olefins collectively having viscosities at 40°C and 100°C that are not more than approximately 25% higher than the respective viscosities of said poly(oxyalkylene) compound at 40°C and 100°C,

wherein the proportions of a) to b) are such that there are from 0.2 to 5 parts by weight of active Mannich base in a) per part by weight of b).
- 15 2. The fuel additive composition of claim 1 wherein the alkyl group has a number average molecular weight within the range of from 800 to 950.
3. The fuel additive composition of claim 1 or claim 2 wherein the amine is a polyalkylene amine selected from diethylene triamine and triethylene tetramine or mixtures thereof.
- 20 4. The fuel additive composition of any one of claims 1 to 3 wherein the poly(oxyalkylene) compound is a monomer derivative of a poly(oxyalkylene) glycol.
5. The fuel additive composition of any one of claims 1 to 4 wherein the proportions of a) to b) are such that there are from 0.5 to 3 parts by weight of active Mannich base in a) per part by weight of b).
- 25 6. The fuel additive composition of claim 5 wherein the proportions of a) to b) are such that there are from 0.8 to 2 parts by weight of active Mannich base in a) per part by weight of b).
- 30 7. The fuel additive composition of any one of claims 1 to 6 wherein said poly(oxyalkylene) compound has an average molecular weight of from 1500 to 2500.
8. The fuel additive composition of claim 1 wherein the alkyl group has a number average molecular weight of from 800 to 1200, the amine is a polyamine, the aldehyde is formaldehyde or a formaldehyde precursor, and the poly
- 35 (oxyalkylene) compound has a viscosity of from 87 to 98 cSt at 40°C and of from 15 to 19 cSt at 100°C, and an average molecular weight of 1700.
9. The fuel additive composition of any one of claims 1 to 8 further comprising, per 100 parts by weight of the composition, 1 to 5 parts by weight of gasoline-soluble antioxidant, 0.1 to 3 parts by weight of gasoline-soluble demulsifier, and 0.025 to 1.0 part by weight of gasoline-soluble corrosion inhibitor.
- 40 10. A composition which comprises a major amount of hydrocarbons of the gasoline boiling range and a minor engine deposit-inhibiting amount of a fuel additive composition in accordance with any one of claims 1 to 8.
- 45 11. A method for controlling intake valve deposits in a gasoline engine comprising fueling and operating the engine with a fuel composition which comprises a major amount of hydrocarbons of the gasoline boiling range and a minor engine deposit-inhibiting amount of a fuel additive composition in accordance with any one of claims 1 to 8.

50 **Patentansprüche**

1. Kraftstoffzusatz-Zusammensetzung zur Kontrolle von Abscheidungen auf Einlaßventilen, umfassend
 - 55 a) ein benzin-lösliches Mannich-Reaktionsprodukt aus
 - (i) einem alkylsubstituierten Phenol mit hohem Molekulargewicht, bei dem die Alkylgruppe ein zahlenmittleres Molekulargewicht von 600 bis 3000 aufweist,
 - (ii) Amin und

(iii) Aldehyd;

b) eine benzin-lösliche Poly(oxyalkylen)-Verbindung mit einer Viskosität im unverdünnten Zustand von mindestens 70 cSt bei 40 °C und mindestens 13 cSt bei 100 °C; und

c) ein oder mehrere Poly-a-olefinkohlenwasserstoff(e), die Viskositäten bei 40 °C und 100 °C aufweisen, welche nicht mehr als etwa 25 % höher sind als die betreffenden Viskositäten der Poly(oxyalkylen)-Verbindung bei 40 °C und 100 °C,

wobei das Verhältnis von a) zu b) so ist, daß 0,2 bis 5 Gew.-Teile der aktiven Mannich-Base in a) pro Gew.-Teil b) vorhanden sind.

2. Kraftstoffzusatz-Zusammensetzung nach Anspruch 1, in der die Alkylgruppe ein zahlenmittleres Molekulargewicht im Bereich von 800 bis 950 hat.

3. Kraftstoffzusatz-Zusammensetzung nach Anspruch 1 oder Anspruch 2, in der das Amin ein Polyalkylenamin ist, ausgewählt aus Diethylentriamin und Triethyltetramin oder deren Gemischen.

4. Kraftstoffzusatz-Zusammensetzung nach einem der Ansprüche 1 bis 3, in der die Poly(oxyalkylen)-Verbindung ein monomeres Derivat von Poly(oxyalkylen)-glykol ist.

5. Kraftstoffzusatz-Zusammensetzung nach einem der Ansprüche 1 bis 4, in der das Verhältnis von a) zu b) so ist, daß 0,5 bis 3 Gew.-Teile aktive Mannich-Base in a) pro Gew.-Teil b) vorhanden sind.

6. Kraftstoffzusatz-Zusammensetzung nach Anspruch 5, in der das Verhältnis von a) zu b) so ist, daß 0,8 bis 2 Gew.-Teile aktive Mannich-Base in a) pro Gew.-Teil b) vorhanden sind.

7. Kraftstoffzusatz-Zusammensetzung nach einem der Ansprüche 1 bis 6, in der die Poly(oxyalkylen)-Verbindung ein zahlenmittleres Molekulargewicht von 1500 bis 2500 hat.

8. Kraftstoffzusatz-Zusammensetzung nach Anspruch 1, in der die Alkylgruppe ein zahlenmittleres Molekulargewicht von 800 bis 1200 aufweist, das Amin ein Polyamin ist, das Aldehyd ein Formaldehyd oder eine Formaldehyd-Vorstufe ist, und die Poly(oxyalkylen)-Verbindung eine Viskosität von 87 bis 98 cSt bei 40 °C und 15 bis 19 cSt bei 100 °C und ein zahlenmittleres Molekulargewicht von 1700 hat.

9. Kraftstoffzusatz-Zusammensetzung nach einem der Ansprüche 1 bis 8, die zusätzlich pro 100 Gew.-Teile der Zusammensetzung 1 bis 5 Gew.-Teile benzin-lösliches Antioxidans, 0,1 bis 3 Gew.-Teile benzin-löslichen Demulgator und 0,025 bis 1,0 Gew.-Teil benzin-löslichen Korrosionsinhibitor aufweist.

10. Zusammensetzung, die einen größeren Anteil von Kohlenwasserstoffen mit einem Siedepunkt im Benzinbereich und eine geringere, Abscheidungen im Motor verhindernde Menge einer Kraftstoffzusatz-Zusammensetzung nach einem der Ansprüche 1 bis 8 aufweist.

11. Verfahren zur Kontrolle von Abscheidungen auf Einlaßventilen in einem Benzinmotor, bei dem man Kraftstoff zuführt und den Motors mit einer Kraftstoffzusammensetzung bereibt, die einen größeren Anteil Kohlenwasserstoffe im Siedebereich von Benzin und eine geringere, Abscheidungen im Motor verhindernde Menge einer Kraftstoffzusatz-Zusammensetzung nach einem der Ansprüche 1 bis 8 aufweist.

Revendications

1. Composition d'additifs pour carburants, destinée à limiter les dépôts sur les soupapes d'admission, comprenant

a) un produit de réaction de Mannich, soluble dans l'essence, (1) d'un phénol à substituant alkyle de haut poids moléculaire dans lequel le groupe alkyle a une moyenne en nombre du poids moléculaire de 600 à 3000, (2) d'une amine et (3) d'un aldéhyde,

b) un dérivé de poly(oxyalkylène), soluble dans l'essence, ayant une viscosité à l'état non dilué d'au moins 70 cSt à 40°C et d'au moins 13 cSt à 100°C ; et

EP 0 647 700 B1

c) une ou plusieurs poly- α -oléfines ayant collectivement des viscosités à 40°C et 100°C qui ne sont pas supérieures de plus d'approximativement 25% aux viscosités respectives dudit dérivé de poly(oxyalkylène) à 40°C et 100°C,

- 5 dans laquelle les proportions des constituants a) et b) sont telles qu'il existe 0,2 à 5 parties en poids de base de Mannich active dans le constituant a) par partie en poids de constituant b).
2. Composition d'additifs pour carburants suivant la revendication 1, dans laquelle le groupe alkyle a une moyenne en nombre du poids moléculaire comprise dans l'intervalle de 800 à 950.
- 10 3. Composition d'additifs pour carburants suivant la revendication 1 ou la revendication 2, dans laquelle l'amine est une polyalkylène-amine choisie entre la diéthylène-triamine et la triéthylène-tétramine ainsi que leur mélange.
- 15 4. Composition d'additifs pour carburants suivant l'une quelconque des revendications 1 à 3, dans laquelle le dérivé de poly(oxyalkylène) est un dérivé monomérique d'un poly(oxyalkylène)glycol.
5. Composition d'additifs pour carburants suivant l'une quelconque des revendications 1 à 4, dans laquelle les proportions du constituant a) et du constituant b) sont telles qu'il existe 0,5 à 3 parties en poids de base de Mannich active dans le constituant a) par partie en poids de constituant b).
- 20 6. Composition d'additifs pour carburants suivant la revendication 5, dans laquelle les proportions des constituants a) et b) sont telles qu'il existe 0,8 à 2 parties en poids de base de Mannich active dans le constituant a) par partie en poids de constituant b).
- 25 7. Composition d'additifs pour carburants suivant l'une quelconque des revendications 1 à 6, dans laquelle le dérivé de poly(oxyalkylène) a un poids moléculaire moyen de 1500 à 2500 en poids.
8. Composition d'additifs pour carburants suivant la revendication 1, dans laquelle le groupe alkyle a une moyenne en nombre du poids moléculaire de 800 à 1200, l'amine consiste en une polyamine, l'aldéhyde consiste en formaldéhyde ou en précurseur de formaldéhyde, et le dérivé de poly(oxyalkylène) a une viscosité comprise dans l'intervalle de 87 à 98 cSt à 40°C et une viscosité comprise dans l'intervalle de 15 à 19 cSt à 100°C et un poids moléculaire moyen de 1700.
- 30 9. Composition d'additifs pour carburants suivant l'une quelconque des revendications 1 à 8, comprenant en outre, pour 100 parties en poids de la composition, 1 à 5 parties en poids d'un antioxydant soluble dans l'essence, 0,1 à 3 parties en poids d'un désémulsionnant soluble dans l'essence et 0,025 à 1,0 parties en poids d'un inhibiteur de corrosion soluble dans l'essence.
- 35 10. Composition qui comprend une quantité dominante d'hydrocarbures dans la plage d'ébullition de l'essence et une petite quantité, inhibant les dépôts dans les moteurs, d'une composition d'additifs pour carburants suivant l'une quelconque des revendications 1 à 8.
- 40 11. Procédé pour limiter les dépôts sur les soupapes d'admission dans un moteur à essence, comprenant l'alimentation et le fonctionnement du moteur avec une composition de carburant qui comprend une quantité dominante d'hydrocarbures dans la plage d'ébullition de l'essence et une petite quantité, inhibant les dépôts dans les moteurs, d'une composition d'additifs pour carburants suivant l'une quelconque des revendications 1 à 8.
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