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Description

Field of the Invention

This invention relates to corrosion inhibiting compositions for use in alcohol and alcohol containing normally liquid hydrocarbon fuels. This invention further relates to alcohol and alcohol containing normally liquid hydrocarbon fuels containing said corrosion inhibiting compositions and characterised by improved corrosion inhibition.

Background of the Invention

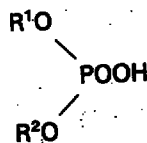
Alcohol fuels and alcohol containing normally liquid hydrocarbon fuels for use in spark-ignited and compression-ignited internal combustion engines possess a high degree of corrosive activity. This higher activity is attributable to the reactive nature of alcohols in general and in some instances, such as for example ethenol, to the presence of acidic and halogen ion containing contaminants. Thus, alcohols are particularly destructive to various nonferrous metals and metal coatings, such as tin/lead alloy coatings employed on internal surfaces of fuel tanks and to zinc/aluminum alloys employed in the construction of carburetors. As a result, motor vehicles employing alcohol and alcohol containing normally liquid hydrocarbon fuels have shown a greater propensity toward corrosion in the fuel tank, fuel line, and fuel induction system areas.

Two patents which are specifically directed toward corrosion inhibition in alcohol or alcohol containing hydrocarbon fuel, e.g., gasohol, are U.S. Patents numbers 4,282,007 and 4,282,008. In the former are disclosed additives comprising the reaction products of aminotriazoles and polyisobutenyl succinic anhydride and in the latter reaction products of an amineotriazole, isatoic anhydride and N-alkylpropylenediamine.

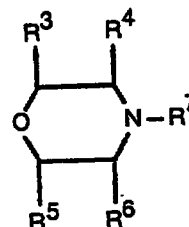
It is an aim of this invention to provide other corrosion inhibiting additives for use in alcohol and alcohol normally liquid hydrocarbon fuels. It is a further aim of this invention to provide alcohol and alcohol containing normally liquid hydrocarbon fuels containing said additives. It is yet a further aim of this invention to provide alcohol and alcohol containing normally liquid hydrocarbon fuels characterized by improved corrosion inhibition.

Summary of the Invention

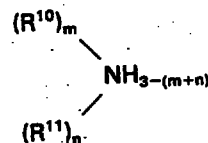
In one aspect the present invention relates to compositions for use in alcohol and alcohol containing normally hydrocarbonaceous petroleum distillate fuels, said compositions comprising a corrosion inhibiting reaction product of (A) at least one phosphoric acid compound having the formula



wherein R¹ is a hydrocarbon based radical containing from about 8 to about 18 carbon atoms and R² is hydrogen or a hydrocarbon based radical containing from about 8 to about 18 carbon atoms and (B) at least one amine compound selected from a group consisting of morpholines of the formula



wherein R³, R⁴, R⁵, and R⁶ are independently hydrogen or alkyl radicals containing from 1 to about 3 carbon atoms and R⁷ is hydrogen or a radical selected from the group consisting of hydrocarbon based radicals containing from 1 to about 20 carbon atoms and $-(\text{R}^8\text{O})_x-\text{R}^9$ radicals where R⁸ is divalent alkyl radical containing from 1 to about 20 carbon atoms, x is a number ranging from 1 to about 10 and R⁹ is hydrogen or aliphatic radicals containing from 1 to about 6 carbon atoms and alkanolamines having the formula



wherein R¹⁰ is a hydrocarbon based radical containing from 2 to about 10 carbon atoms, said radical R¹⁰ further containing at least hydroxyl group, R¹¹ is a hydrocarbon based radical containing from 1 to about 20 carbon atoms, m is a number equal to 1, 2, or 3, n is a number equal to 0, 1, or 2 and the sum of m+n is a number ranging from 1 to 2 to provide alcohol and alcohol containing normally liquid hydrocarbonaceous petroleum distillate fuels with improved corrosion inhibition.

The invention further relates to compositions for use in internal combustion engines comprising (A) a major portion of a fuel containing (i) from about 2 to 100 percent by volume of an alcohol containing from 1 to about 5 carbon atoms and (ii) from about 98 to 0 volume percent of a normally liquid hydrocarbonaceous petroleum distillate fuel and (B) a minor portion of the corrosion inhibiting products generally described hereinabove.

Detailed Description of Preferred Embodiments

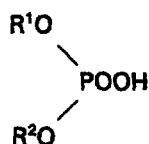
The corrosion inhibiting additives comprising one aspect of this invention are amine salts prepared by the reaction of phosphoric acids and monoamines, both of which are defined in detail below.

As used herein, the term "hydrocarbon based" or "hydrocarbon based radicals" denotes a radical having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Such radicals include the following:

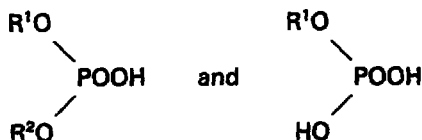
1. Hydrocarbon radicals; that is, aliphatic, (e.g. alkyl or alkenyl), alicyclic (e.g., cycloalkyl or cycloalkenyl), aromatic aliphatic- and alicyclic substituted aromatic, aromatic substituted aliphatic and alicyclic radicals, cyclic radicals wherein the ring is completed through another portion of the molecule (i.e., any two indicated substituents may together form an alicyclic radical) and the like as well as two or more used benzene nuclei. Such radicals are known to those skilled in the art, represented examples of which include methyl, ethyl, propyl, butyl, octyl, decyl, dodecyl, cyclohexyl, phenyl, tolyl, benzyl, naphthyl, anthryl, phenanthryl and the like, and

2. Substituted hydrocarbon radicals; that is radicals containing non-hydrocarbon substituents which, in the context of this invention do not alter the predominantly hydrocarbon character of the radical. Those skilled in the art will be aware of the suitable substituents (hydroxy, alkoxy, carbal-koxy, etc.).

The phosphoric acids which are useful in the preparation of the amine salts in this invention are partially esterified orthophosphoric acids having the formula

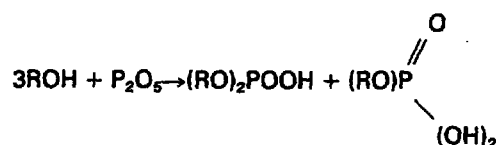


wherein R¹ is a hydrogen based radical containing from about 8 to about 18 carbon atoms and R² is hydrogen or a hydrocarbon radical containing from about 8 to about 18 carbon atoms. Thus, it is contemplated that the phosphoric acids may be monoesters or diesters of orthophosphoric acids or mixtures thereof represented by the formulae



wherein R¹ and R² are hydrocarbon based radicals as defined above. For reasons of economy a mixture of mono- and di-phosphate esters is preferred. Such a mixture can be prepared by the reaction of one mole of phosphorus pentoxide with three moles of a hydrocarbon alcohol having from about 8 to about 18 carbon atoms. The

reaction may be illustrated by the following equation:

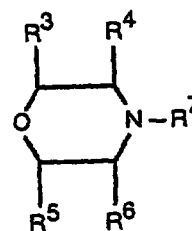


Alternatively, from about two to four moles of the hydrocarbon alcohol or a mixture of such alcohols can be employed per mole of the phosphorus pentoxide.

Generally, R¹ will be unsubstituted aliphatic radicals and preferably unsubstituted alkyl radicals such as, e.g., octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, hexadecyl, and octadecyl and R² will be hydrogen or R¹.

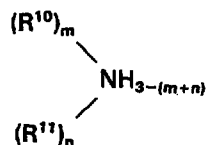
For the preparation of the phosphoric acids, the alcohol will be primary alcohol and preferably branched primary alcohol having from about 8 to about 18 carbon atoms. Examples of such alcohol are the normal alcohols derived from coconut kernel oils. One such commercially available fraction consists mainly of the n-octyl and n-decyl alcohols. Another consists largely of n-dodecyl alcohol, but contains other alcohols having from about 10 to about 18 carbon atoms. Preferably, the alcohol will be a mixture of branched-chain primary alcohols such as those produced by the well known "Oxo" process. Examples of such alcohols include the "Oxo" octyl, decyl, tridecyl, and octyldecyl alcohols, all of which are mixtures consisting predominantly of branched-chain primary alcohols obtained from propylene-butylene dimer, tri-propylene, tetra-propylene, and penta-propylene, respectively.

The amines, which are useful in preparing the corrosion inhibiting additive compositions which comprise one aspect of the present invention are monoamines selected from the group consisting of the group morphylenes of the formula

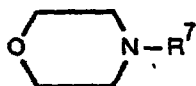


wherein R³, R⁴, R⁵, and R⁶ are independently hydrogen or alkyl radicals containing from 1 to about 3 carbon atoms and R⁷ is hydrogen or a radical selected from the group consisting of hydrocarbon based radicals containing from 1 to about 20 carbon atoms and $-(\text{R}^8\text{O})_x-\text{R}^9$ radicals where R⁸ is a divalent aliphatic hydrocarbon radical containing from 1 to about 20 carbon atoms, x is a number ranging from 1 to about 10,

and R^9 is hydrogen or an aliphatic hydrocarbon radical containing from 1 to about 6 carbon atoms, and alkanolamines having the formula



wherein R^{10} is a hydrocarbon based radical containing from about 2 to about 10 carbon atoms, said radical R^{10} further containing at least one hydroxyl group, R^{11} is a hydrocarbon based radical containing from 1 to about 20 carbon atoms, m is a number equal to 1, 2, or 3, n is a number equal to 0, 1, or 2, and the sum of $m + n$ is a number ranging from 1 to 3. In a preferred embodiment, the amine compounds useful in preparing the additive compositions described herein are selected from the group consisting of morpholines of the above formula wherein R^3 , R^4 , R^5 , and R^6 are all hydrogen atoms and R^7 is hydrogen or a radical selected from the group consisting of hydrocarbon based radicals containing from 1 to about 10 carbon atoms and $-(R^8O)_xR^9$ radicals where R^8 is a divalent alkyl radical containing from 1 to about 10 carbon atoms, x is a number ranging from 1 to about 6 and R^9 is hydrogen or alkyl radical containing from 1 to about 3 carbon atoms and alkanolamines of the above formula wherein R^{10} is an aliphatic hydrocarbon radical containing from about 2 to 5 carbon atoms, said radical R^{10} containing at least one hydroxyl group, R^{11} is a hydrocarbon based radical containing from 1 to about 10 carbon atoms, and m and n and the sum of $m + n$ are as set forth above. The most preferred amine compounds is useful in preparing the additive compositions of this invention are morpholines having the following formula



wherein R^7 is hydrogen or a radical selected from the group consisting of straight-chain or branched-chain aliphatic radicals containing from 1 to about 5 carbon atoms and $-(R^8O)_xR^9$ radicals where R^8 is a divalent alkyl radical containing from 1 to about 6 carbon atoms, x is a number ranging from 1 to about 4, and R^9 is hydrogen or alkyl radicals containing from 1 to about 3 carbon atoms and alkanolamines of the formula above wherein R^{10} is a straight-chain or branched-chain alkyl radical containing from about 2 to 3 carbon atoms, said radical R^{10} further containing one hydroxyl group, R^{11} is a straight-chain or branched-chain alkyl radical containing from 1 to

about 3 carbon atoms and m and n and the sum of $m + n$ are the same as set forth above.

Representative, but non-limited examples of amine compounds useful in the preparation of the additive compositions comprising of one aspect of this invention and falling within the description of the amines set forth above are Morpholine, 4-methylmorpholine, 4-ethylmorpholine, 4-propylmorpholine, 4-butylmorpholine, 2-methylmorpholine, 2-ethylmorpholine, 2,5-dimethylmorpholine, 2-ethyl-5-methyl-morpholine, 2,6-diethylmorpholine, 4-heptylmorpholine, 4-dodecylmorpholine, 4-hexyldecylmorpholine, 4-cyclohexylmorpholine, 4-cyclohexyl-2,6-dimethylmorpholine, 4-cyclopentylmorpholine, 4-(3-butenyl)morpholine, 4-(1-hexenyl)morpholine, 4-(2-ethylhexyl)morpholine, 4-eicosylmorpholine, 4-(2-methoxy)morpholine, 4-(2-cyclohexyloxyethyl)morpholine, 4-(2-methoxymethyl)morpholine, 4-(2-methylpentyl)morpholine, 4-(3-methylphenyl)morpholine, 4-phenylmorpholine, 4-(2-phenylethyl)morpholine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, triisopropanolamine, mono-sec-butenylamine, di-sec-butenylamine, di-methylethanolamine, di-methylisopropanolamine, di-ethylethanolamine, methyl-ethanolamine, butylethanolamine, phenylethanolamine, phenylethylethanolamine, methyl-diethanolamine, tris(hydroxy methyl) methylamine, and the like. The most preferred amines for use in preparing the additive compositions of this invention are selected from the group consisting of morpholine, ethylmorpholine, diethanolamine, and triethanolamine.

The amine salts comprising the corrosion inhibiting additive compositions of the present invention can be prepared simply by mixing the organic substituted phosphoric acid and the amine reactant at a temperature below about 100°C. The reaction in most instances is slightly exothermic and is preferably carried out in the presence of a solvent. Solvents which have been found to be useful are the hydrocarbons or polar salts, such as, benzene, naphtha, toluene, xylene, n-hexane, dioxane, chlorobenzene, kerosene, or a fuel oil. Ordinarily, the relative proportions of the reactants used to prepare the salts are one equivalent of the phosphoric acid compound and one equivalent of the amine so that all of the free amino groups are converted to salts. In some instances, however, only one acidic hydrogen on a mono-organic substituted phosphoric acid may be utilized to form a salt. Thus, amine salts which are useful in this invention are prepared by reacting the amine with one to two equivalents of the phosphoric acid.

The following examples illustrate the preparation of the additive compositions comprising one aspect of this invention and improved corrosion characteristics of alcohol or alcohol containing normally liquid fuels containing these compositions. In the following examples, all parts are by weight unless otherwise specified.

Example 1

A reaction vessel equipped with a stirrer, thermometer and reflux condenser is charged with 1000 parts (5.0 moles) tridecyl alcohol. The vessel is purged with nitrogen while the alcohol is heated to 35°C. Phosphorus pentoxide, 248 parts (1.74 moles), is added in increments over a period of 5 hours. The reaction is exothermic and the temperature is allowed to rise to 50°C. during the addition. The materials are then reacted at 60°C. for 8 hours. The reaction mixture is then filtered and collected. The product obtained contains 8.5 percent phosphorus.

Example 2

To a solution of 14.8 parts of diethanolamine in 50 parts of xylene is added, over a period of one hour, 35.2 parts of the product of Example 1. The temperature of the reaction mixture rises exothermically from room temperature to 50°C. during the addition. The materials are then stirred for an additional 0.25 hour at 50°C.

Example 3

To 18.7 parts of triethanolamine is added, over a period of one hour, 31.3 parts of the product of Example 1. The temperature rises exothermically from room temperature to 51°C. during the addition. Xylene, 50 parts, is then added and the materials are mixed at 50°C. for an additional 0.25 hour.

Example 4

Following the procedure of Example 3, 9.85 parts of ethanolamine is reacted with 40.15 parts of the product of Example 1, and diluted with 50 parts xylene.

Example 5

Following the procedure of Example 2, a solution consisting of 12.95 parts of morpholine and 50 parts xylene is reacted with 37.05 parts of the product of Example 1.

Example 6

A series of alcohol fuels are prepared by blending from 10 to 450 parts by weight of one of the reaction products of examples 2 through 5 with one million parts by weight of hydrated ethanol containing about 7.5 percent by weight water.

Example 7

A series of alcohol containing gasoline fuels is prepared by blending from 10 to 450 parts by weight of one of the reaction products of examples 2 through 5 with one million parts by weight of a gasohol which comprises 20 percent by volume of hydrated ethanol containing 7.5 percent by weight of water and 80 percent by volume of gasoline having an ASTM distillation range of from about 60°C at the 10 percent distillation point to about 205°C at the 90 percent distillation point.

The corrosion inhibiting effectiveness of the additive compositions were tested in accordance

with Method K, Test C of the Brazilian Association of Technical Norms (ABNT). In this test, various metal specimens (e.g., steel, brass, zinc/aluminum alloys) are immersed in commercially available hydrated ethanol for a continuous period of 144 hours at a temperature of 50°C ± 3°C. At the end of the test period each test specimen is then rinsed first with water and then with a ketone or other suitable solvent and dried. After drying, each test specimen is weighed and its visual appearance noted. The weight loss, if any, and visual appearance of the specimens are then compared to those of specimens treated in the same manner in a control or reference gasoline/alcohol blend comprised of 78 to 82 percent by volume of gasoline and 22 to 18 percent by volume of 100 percent absolute ethanol. For a corrosion inhibiting additive composition to be considered effective, neither the weight loss nor the visual appearance of specimens tested with additive containing hydrated ethanol can vary from those treated in the controlled or referenced gasohol/alcohol blend by more than 10 percent. The corrosion inhibiting additive compositions described in examples 2 through 5 above are found to be effective when tested in accordance with this Brazilian method.

Another aspect of this invention comprises fuel compositions for use in internal combustion engines comprising (A) a major portion of a fuel containing (i) at least one alcohol having from 1 to about 5 carbon atoms and (ii) a normally liquid hydrocarbonaceous petroleum distillate fuel and (B) a minor portion of a corrosion inhibiting reaction product as described hereinabove, i.e., the reaction product of (i) at least one phosphoric acid reactant having the formula as set forth hereinabove, and (ii) at least one amine reactant selected from the group consisting of morpholines and alkanolamines corresponding to the formulae also set forth hereinabove.

Alcohol fuels useful in combination with the corrosion inhibiting reaction products of phosphoric acids and amines as defined herein to provide fuel compositions having improved corrosion inhibiting characteristics include such commercially available alcohols as methanol, ethanol, propanol, isopropanol, butyl alcohol and its isomers and amyl alcohol and its isomers and mixtures of these various alcohols. As produced commercially, the preferred alcohols for use in the present invention are methanol and ethanol. The hydrated forms of the above alcohol are particularly suited for accomplishing the objectives of this invention.

The normally liquid hydrocarbonaceous petroleum distillate fuels which are useful in combination with alcohols and the corrosion inhibiting reaction product as described hereinabove include motor gasoline as defined by (ASTM) Specification D439 and diesel fuel or fuel oil as defined by ASTM Specification D396. A particularly preferred petroleum distillate fuel, however, is gasoline, that is a mixture of hydrocarbons having an ASTM distillation range of

from about 60°C at the 10 percent distillation point to about 205°C at the 90 percent distillation point.

The fuel portion of the fuel composition of this invention comprise of about 2 to 100 percent by volume of at least one alcohol containing 1 to about 5 carbon atoms, and from about 98 to 0 percent by volume of the normally liquid hydrocarbonaceous petroleum distillate fuel. In a preferred embodiment, this fuel portion will comprise from about 10 to 100 percent by volume of at least one alcohol containing from 1 to about 5 carbon atoms and from 90 percent to 0 percent by volume of the petroleum distillate fuel. In a more preferred embodiment, the ranges of the alcohol and petroleum distillate fuels employed in the fuel compositions of this invention will be from about 20 to 100 percent by volume and from about 80 to 0 percent by volume respectively. Particularly useful compositions are those based on a mixture of alcohol, especially methanol or ethanol, and a petroleum distillate fuel, especially gasoline, in which mixture the alcohol component ranges from about 10 to about 20 percent by volume and the petroleum distillate fuel ranges from about 90 to 80 percent by volume.

The amount of the corrosion inhibiting reaction products disclosed herein, to be added to the above described fuel portion to provide the fuel compositions of this invention will be an amount sufficient to impart improved corrosion inhibiting characteristics to these fuel compositions. Broadly this amount will arrange from about 10 to 1,000 parts by weight of said additives reaction product per million part by weight of said fuel portion. Preferably this amount will range from about 10 to about 450 parts by weight with a range from about 175 to about 450 parts by weight of said additive reaction product per million parts by weight of said fuel portion being the most preferred. It is to be understood that these amounts are based on additive in pure form and not in a diluted form such as in a concentrate form as described below.

The fuel compositions of this invention can be prepared by merely adding the reaction product of the phosphoric acid and amine directly to the fuel portion or it can be diluted with a substantially inert normally liquid diluent such as naphtha, benzene, toluene, xylene, or a petroleum distillate fuel as described above to form a concentrate of said reaction product which is then added to the fuel portion. These concentrates which constitute yet another embodiment of the invention generally contain from about 20 percent to about 90 percent of the additive reaction products.

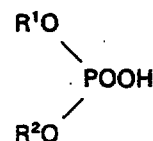
The fuel compositions described hereinabove, may also contain additional materials normally added to liquid fuels to obtain specific benefits. Therefore, the fuel compositions which represent one aspect of this invention may also contain additional materials normally added to liquid fuels to obtain specific benefits. Therefore the fuel compositions which represent one aspect of this

invention may contain anti-knock agents such as tetraalkyl lead compounds, lead scavengers such as halo alkanes (e.g., ethylene dichloride and ethylene dibromide) deposit preventers or modifiers such as triaryl phosphates, dyes, octane improvers, antioxidants such as 2,6-di-tertiary-butyl-4-methylphenol, bacteriostatic agents, gum inhibitors, metal deactivators, demulsifiers, dispersants, detergents, upper cylinder lubricants and anti-icing agents.

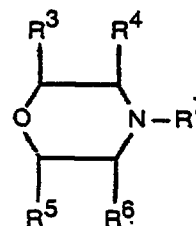
The compositions for use in alcohol and alcohol containing normally liquid hydrocarbonaceous petroleum distillate fuels and the fuel compositions based thereon as well as their methods of preparation have been specifically set forth above to assist those skilled in the art in understanding and practicing the invention. Based on the teachings herein, many various and departures from these specific disclosures will be obvious to those skilled in the art. The term "composition" as used herein includes, where the context permits, a single compound or a mixture of compounds produced by a chemical process.

Claims

1. Compositions for use in alcohol and alcohol containing normally liquid hydrocarbonaceous petroleum distillate fuels comprising reaction products of (A) at least one phosphoric acid compound having the formula



wherein R^1 is a hydrocarbon based radical containing from 8 to 18 carbon atoms and R^2 is hydrogen or a hydrocarbon based radical containing from 8 to 18 carbon atoms and (B) at least one amine compound selected from the group consisting of morpholines of the formula



wherein R^3 , R^4 , R^5 and R^6 are independently hydrogen or alkyl radicals containing from 1 to 3 carbon atoms and R^7 is hydrogen or a radical selected from the group consisting of hydrocarbon based radicals containing from 1 to 20 carbon atoms and $-(\text{R}^8\text{O})_x\text{R}^9$ radicals where R^8 is a divalent aliphatic hydrocarbon radical containing from 1 to 20 carbon atoms, x is a number ranging

from about 60°C at the 10 percent distillation point to about 205°C at the 90 percent distillation point.

The fuel portion of the fuel composition of this invention comprise of about 2 to 100 percent by volume of at least one alcohol containing 1 to about 5 carbon atoms, and from about 98 to 0 percent by volume of the normally liquid hydrocarbonaceous petroleum distillate fuel. In a preferred embodiment, this fuel portion will comprise from about 10 to 100 percent by volume of at least one alcohol containing from 1 to about 5 carbon atoms and from 90 percent to 0 percent by volume of the petroleum distillate fuel. In a more preferred embodiment, the ranges of the alcohol and petroleum distillate fuels employed in the fuel compositions of this invention will be from about 20 to 100 percent by volume and from about 80 to 0 percent by volume respectively. Particularly useful compositions are those based on a mixture of alcohol, especially methanol or ethanol, and a petroleum distillate fuel, especially gasoline, in which mixture the alcohol component ranges from about 10 to about 20 percent by volume and the petroleum distillate fuel ranges from about 90 to 80 percent by volume.

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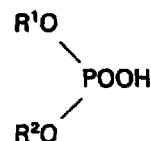
The fuel compositions described hereinabove, may also contain additional materials normally added to liquid fuels to obtain specific benefits. Therefore, the fuel compositions which represent one aspect of this invention may also contain additional materials normally added to liquid fuels to obtain specific benefits. Therefore the fuel compositions which represent one aspect of this

invention may contain anti-knock agents such as tetraalkyl lead compounds, lead scavengers such as halo alkanes (e.g., ethylene dichloride and ethylene dibromide) deposit preventers or modifiers such as triaryl phosphates, dyes, octane improvers, antioxidants such as 2,6-di-tertiary-butyl-4-methylphenol, bacteriostatic agents, gum inhibitors, metal deactivators, demulsifiers, dispersants, detergents, upper cylinder lubricants and anti-icing agents.

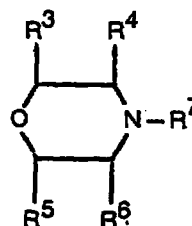
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Claims

1. Compositions for use in alcohol and alcohol containing normally liquid hydrocarbonaceous petroleum distillate fuels comprising reaction products of (A) at least one phosphoric acid compound having the formula



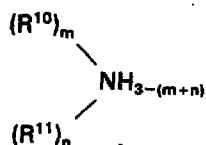
wherein R¹ is a hydrocarbon based radical containing from 8 to 18 carbon atoms and R² is hydrogen or a hydrocarbon based radical containing from 8 to 18 carbon atoms and (B) at least one amine compound selected from the group consisting of morpholines of the formula



wherein R³, R⁴, R⁵ and R⁶ are independently hydrogen or alkyl radicals containing from 1 to 3 carbon atoms and R⁷ is hydrogen or a radical selected from the group consisting of hydrocarbon based radicals containing from 1 to 20 carbon atoms and $-(\text{R}^8\text{O})_x-\text{R}^9$ radicals where R⁸ is a divalent aliphatic hydrocarbon radical containing from 1 to 20 carbon atoms, x is a number ranging

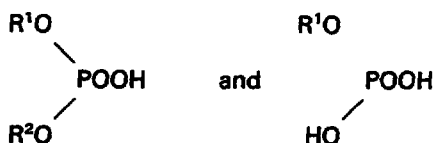


from 1 to 10, R^9 is hydrogen or an aliphatic hydrocarbon radical containing from 1 to 6 carbon atoms and alkanolamines having the formula

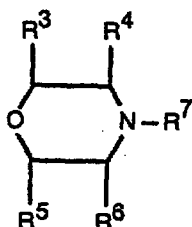


wherein R^{10} is a hydrocarbon based radical containing from 2 to 10 carbon atoms said radical R^{10} further containing at least one hydroxyl group, R^{11} is a hydrocarbon based radical containing from 1 to 20 carbon atoms, m is a number equal to 1, 2 or 3, n is a number equal to 0, 1 or 2 and the sum of $m+n$ is a number ranging from 1 to 3.

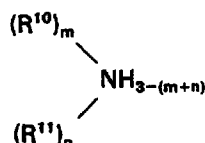
2. The compositions of Claim 1 wherein the phosphoric acid reactant (A) is a mixture of compounds having the formulae



wherein R^1 and R^2 are aliphatic hydrocarbon radicals containing from 8 to 18 carbon atoms and the amine reactant (B) is selected from the group consisting of morpholines having the formula



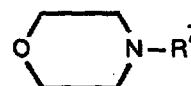
wherein R^3 , R^4 , R^5 and R^6 are hydrogen and R^7 is hydrogen or a radical selected from the group consisting hydrocarbon based radicals containing from 1 to 10 carbon atoms and $-(R^8O)_xR^9$ radicals wherein R^8 is a divalent alkyl radical containing from 1 to 10 carbon atoms, x is a number ranging from 1 to 6 and R^9 is hydrogen or an alkyl radical containing from 1 to 3 carbon atoms and alkanolamines having the formula



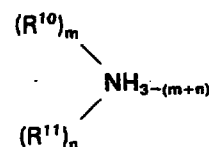
wherein R^{10} is an aliphatic hydrocarbon radical

containing from 2 to 5 carbon atoms, said radical R^{10} containing at least one hydroxyl group, R^{11} is a hydrocarbon based radical containing from 1 to 10 carbon atoms, m is a number equal to 1, 2 or 3, n is a number equal to 0, 1 or 2 and the sum of $m+n$ is a number ranging from 1 to 3.

3. The compositions of either of claims 1 and 2 wherein the amine reactant (B) is selected from the group consisting of morpholines having the formula



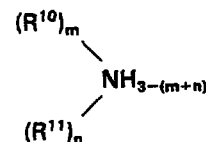
wherein R^7 is hydrogen or a radical selected from the group consisting of straight-chain or branched-chain aliphatic hydrocarbon radicals containing from 1 to 5 carbon atoms and $-(R^8O)_xR^9$ radicals where R^8 is a divalent alkyl radical containing from 1 to 6 carbon atoms, x is a number ranging from 1 to 4 and R^9 is hydrogen or alkyl radical containing from 1 to 3 carbon atoms and alkanolamines having the formula



wherein R^{10} is a straight-chain or branched-chain alkyl radical containing from 2 to 5 carbon atoms, said radical R^{10} further containing one hydroxyl group, R^{11} is a straight-chain or branched-chain alkyl radical containing from 1 to 4 carbon atoms, m is a number equal to 1, 2 or 3, n is a number equal to 0, 1 or 2 and the sum of $m+n$ is a number ranging from 1 to 3.

4. The compositions of Claim 3 wherein the amine reactant (B) is morpholine.

5. The compositions of Claim 3 wherein the amine reactant (B) is an alkanol amine having the formula



wherein R^{10} is a straight-chain alkyl radical containing 2 or 3 carbon atoms, said radical R^{10} containing one hydroxyl group, R^{11} is a straight-chain alkyl radical containing from 1 to 3 carbon



atoms, m is a number equal to 1, 2 or 3, n is a number equal to 0, 1 or 2 and the sum of m+n is a number ranging from 1 to 3.

6. The compositions of Claim 5 wherein the amine reactant (B) is selected from the group consisting of monoethanolamine, diethanolamine and triethanolamine.

7. The compositions of Claims 2, 3, 4, 5 or 6 wherein the phosphoric acid reactant (A) is a mixture of mono- and di-tridecyl phosphoric acids.

8. Fuel compositions for use in internal combustion engines comprising (A) a major portion of a fuel containing (i) from 2.0 to 100 percent by volume of at least one alcohol containing from 1 to 5 carbon atoms and (ii) from 98.0 to 0 percent by volume of a normally liquid hydrocarbonaceous petroleum distillate fuel and (B) a minor portion of a composition according to any one of the preceding claims.

9. The fuel compositions of claim 8, wherein the fuel portion (A) of said compositions comprises (i) from 10 to 100 percent by volume of an alcohol containing from 1 to 5 carbon atoms and (ii) from 90 to 0 percent by volume of a normally liquid hydrocarbonaceous petroleum distillate fuel.

10. The fuel compositions of claim 9 wherein the fuel portion (A) of said compositions comprises (i) from 20 to 100 percent of an alcohol containing from 1 to 5 carbon atoms and (ii) from 80 to 0 percent by volume of a normally liquid hydrocarbonaceous petroleum distillate fuel.

11. The fuel compositions of claims 8, 9 or 10 wherein in said fuel portion (A) the alcohol component (A)(i) is selected from the group consisting of methanol and ethanol and the normally liquid hydrocarbonaceous petroleum fuel component (A)(ii) is gasoline.

12. The fuel compositions of claim 11 wherein in said fuel portion (A), the alcohol component (A)(i) is ethanol.

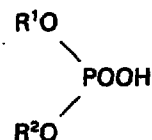
13. The fuel compositions of claims 8, 9, 10, 11 or 12 wherein the phosphoric acid compound is a mixture of mono- and di-tridecylphosphoric acids.

14. Fuel compositions according to claim 8 for use in internal combustion engines comprising (A) a major portion of a fuel containing (i) 10 percent by volume of ethanol and (ii) 90 percent by volume of gasoline and (B) a minor portion of a corrosion inhibiting reaction product of (i) a mixture of mono- and di-tridecylphosphoric acid and (ii) at least one amine selected from the group consisting of morpholine and mono, di- and triethanolamine.

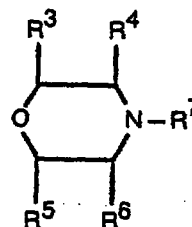
15. Fuel compositions according to claim 8 for use in internal combustion engines comprising (A) a major portion of a fuel containing (i) 20 percent by volume of ethanol and (ii) 80 percent by volume of gasoline and (B) a minor portion of a corrosion inhibiting reaction product of (i) a mixture of mono- and di-tridecylphosphoric acids and (ii) at least one amine selected from the group consisting of morpholine and mono-, di- and triethanol amine.

Patentansprüche

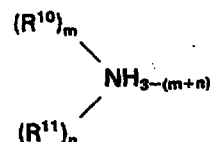
1. Zusammensetzungen zur Verwendung in Alkohol und Alkohol enthaltenden, normalerweise flüssigen Erdöldestillat-Treibstoffen auf Kohlenwasserstoffbasis, umfassend Reaktionsprodukte von (A) mindestens einer Phosphorsäureverbindung der Formel



in der R^1 einen Rest auf Kohlenwasserstoffbasis mit 8 bis 18 Kohlenstoffatomen darstellt und R^2 ein Wasserstoffatom oder einen Rest auf Kohlenwasserstoffbasis mit 8 bis 18 Kohlenstoffatomen bedeutet und (B) mindestens einer Aminverbindung aus der Gruppe Morpholine der Formel



in der R^3 , R^4 , R^5 und R^6 unabhängig voneinander Wasserstoffatome oder Alkylreste mit 1 bis 3 Kohlenstoffatomen darstellen und R^7 ein Wasserstoffatom oder ein Rest auf Kohlenwasserstoffbasis mit 1 bis 20 Kohlenstoffatomen oder ein Rest $-(\text{R}^8\text{O})_x-\text{R}^9$ ist, in dem R^8 einen zweiwertigen aliphatischen Kohlenwasserstoffrest mit 1 bis 20 Kohlenstoffatomen bedeutet, x eine Zahl von 1 bis 10 ist und R^9 ein Wasserstoffatom oder einen aliphatischen Kohlenwasserstoffrest mit 1 bis 6 Kohlenstoffatomen darstellt, und Alkanolamine der Formel

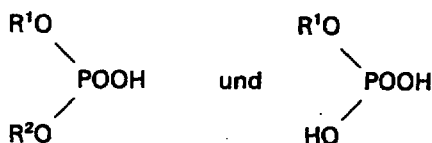


in der R^{10} einen rest auf Kohlenwasserstoffbasis mit 2 bis 10 Kohlenstoffatomen bedeutet, wobei der Rest R^{10} außerdem mindestens eine Hydroxylgruppe enthält, R^{11} einen Rest auf Kohlenwasserstoffbasis mit 1 bis 20 Kohlenstoffatomen bedeutet, m eine Zahl im Wert von 1, 2 oder 3 ist, n eine Zahl im Wert von 0, 1 oder 2 ist und die Summe von m + n eine Zahl im Wert von 1 bis 3 darstellt.

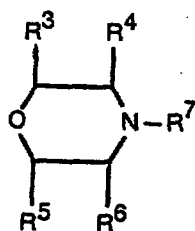
2. Zusammensetzungen nach Anspruch 1, in denen der Phosphorsäure-Umsetzungsteilneh-



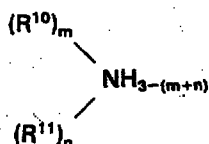
mer (A) ein Gemisch von Verbindungen der Formeln ist



in denen R^1 und R^2 aliphatische Kohlenwasserstoffreste mit 8 bis 18 Kohlenstoffatomen sind, und der Amin-Umsetzungsteilnehmer (B) ein Morpholin der Formel

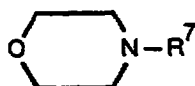


in der R^3 , R^4 , R^5 und R^6 Wasserstoffatome sind und R^7 ein Wasserstoffatom oder ein Rest auf Kohlenwasserstoffbasis mit 1 bis 10 Kohlenstoffatomen oder ein Rest $-(\text{R}^8\text{O})_x\text{R}^9$ ist, wobei R^8 ein Zweiwertiger Alkylrest mit 1 bis 10 Kohlenstoffatomen ist, x eine Zahl von 1 bis 6 ist und R^9 ein Wasserstoffatom oder einen Alkylrest mit 1 bis 3 Kohlenstoffatomen bedeutet, oder ein Alkanolamin der Formel



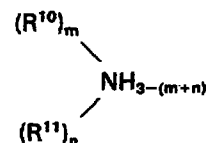
ist, in der R^{10} einen aliphatischen Kohlenwasserstoffrest mit 2 bis 5 Kohlenstoffatomen bedeutet, wobei der Rest R^{10} mindestens eine Hydroxylgruppe enthält, R^{11} einen Rest auf Kohlenwasserstoffbasis mit 1 bis 10 Kohlenstoffatomen darstellt, m eine Zahl im Wert von 1, 2 oder 3 ist, n eine Zahl im Wert von 0, 1 oder 2 ist und die Summe von $m + n$ eine Zahl von 1 bis 3 ist.

3. Zusammensetzungen nach Anspruch 1 und 2, in denen der Amin-Umsetzungsteilnehmer (B) ein Morpholin der Formel



in der R^7 ein Wasserstoffatom oder einen geradkettigen oder verzweigten aliphatischen Kohlenwasserstoffrest mit 1 bis 5 Kohlenstoffatomen

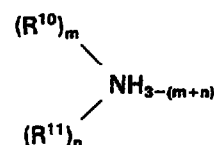
oder einen Rest $-(\text{R}^8\text{O})_x\text{R}^9$ bedeutet, in dem R^8 einen zweiwertigen Alkylrest mit 1 bis 6 Kohlenstoffatomen darstellt, x eine Zahl von 1 bis 4 ist und R^9 ein Wasserstoffatom oder einen Alkylrest mit 1 bis 3 Kohlenstoffatomen darstellt, oder ein Alkanolamin der Formel



ist, in der R^{10} einen geradkettigen oder verzweigten Alkylrest mit 2 bis 5 Kohlenstoffatomen bedeutet, wobei der Rest R^{10} außerdem eine Hydroxylgruppe enthält, R^{11} einen geradkettigen oder verzweigten Alkylrest mit 1 bis 4 Kohlenstoffatomen darstellt, m eine Zahl im Wert von 1, 2 oder 3 ist, n eine Zahl im Wert von 0, 1 oder 2 ist und die Summe von $m + n$ eine Zahl von 1 bis 3 ist.

4. Zusammensetzungen nach Anspruch 3, in denen der Amin-Umsetzungsteilnehmer (B) Morpholin ist.

5. Zusammensetzungen nach Anspruch 3, in denen der Amin-Umsetzungsteilnehmer (B) ein Alkanolamin der Formel



ist, in der R^{10} einen unverzweigten Alkylrest mit 2 oder 3 Kohlenstoffatomen bedeutet, wobei der Rest R^{10} eine Hydroxylgruppe enthält, R^{11} einen unverzweigten Alkylrest mit 1 bis 3 Kohlenstoffatomen darstellt, m eine Zahl im Wert von 1, 2 oder 3 ist, n eine Zahl im Wert von 0, 1 oder 2 ist und die Summe von $m + n$ eine Zahl von 1 bis 3 ist.

6. Zusammensetzungen nach Anspruch 5, in denen der Amin-Umsetzungsteilnehmer (B) Monoäthanolamin, Diäthanolamin oder Triäthanolamin ist.

7. Zusammensetzungen nach den Ansprüchen 2, 3, 4, 5 oder 6, in denen der Phosphorsäure-Umsetzungsteilnehmer (A) ein Gemisch von Mono- und Di-Tridecylphosphorsäuren ist.

8. Treibstoffzusammensetzungen zur Verwendung in Innenverbrennungsmotoren, umfassend (A) einen größeren Anteil eines Treibstoffs, der (i) 2,0 bis 100 Vol.-% mindestens eines Alkohols mit 1 bis 5 Kohlenstoffatomen und (ii) 98,0 bis 0 Vol.-% eines normalerweise flüssigen Erdöldestillat-Treibstoffs auf Kohlenwasserstoffbasis enthält, und (B) einen kleineren Anteil einer Zusammensetzung nach einem der vorangehenden Ansprüche.

9. Treibstoffzusammensetzungen nach Anspruch 8, in denen der Treibstoffanteil (A) der Zusammensetzungen (i) 10 bis 100 Vol.-% eines



Alkohols mit 1 bis 5 Kohlenstoffatomen und (ii) 90 bis 0 Vol.-% eines normalerweise flüssigen Erdöldestillat-Treibstoffs auf Kohlenwasserstoffbasis umfaßt.

10. Treibstoffzusammensetzungen nach Anspruch 9, in denen der Treibstoffanteil (A) der Zusammensetzungen (i) 20 bis 100 % eines Alkohols mit 1 bis 5 Kohlenstoffatomen und (ii) 80 bis 0 Vol.-% eines normalerweise flüssigen Erdöldestillat-Treibstoffs auf Kohlenwasserstoffbasis umfaßt.

11. Treibstoffzusammensetzungen nach Anspruch 8, 9 oder 10, in denen im Treibstoffanteil (A) die Alkoholkomponente (A) (i) Methanol oder Äthanol ist und die normalerweise flüssige Erdöl-Treibstoffkomponente auf Kohlenwasserstoffbasis (A) Benzin ist.

12. Treibstoffzusammensetzungen nach Anspruch 11, in denen in dem Treibstoffanteil (A) die Alkoholkomponente (A) (i) Äthanol ist.

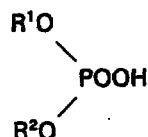
13. Treibstoffzusammensetzungen nach den Ansprüchen 8, 9, 10, 11 oder 12, in denen die Phosphorsäureverbindung ein Gemisch von Mono- und Di-Tridecylphosphorsäuren ist.

14. Treibstoffzusammensetzungen nach Anspruch 8 zur Verwendung in Innenverbrennungsmotoren, umfassend (A) einen größeren Anteil an einem Treibstoff, der (i) 10 Vol.-% Äthanol und (ii) 90 Vol.-% Benzin enthält, und (B) einen geringeren Anteil eines korrosionsinhibierenden Reaktionsproduktes von (i) einem Gemisch von Mono- und Di-Tridecylphosphorsäure und (ii) mindestens einem Amin aus der Gruppe Morpholin und Mono-, Di- und Triäthanolamin.

15. Treibstoffzusammensetzungen nach Anspruch 8 zur Verwendung in Innenverbrennungsmotoren, umfassend (A) einen größeren Anteil eines Treibstoffs, der (i) 20 Vol.-% Äthanol- und (ii) 80 Vol.-% Benzin enthält, und (B) einen kleineren Anteil eines korrosionsinhibierenden Reaktionsproduktes von (i) einem Gemisch aus Mono- und Di-Tridecylphosphorsäuren und (ii) mindestens einem Amin aus der Gruppe Morpholin und Mono-, Di und Triäthanolamin.

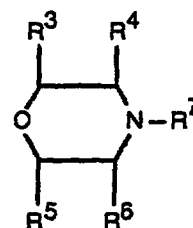
Revendications

1. Compositions utilisables dans un alcool et dans des combustibles hydrocarbonés de distillation de pétrole normalement liquides contenant un alcool comprenant des produits de réaction de (A) au moins un dérivé d'acide phosphorique ayant la formule

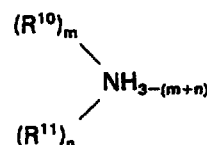


où R^1 est un radical à base d'hydrocarbure contenant de 8 à 18 atomes de carbone et R^2 est de

l'hydrogène ou un radical à base d'hydrocarbure contenant de 8 à 18 atomes de carbone et de (B) au moins un composé aminé choisi dans le groupe constitué par les morpholines de formule

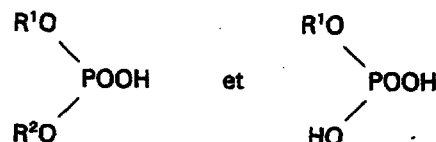


où R^3 , R^4 , R^5 et R^6 sont indépendamment de l'hydrogène ou des radicaux alcoyle contenant de 1 à 3 atomes de carbone et R^7 est de l'hydrogène ou un radical choisi dans le groupe constitué par les radicaux à base d'hydrocarbures contenant de 1 à 20 atomes de carbone et les radicaux $-(R^8O)_x-R^9$ où R^8 est un radical d'hydrocarbure aliphatique divalent contenant de 1 à 20 atomes de carbone, x est un nombre allant de 1 à 10, R^9 est de l'hydrogène ou un radical d'hydrocarbure aliphatique contenant de 1 à 6 atomes de carbone et les alcanolamines ayant la formule



où R^{10} est un radical à base d'hydrocarbure contenant de 2 à 10 atomes de carbone, ce radical R^{10} contenant en outre au moins un groupe hydroxyle, R^{11} est un radical à base d'hydrocarbure contenant de 1 à 20 atomes de carbone, m est un nombre égal à 1, 2 ou 3, n est un nombre égal à 0, 1 ou 2 et la somme de $m + n$ est un nombre allant de 1 à 3.

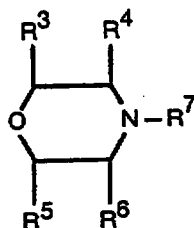
2. Les compositions selon la revendication 1 dans lesquelles le corps en réaction acide phosphorique (A) est un mélange de composés ayant les formules



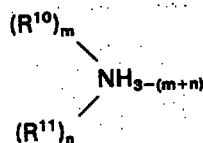
où R^1 et R^2 sont des radicaux d'hydrocarbures aliphatiques contenant de 8 à 18 atomes de carbone et le corps en réaction amine (B) est



choisi dans le groupe constitué par les morpholines ayant la formule



où R^3 , R^4 , R^5 et R^6 sont de l'hydrogène et R^7 est de l'hydrogène ou un radical choisi dans le groupe constitué par les radicaux à base d'hydrocarbures contenant de 1 à 10 atomes de carbone et les radicaux $-(R^8O)_xR^9$ où R^8 est un radical alcoyle divalent contenant de 1 à 10 atomes de carbone, x est un nombre allant de 1 à 6 et R^9 est de l'hydrogène ou un radical alcoyle contenant de 1 à 3 atomes de carbone et les alcanolamines ayant la formule



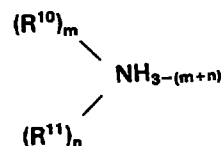
où R^{10} est un radical d'hydrocarbure aliphatique contenant de 2 à 5 atomes de carbone, ce radical R^{10} contenant au moins un groupe hydroxyle, R^{11} est un radical à base d'hydrocarbure contenant de 1 à 10 atomes de carbone, m est un nombre égal à 1, 2 ou 3, n est un nombre égal à 0, 1 ou 2 et la somme de $m + n$ est un nombre allant de 1 à 3.

3. Les compositions selon l'une des revendications 1 et 2 dans lesquelles le corps en réaction amine (B) est choisi dans le groupe constitué par les morpholines ayant la formule



où R^7 est de l'hydrogène ou un radical choisi dans le groupe constitué par les radicaux d'hydrocarbures aliphatiques à chaîne ramifiée contenant de 1 à 5 atomes de carbone et les radicaux $-(R^8O)_xR^9$ où R^8 est un radical alcoyle divalent contenant de 1 à 6 atomes de carbone, x est un nombre allant de 1 à 4 et R^9 est de l'hydrogène ou

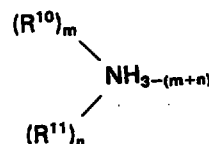
un radical alcoyle contenant de 1 à 3 atomes de carbone et les alcanolamines ayant la formule



où R^{10} est un radical alcoyle à chaîne droite ou à chaîne ramifiée contenant de 2 à 5 atomes de carbone, ce radical R^{10} contenant en outre un groupe hydroxyle, R^{11} est un radical alcoyle à chaîne droite ou à chaîne ramifiée contenant de 1 à 4 atomes de carbone, m est un nombre égal à 1, 2 ou 3, n est un nombre égal à 0, 1 ou 2 et la somme de $m + n$ est un nombre allant de 1 à 3.

4. Les compositions selon la revendication 3 dans lesquelles le corps en réaction amine (B) est la morpholine.

5. Les compositions selon la revendication 3 dans lesquelles le corps en réaction amine (B) est une alcanolamine ayant la formule



où R^{10} est un radical alcoyle à chaîne droite contenant 2 ou 3 atomes de carbone, ce radical R^{10} contenant un groupe hydroxyle, R^{11} est un radical alcoyle à chaîne droite contenant de 1 à 3 atomes de carbone, m est un nombre égal à 1, 2 ou 3, n est un nombre égal à 0, 1 ou 2 et la somme de $m + n$ est un nombre allant de 1 à 3.

6. Les compositions selon la revendication 5 dans lesquelles le corps en réaction amine (B) est choisi dans le groupe constitué par la monoéthanolamine, la diéthanolamine et la triéthanolamine.

7. Les compositions selon les revendications 2, 3, 4, 5 ou 6 dans lesquelles le corps en réaction acide phosphorique (A) est un mélange d'acides mono- et di-tridécyli phosphoriques.

8. Des compositions combustibles utilisables dans des moteurs à combustion interne comprenant (A) une portion majeure d'un combustible contenant (1) de 2, 0 à 100% en volume d'au moins un alcool contenant de 1 à 5 atomes de carbone et (2) de 98, 0 à 0% en volume d'un combustible hydrocarboné de distillation de pétrole normalement liquide et (B) une portion mineure d'une composition selon l'une quelconque des revendications précédentes.

9. Les compositions combustibles selon la revendication 8 dans lesquelles la portion combustible (A) des dites compositions comprend (1) de 10 à 100% en volume d'un alcool contenant de 1 à 5 atomes de carbone et (2) de 90 à 0% en volume d'un combustible hydrocarboné de distillation de pétrole normalement liquide.



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10. Les compositions combustibles selon la revendication 9 dans lesquelles la portion combustible (A) des dites compositions comprend (1) de 20 à 100% d'un alcool contenant de 1 à 5 atomes de carbone et (2) de 80 à 0% en volume d'un combustible hydrocarboné de distillation de pétrole normalement liquide.

11. Les compositions combustibles selon les revendications 8, 9 ou 10 dans lesquelles dans la portion combustible (A), le constituant alcool (A) (1) est choisi dans le groupe constitué par le méthanol et l'éthanol et le constituant combustible hydrocarboné dérivé du pétrole normalement liquide (A) (2) est de l'essence.

12. Les compositions combustibles selon la revendication 11 dans lesquelles dans la portion combustible (A) le constituant alcool (A) (1) est de l'éthanol.

13. Les compositions combustibles selon les revendications 8, 9, 10, 11 ou 12 dans lesquelles le composé acide phosphorique est un mélange d'acides mono- et di-tridécyolphosphoriques.

14. Compositions combustibles selon la revendication utilisables dans des moteurs à combustion interne comprenant (A) une portion majeure d'un combustible contenant (1) 10% en volume d'éthanol et (2) 90% en volume d'essence et (B) une portion mineure d'un produit de réaction inhibiteur de corrosion de (1) un mélange d'acides mono- et di-tridécyolphosphorique et de (2) au moins une amine choisie dans le groupe constitué par la morpholine et la mono-, la di- et la triéthanolamine.

15. Compositions combustibles selon la revendication 8 utilisables dans des moteurs à combustion interne comprenant (A) une portion majeure d'un combustible contenant (1) 20% en volume d'éthanol et (2) 80% en volume d'essence et (B) une portion mineure d'un produit de réaction inhibiteur de corrosion de (1) un mélange d'acides mono- et di-tridécyolphosphorique et de (2) au moins une amine choisie dans le groupe constitué par la morpholine et les mono-, di- et triéthanol amine.

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