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(64) Compositions for use in alcohol and alcohol containing fuels.

(67) Corrosion inhibiting additive compositions for use in alcohol and alcohol containing normally liquid hydrocarbon fuels derived by the reaction of at least one succinic acylating agent and at least one monoamine having the formula $(R_1)(R_2)(R_3)N$ wherein R_1 is a hydrocarbon based radical and R_2 and R_3 are independently hydrogen or hydrocarbon based radicals and alcohol and alcohol containing normally liquid hydrocarbonaceous petroleum distillate fuels containing said additive compositions are disclosed.

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COMPOSITIONS FOR USE IN ALCOHOL AND
ALCOHOL CONTAINING FUELS

Field of the Invention

This invention relates to corrosion inhibiting
5 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 compositions and characterized by improved corrosion inhibition.

10 Background of the Invention

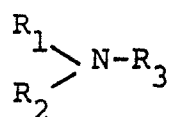
Alcohol fuels and alcohol containing normally liquid hydrocarbon fuels for use in spark-ignited and compression-ignited internal combustion engines possess a high degree of corrosive activity. This higher activity is generally attributed to the presence of acidic and halogen ion
15 containing contaminants present in alcohols but not present in normally liquid hydrocarbon fuels. These alcohol contaminants are particularly destructive to various non-ferrous metals and metal coatings such as tin/lead alloy
20 coatings (i.e.terne coatings) employed on internal surfaces of fuel tanks and fuel lines and to zinc/aluminum metal alloys employed in the construction of carburetors. As a result motor vehicles employing alcohol and alcohol containing normally liquid hydrocarbon fuels have shown a
25 greater propensity toward corrosion in the fuel tank, fuel line and fuel induction system areas.

As is well known, many patents exist which disclose various corrosion inhibiting additives for use in normally liquid hydrocarbon fuels. See, for example, U.S. Pat. No. 2,993,771 which relates to a process for preventing deposit formation and corrosion of internal combustion engines from substantially hydrocarbon fuels and particularly gasoline, by the addition of additives to such fuels. Two patents which are specifically directed to corrosion inhibition in alcohol or alcohol containing hydrocarbon fuels, e.g., gasohol, are U.S. Pat. Nos. 4,282,007 and 4,282,008. In the former are disclosed additives comprising the reaction product of aminotriazoles and polyisobut-enyl succinic acid anhydride and in the latter reaction products of an aminotriazole, isatoic anhydride and N-alkylpropylene diamine.

It is an aim of this invention to provide other corrosion inhibiting additives for use in alcohol and alcohol containing 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.

25 Summary of the Invention

In its broadest sense the present invention relates to compositions for use in alcohol and alcohol containing normally liquid hydrocarbonaceous petroleum distillate fuels said compositions comprising a corrosion inhibiting reaction product of (A) at least one succinic acylating agent selected from the group consisting of unsubstituted succinic acylating agents and aliphatic hydrocarbon based substituted succinic acylating agents and (B) at least one amine of the formula



wherein R_1 is a hydrocarbon based radical and R_2 and R_3 are independently hydrogen or hydrocarbon based radicals with the proviso that when R_2 and R_3 are both hydrogen, R_1 is a hydrocarbon based radical selected from the group consisting of tertiary alkyl, cycloalkyl, aryl, aralkyl and alkaryl radicals to provide said alcohol and alcohol containing hydrocarbonaceous petroleum distillate fuels with improved corrosion inhibition.

10 The invention further relates to fuel 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 percent by volume of
15 a normally liquid hydrocarbonaceous petroleum distillate fuel and (B) a minor portion of the corrosion inhibiting reaction product generally described hereinabove.

Detailed Description of Preferred Embodiments

20 The corrosion inhibiting additives comprising one aspect of this invention are prepared by the reaction of a succinic acylating agent selected from the group consisting of unsubstituted succinic acylating agent and aliphatic hydrocarbon based substituted succinic acylating agents, and a monoamine as defined hereinbelow.

25 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 within the context of this invention. Such radicals include the
30 following:

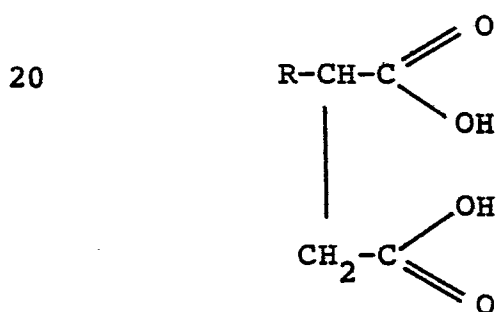
(1) Hydrocarbon radicals; that is, aliphatic, (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl or cycloalkenyl), aromatic, aliphatic- and alicyclic-substituted aromatic, aromatic-substituted aliphatic and alicyclic
35 radicals, cyclic radicals wherein the ring is completed

through another portion of the molecule (that is, any two indicated substituents may together form an alicyclic radical) and the like as well as two or more fused benzene nuclei. Such radicals are known to those skilled in the art, representative examples of which include methyl, ethyl, propyl, butyl, octyl, decyl, dodecyl, cyclohexyl, phenyl, tolyl, benzyl, naphthyl, anthryl, phenanthryl and the like.

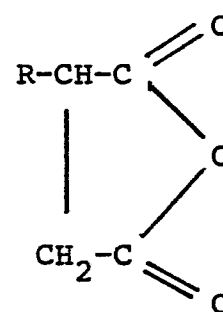
(2) Substituted hydrocarbon radicals; that is, radicals containing non-hydrocarbon substituents which, in the context of this invention, do not alter the predominantly hydrocarbon character of the radical. Those skilled in the art will be aware of suitable substituents (hydroxy, alkoxy, carbalkoxy, etc.).

The succinic acylating agents useful in preparing the additive compositions of this invention are the unsubstituted and aliphatic hydrocarbon based substituted succinic acids and anhydrides thereof having the following structural formulae

Acid



Anhydride



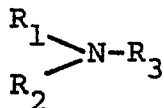
where R is hydrogen or an aliphatic hydrocarbon based radical containing from about 3 to about 100 carbon atoms, preferably from about 8 to about 30 carbon atoms and most preferably from about 9 to about 15 carbon atoms. Although the source of the aliphatic hydrocarbon based substituent is not a critical aspect of the invention, this substituent will generally be a 1-mono-olefin or oligomers, prepolymers or low molecular weight polymers thereof. Representative examples of such 1-monoolefins include ethylene, propylene,

1-butene, isobutene, 1-hexene, 1-octene, 2-methyl-1-heptene, 3-cyclohexyl-1-butene, 2-methyl-5-propyl-1-hexene and the like. Medial monoolefins, i.e., olefins in which the olefinic linkage is not at the terminal position, and oligomers, prepolymers and low molecular weight polymers and low molecular weight polymers thereof are also useful. Illustrative examples of such medial olefins include 2-butene, 3-pentene and 4-octene.

Although both unsubstituted succinic acylating agents and aliphatic hydrocarbon based substituted succinic acylating agents can be used in preparing the additive compositions of this invention the aliphatic hydrocarbon based substituted succinic acylating agents are preferred. They are well-known and can be prepared by various known procedures. One particularly useful procedure is to react a monoolefin monomer or oligomer, prepolymer or low molecular weight polymer thereof as described above with maleic anhydride at 100°C to 200°C with or without a catalyst to form the corresponding substituted succinic anhydride. The monoolefin also can be replaced by an alkyl halide which is capable of being substituted onto the unsaturated anhydride or the equivalent free acid thereof.

The aliphatic hydrocarbon based substituent can be saturated or unsaturated, straight-chain or branched-chain and may contain polar groups provided, however, that such groups are not present in significantly large proportions as to alter the hydrocarbon character of the substituent. Polar groups are typified by halo, carbonyl, nitro and similar groups. In a preferred embodiment, the aliphatic hydrocarbon based substituent is a polyisopropenyl radical containing 12 carbon atoms.

The amines which are useful in preparing the additive compositions are monoamines which have the formula



wherein R_1 is a hydrocarbon based radical and R_2 and R_3 are independently hydrogen or hydrocarbon based radicals with the proviso that when R_2 and R_3 are both hydrogen, R_1 is a hydrocarbon based radical selected from the group consisting of tertiary alkyl, cycloalkyl, aryl, alkaryl and aralkyl radicals. In the inventions broader scope, the monoamines of the formula above can be straight-chain or branched-chain aliphatic, alicyclic and aromatic amines; mono-amines wherein each of R_1 , R_2 and R_3 are dissimilar such as aliphatic-
10 alicyclic, aliphatic-aromatic and alicyclic-aromatic amines and substituted amines such as aliphatic substituted alicyclic, aliphatic substituted aromatic, alicyclic substituted aliphatic, alicyclic substituted aromatic, aromatic substituted aliphatic and aromatic substituted alicyclic
15 amines. More specifically, the monoamines useful in preparing the compositions comprising one aspect of the invention are those amines defined by the above formula wherein R_1 is a hydrocarbon based radical containing from 1 to about 24 carbon atoms selected from the group consisting
20 of straight-chain and branched-chained alkyl radicals containing from 1 to about 24 carbon atoms, cycloalkyl radicals containing from about 5 to about 7 carbon atoms, aryl radicals containing from about 6 to about 14 carbon atoms and alkaryl and aralkyl radicals containing from about 7 to
25 about 20 carbon atoms and R_2 and R_3 are hydrogen or hydrocarbon based radicals selected from the group consisting of straight-chain or branched alkyl radicals containing from 1 to about 24 carbon atoms, cycloalkyl radicals containing from about 5 to about 7 carbon atoms, aryl radicals con-
30 taining from about 6 to about 14 carbon atoms and alkaryl and aralkyl radicals containing from about 7 to about 20 carbon atoms. When R_2 and R_3 are both hydrogen, thereby making the amine defined above a primary amine, then R_1 is a hydrocarbon based radical selected from the group consisting
35 of tertiary alkyl radicals containing from about 5 to about 7 carbon atoms, cycloalkyl radicals containing from 4 to about 24 carbon atoms, aryl radicals containing from about

6 to about 14 carbon atoms and alkaryl and aralkyl radicals containing from about 5 to about 7 carbon atoms. The purpose of the proviso described above is to ensure that R_1 will possess sufficient inherent steric hindrance to inhibit any imide formation, the additive compositions of the present invention being primarily amidic acid salts or mixtures of amidic acid and amidic acid salts depending on the nature of the starting reactants and the relative ratios employed thereof. The amines will be free of any acetylenic unsaturation in the event any of the R groups of the amine should be unsaturated.

Representative, but nonlimiting examples of monoamines useful in the preparation of the additive compositions comprising one aspect of this invention include dimethylamine, triethylamine, diethylamine, triethylamine, dipropylamine, tripropylamine, diisopropylamine, dibutylamine, tributylamine, diisobutylamine, triisobutylamine, tertiary butylamine, ethyl-n-butylamine, dimethyl butylamine, di-n-amylamine, tri-n-amylamine, dihexylamine, trihexylamine, dioctylamine, trioctylamine, N-dodecyl-1-dodecanamine, N-octadecyl-1-octadecanamine, N,N-dimethyl-1-octadecanamine, cyclopentylamine, cyclopentenylamine, cyclohexylamine, dicyclohexylamine, methyl ethanolamine, benzylamine, aniline, o-phenylaniline, diphenylamine, 2-methyldiphenylamine, 3-methyldiphenylamine, 4,4'-dimethyldiphenylamine, 2,2'-diethyldiphenylamine, 4,4'-dioctyldiphenylamine, N-phenyl-1-naphthylamine, N-phenyl-2-naphthylamine and the like.

In one embodiment, the additive compositions are prepared by the reaction of the succinic acylating agent with secondary amines, or mixtures of secondary and tertiary amines in the manner described hereinbelow. In a preferred embodiment the additive compositions are prepared by the reaction of the succinic acylating agent with secondary amines. A most preferred secondary amine for use

, in preparing the additive compositions comprising one aspect of this invention is dicyclohexylamine.

The corrosion inhibiting additive compositions of the present invention may be readily prepared by heating
5 mixtures of the unsubstituted or aliphatic hydrocarbon based substituted succinic acylating agent with the amine at elevated temperatures ranging from about 30°C to about 200°C. A more preferred range of temperatures is from about 50°C to about 150°C. Generally, however, very reasonable
10 rates of reaction can be achieved from about 50°C to about 120°C.

The proportions of the reactants can vary widely. For example, the molar ratios of the unsubstituted or aliphatic hydrocarbon-based substituted succinic acylating
15 agent to the monoamine can range from about 1.0/0.5 to about 1.0/3.0. However, the preferred molar ratios range from about 1.0/1.0 to about 1.0/2.0 with the most preferred molar ratio being 1.0/2.0.

The preparation of the additive compositions
20 herein described can be carried out either in the absence or presence of a solvent. Preferably the compositions are prepared in the presence of solvent. Useful solvents can be hydrocarbon or polar solvents including, for example benzene naphtha, toluene, xylene, n-hexane, dioxane, chlorobenzene,
25 kerosene, gasoline or a fuel oil or oil of lubricating viscosity.

The following examples illustrate the preparation of the additive compositions comprising one aspect of this invention and the improved corrosion inhibiting character-
30 istics of alcohol or alcohol containing normally liquid fuels containing these compositions, which fuels comprise another aspect of this invention. In the following examples all parts are by weight unless otherwise specified.

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Example 1

Three hundred sixty-seven parts of tetrapropenyl-substituted succinic anhydride (prepared by reacting maleic anhydride with a polypropylene tetramer and having an average M.W. of about 248) is charged to a reaction vessel equipped with a stirrer, thermometer, reflux condenser and addition funnel. Starting at room temperature, 500 parts dicyclohexylamine is added over a period of 0.5 hour. The temperature of the reaction mixture rises to 45°C during the addition. The reaction is continued for 4.5 hours at 45°C. The temperature is increased to 60°C. over 0.5 hour. The reaction product is then filtered and collected.

Example 2

Two hundred sixty-five parts of tetrapropenyl-substituted succinic anhydride, as described in Example 1, is charged to a reaction vessel equipped with a stirrer, thermometer, reflux condenser and addition funnel. Three hundred sixty-two parts of dicyclohexylamine is then added to the reaction vessel over a period of 2 hours while heating the reaction mixture to 120°C. The addition of the amine to the succinic anhydride is exothermic. The reaction is continued for 3 hours at 120°C. Three hundred twenty-two parts kerosene is then added to the reaction mixture. The materials are mixed thoroughly, filtered and collected.

Example 3

Two hundred sixty-six parts of tetrapropenyl-substituted succinic anhydride, as described in Example 1, and 338 parts of xylene are charged to a reaction vessel as described in the previous examples. The mixture is heated to 110°C. with stirring, followed by the addition of 362 parts dicyclohexylamine over a period of one hour at 110-120°C. The reaction is continued for 3.25 hours at 110°C. The reaction mixture is then filtered and collected.

Example 4

Two hundred forty-eight parts of an oil solution of tetrapropenyl-substituted succinic acid (prepared by reacting tetrapropenyl-substituted succinic anhydride with 5 water) are charged to a reaction vessel equipped as described in Example 1. Two hundred parts of dicyclohexylamine are then added over a period of 0.5 hour. The temperature of the reaction mixture rises from room temperature to 49°C. during the amine addition. One hundred sixteen 10 parts of mineral oil are then added and the mixture stirred for an additional 0.5 hour. The materials are then filtered and collected.

Example 5

Two hundred sixty-six parts of tetrapropenyl- 15 substituted succinic anhydride is charged to a reaction vessel as described in Example 1. The anhydride is heated to 100°C., followed by the addition of 20 parts of distilled water. The materials are reacted for 1.75 hours at 100°C. The reaction product (i.e., tetrapropenyl-substituted succinic acid) is then cooled to 55°C., at which time 362 parts 20 dicyclohexylamine are then added to the acid. The addition of the amine is exothermic and the temperature of the reaction mixture increases to about 65°C. The reaction mixture is then heated to 70°C. and reacted at this temperature 25 for 4 hours. After cooling, 349 parts xylene are added. The xylene solution of reaction product is stirred thoroughly, filtered and collected.

Example 6

A reaction vessel equipped in the manner as described in Example 1 is charged with 98 parts of tetrapropenyl-substituted succinic anhydride (average M.W. 268) and 60 parts xylene. A solution consisting of 134 parts dicyclohexylamine and 65 parts xylene is then added over 0.5 hour. With addition of the amine solution the temperature 35 of the reaction mixture increases from room temperature to

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about 34°C. The reaction mixture is then heated to 75°C. and reacted at that temperature for a total of 5 hours. The solution containing the reaction product is then cooled, 5 filtered and collected.

Example 7

Two hundred sixty-six parts of tetrapropenyl-substituted succinic anhydride are charged to a reaction vessel equipped as described in Example 1. Then 374 parts 10 Primene 81R (a mixture of C₁₂₋₁₄ t-alkyl primary amines available commercially from Rohm & Haas Co.) are added dropwise over 3 hours. The reaction is exothermic and the temperature of the reactant increases from room temperature to about 59°C. over the course of the amine addition. One 15 hundred sixty parts of diluent oil are then added to the reaction product and stirring is continued for an additional hour at 55°C. After cooling to 40°C. the material is filtered and collected.

Example 8

20 Two hundred twenty-six parts of tetrapropenyl-substituted succinic anhydride is charged to a reaction vessel as described in Example 1. Then 362.6 parts of dicyclohexylamine is added dropwise to the reaction vessel over one hour. The reaction of the anhydride and amine is 25 exothermic and the temperature of the reaction mixture increases to 36°C. The mixture is reacted at 36-45°C. while heating for one hour. The product is then filtered and collected.

Example 9

30 To a solution of 266 parts tetrapropenyl-substituted succinic anhydride in 253 parts xylene contained in a reaction vessel as described in Example 1 is added a solution of 362.6 parts dicyclohexylamine in 85 parts xylene over a period of one hour. The temperature increases exo- 35 thermically to 32°C. during the addition. The materials are then reacted at 32-50°C. for one hour, filtered and collected. Sixty parts of this product is then diluted further with 40 parts xylene and mixed thoroughly.

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Example 10

A series of alcohol fuels are prepared by blending from 35 to 450 parts by weight of one of the reaction products of Examples 1 through 9 with hydrated ethanols containing about 7.5 percent by weight water.

Example 11

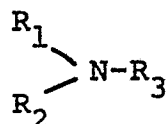
A series of alcohol containing gasoline fuels is prepared by blending from 35 to 450 parts by weight of one of the reaction products of Examples 1 through 9 with a gasohol which comprises 20 percent by volume of hydrated ethanol and 80 percent by volume of a gasoline having an ASTM distillation range 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 and zinc/aluminum alloy) are immersed in commercially available hydrated ethanol for a continuous period of 144 hours at a temperature of 50°C $\pm$ 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 control or reference gasoline/alcohol blend by more than 10 percent. The corrosion inhibiting additive compositions described in Examples 1 through 9 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

5 (i) at least one alcohol having from 1 to about five 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 succinic acylating

10 agent selected from the group consisting of unsubstituted and aliphatic hydrocarbon based substituted succinic acylating agent and (ii) at least one amine of the formula



wherein R_1 , R_2 and R_3 have the same meanings as set forth

15 above.

Alcohol fuels useful in combination with the corrosion inhibiting reaction products of succinic acylating agents and amines as described herein to provide fuel compositions having improved corrosion inhibiting characteristics include such commercially available alcohols as

20 methanol, ethanol, propanol, isopropanol, butanol and its isomer and amyl alcohol and its isomers and mixtures of these various alcohols. As produced commercially the preferred alcohols are methanol and ethanol.

25 The normally liquid hydrocarbonaceous petroleum distillate fuels which are useful in combination with alcohols and the corrosion inhibiting reaction products described herein above include motor gasoline as defined by ASTM Specification D439 and diesel fuel or fuel oil as

30 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 compositions of this invention comprise from about 2.0 to 100 percent by volume of at least one alcohol containing from 1 to about 5 carbon atoms and from about 98.0 to 0 percent by volume of the normally liquid hydrocarbonaceous petroleum distillate fuel. In a preferred embodiment, this fuel portion will comprise from about 10.0 to 100 percent by volume of at least one alcohol containing from 1 to about 5 carbon atoms and from about 90.0 percent to 0 percent 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 20.0 to 100 percent by volume and from about 80.0 to 0 percent by volume respectively. Particularly preferred fuel compositions are those based on a mixture of an alcohol, especially methanol or ethanol, and a petroleum distillate fuel, especially gasoline, in which mixture the alcohol component ranges from about 10.0 to about 20.0 percent by volume and the petroleum distillate fuel ranges from about 90.0 to about 80.0 percent by volume.

The amount of the additive reaction product of the succinic acylating agent and amine added to the above described fuel portion to provide the fuel compositions of the invention will be an amount sufficient to impart improved corrosion inhibiting characteristics to these fuel compositions. Broadly this amount will range from about 10 to about 1000 parts by weight of said additive reaction product per million parts by weight of the fuel portion. Preferably this amount will range from about 10 to about 450 parts by weight with a range of from about 175 to about 450 parts by weight of said additive reaction product per million parts by weight of said fuel portion being most preferred.

The fuel compositions of this invention can be prepared by merely adding the reaction product of the succinic acylating agent and amine directly to the fuel portion or it can be diluted with a substantially inert, normally

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liquid organic 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

5 constitute yet another embodiment of the invention, generally contain from about 20 percent to about 90 percent of the additive reaction products of the invention.

The fuel compositions described hereinabove, may also contain additional materials normally added to liquid
10 fuels to obtain specific benefits. Therefore, the fuel compositions, representing one aspect of this invention, may contain antiknock agents such as tetraalkyl lead compounds, lead scavengers such as haloalkanes (e.g., ethylene dichloride and ethylene dibromide) deposit preventers or
15 modifiers such triaryl phosphates, dyes, octane improvers, antioxidants such as 2,6-di-tertiary-butyl-4-methylphenol, bacteriostatic agents, gum inhibitors, metal deactivators, demulsifiers, upper cylinder lubricants and anti-icing agents.

20 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
25 understanding and practicing the invention. Based on the teachings herein, many variations 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
30 chemical process.

CLAIMS

1 1. Compositions for use in alcohol and alcohol
2 containing normally liquid hydrocarbonaceous petroleum dis-
3 tillate fuels comprising a reaction product of (A) at least
4 one succinic acylating agent selected from the group con-
5 sisting of unsubstituted and aliphatic hydrocarbon based
6 substituted succinic acylating agents and (B) at least one
7 amine of the formula



9 wherein R_1 is a hydrocarbon based radical and R_2 and R_3 are
10 independently hydrogen or hydrocarbon based radicals with
11 the proviso that when R_2 and R_3 are both hydrogen R_1 is a
12 hydrocarbon based radical selected from the group consisting
13 of tertiary alkyl, cycloalkyl, aryl, alkaryl and aralkyl
14 radicals to provide said alcohol and alcohol containing
15 normally liquid hydrocarbonaceous petroleum distillate fuels
16 with improved corrosion inhibition.

1 2. The compositions of Claim 1 wherein the
2 succinic acylating agent (A) is an aliphatic hydrocarbon
3 based substituted succinic anhydride or acid.

1 3. The compositions of Claim 2 wherein the
2 aliphatic hydrocarbon based substituent on the succinic
3 anhydride or acid acylating agent (A) is a straight-chain or
4 branched-chain alkyl or alkenyl radical containing from 3 to
5 100 carbon atoms.

1 4. The compositions of Claim 2 wherein the
2 aliphatic hydrocarbon based substituent on the succinic
3 anhydride or acid acylating agent (A) is a straight-chain or
4 branched-chain alkyl or alkenyl radical containing from
5 about 8 to about 30 carbon atoms.

1 5. The compositions of Claim 2 wherein the
2 aliphatic hydrocarbon based substituent on the succinic
3 anhydride or acid acylating agent (A) is a straight-chain or
4 branched-chain alkyl or alkenyl radical containing from

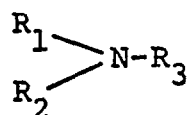
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5 about 9 to about 15 carbon atoms.

1 6. The compositions of Claims 3, 4 or 5 wherein
2 the aliphatic hydrocarbon based substituent on the succinic
3 anhydride or acid acylating agent (A) is a straight-chain or
4 branched-chain alkenyl radical.

1 7. The compositions of Claim 6 wherein the
2 aliphatic hydrocarbon based substituent on the succinic
3 anhydride or acid acylating agent (A) is polypropenyl rad-
4 ical containing 12 carbon atoms.

1 8. The compositions of Claims 1, 2, 3, 4 or 5
2 wherein (B) is an amine having the formula



4 wherein R_1 is a hydrocarbon based radical containing from 1
5 to about 24 carbon atoms and R_2 and R_3 are independently
6 hydrogen or hydrocarbon based radicals containing from 1 to
7 about 24 carbon atoms with the proviso that when R_2 and R_3
8 are both hydrogen R_1 is a hydrocarbon based radical selected
9 from the group consisting of tertiary alkyl radicals con-
10 taining from about 4 to about 24 carbon atoms, cycloalkyl
11 radicals containing from about 5 to about 7 carbon atoms,
12 aryl radicals containing from about 6 to about 14 carbon
13 atoms and alkaryl and aralkyl radicals containing from about
14 7 to about 20 carbon atoms.

1 9. The compositions of Claim 8 wherein R_2 is a
2 hydrocarbon based radical and R_3 is hydrogen.

1 10. The compositions of Claim 8 wherein the
2 hydrocarbon based radical R_1 is selected from the group
3 consisting of straight-chain or branched-chain alkyl rad-
4 icals containing from 1 to about 24 carbon atoms, cycloalkyl
5 radicals having from about 5 to about 7 carbon atoms, aryl
6 radicals having from about 6 to about 14 carbon atoms and
7 alkaryl and aralkyl radicals containing from about 7 to
8 about 20 carbon atoms and R_2 and R_3 are independently hy-
9 drogen or hydrocarbon radicals selected from the group

10 consisting of straight-chain or branched-chain alkyl rad-
 11 icals having from 1 to about 24 carbon atoms, cycloalkyl
 12 radicals having from about 5 to about 7 carbon atoms, aryl
 13 radicals containing from about 6 to about 14 carbon atoms
 14 and alkaryl and aralkyl radicals containing about 7 to about
 15 20 carbon atoms.

1 11. The compositions of Claim 10 wherein R_2 is a
 2 hydrocarbon based radical selected from the group consisting
 3 of straight-chain or branched-chain alkyl radicals having
 4 from 1 to about 24 carbon atoms, cycloalkyl radicals having
 5 from about 5 to about 7 carbon atoms, aryl radicals con-
 6 taining from about 6 to about 14 carbon atoms and alkaryl
 7 and aralkyl radicals containing from about 7 to about 20
 8 carbon atoms, and R_3 is hydrogen.

1 12. The compositions of Claim 11 wherein R_1 and
 2 R_2 are cycloalkyl radicals containing from about 5 to about
 3 7 carbon atoms.

1 13. The compositions of Claim 12 wherein R_1 and
 2 R_2 are cyclohexyl radicals.

1 14. Compositions for use in alcohol and alcohol
 2 containing normally liquid hydrocarbonaceous petroleum
 3 distillate fuels comprising a reaction product of (A) at
 4 least one straight-chain or branched-chain alkenyl substi-
 5 tuted succinic anhydride or acid and (B) at least one amine
 6 of the formula



8 wherein R_1 is a hydrocarbon based radical containing from 1
 9 to about 24 carbon atoms and R_2 and R_3 are independently
 10 hydrogen or hydrocarbon based radicals containing from 1 to
 11 about 24 carbon atoms with the proviso that when R_2 and R_3
 12 are both hydrogen R_1 is a hydrocarbon based radical selected
 13 from the group consisting of tertiary alkyl radicals having
 14 from about 4 to about 24 carbon atoms, cycloalkyl radicals
 15 having from about 5 to about 7 carbon atoms, aryl radicals
 16 having from about 6 to about 14 carbon atoms, and alkaryl
 17 and aralkyl radicals having from about 7 to about 20 carbon

18 atoms to provide said alcohol and alcohol containing nor-
19 mally liquid hydrocarbonaceous petroleum distillate fuels
20 with improved corrosion inhibition.

1 15. The compositions of Claim 14 wherein R_2 is a
2 hydrocarbon based radical containing from 1 to about 24
3 carbon atoms and R_3 is hydrogen.

1 16. The compositions of Claim 14 wherein the
2 hydrocarbon based radical R_1 is selected from the group
3 consisting of straight-chain or branched-chain alkyl rad-
4 icals containing from 1 to about 24 carbon atoms, cycloalkyl
5 radicals having from about 5 to about 7 carbon atoms, aryl
6 radicals containing from about 6 to about 14 carbon atoms
7 and alkaryl and aralkyl radicals containing from about 7 to
8 about 20 carbon atoms and R_2 and R_3 are independently hy-
9 drogen or hydrocarbon radicals selected from the group
10 consisting of straight-chain or branched-chain alkyl rad-
11 icals having from 1 to about 24 carbon atoms, cycloalkyl
12 radicals having from about 5 to about 7 carbon atoms, aryl
13 radicals containing from about 6 to about 14 carbon atoms
14 and alkaryl or aralkyl radicals containing from about 7 to
15 about 20 carbon atoms.

1 17. The compositions of Claim 16 wherein R_2 is a
2 hydrocarbon radical selected from the group consisting of
3 straight-chain or branched-chain alkyl radicals containing
4 from 1 to about 24 carbon atoms, cycloalkyl radicals con-
5 taining from about 5 to about 7 carbon atoms, aryl radicals
6 containing from about 6 to about 14 carbon atoms and alkaryl
7 and aralkyl containing from about 7 to about 20 carbon atoms
8 and R_3 is hydrogen.

1 18. The compositions of Claim 17 wherein R_1 and
2 R_2 are cycloalkyl radicals containing from about 5 to about
3 7 carbon atoms.

1 19. The compositions of Claim 18 wherein R_1 and
2 R_2 are cyclohexyl radicals.

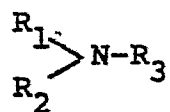
1 20. The compositions of Claims 14, 15, 16, 17, 18
2 or 19 wherein the straight-chain or branched-chain alkenyl
3 substituent on the succinic anhydride or acid (A) contains
4 from about 3 to about 100 carbon atoms.

1 21. The compositions of Claim 20 wherein the
2 straight-chain or branched-chain alkenyl substituent on the
3 succinic anhydride or acid (A) contains from about 8 to
4 about 30 carbon atoms.

1 22. The compositions of Claim 20 wherein the
2 straight-chain or branched-chain alkenyl substituent on the
3 succinic anhydride or acid (A) contains from about 9 to
4 about 15 carbon atoms.

1 23. The compositions of Claim 20 wherein the
2 straight-chain or branched-chain alkenyl substituent on the
3 succinic anhydride or acid (A) is polypropenyl radical
4 containing about 12 carbon atoms.

1 24. Fuel compositions for use in an internal
2 combustion engine comprising (A) a major portion of a fuel
3 containing (i) from about 2.0 to 100 percent by volume of at
4 least one alcohol containing from 1 to about 5 carbon atoms
5 and (ii) from about 98.0 to 0 percent by volume of a nor-
6 mally liquid hydrocarbonaceous petroleum distillate fuel and
7 (B) a minor portion of a corrosion inhibiting reaction
8 product of (i) at least one succinic acylating agent se-
9 lected from the group consisting of unsubstituted and
10 aliphatic hydrocarbon substituted succinic acylating agents
11 and (ii) at least one amine of the formula
12



13 wherein R_1 is a hydrocarbon based radical and R_2 and R_3 are
14 independently hydrogen or hydrocarbon based radicals with
15 the proviso that when R_2 and R_3 are both hydrogen, R_1 is a
16 hydrocarbon based radical selected from the group consisting
17 of tertiary alkyl, cycloalkyl, aryl, alkaryl and aralkyl
18 radicals.

1 25. The fuel compositions of Claim 24 wherein the
2 succinic acylating agent (B)(i) is an aliphatic hydrocarbon
3 based substituted succinic anhydride or acid.

1 26. The fuel compositions of Claim 25 wherein the
2 aliphatic hydrocarbon based substituent on the succinic

3 anhydride or acid acylating agent (B)(i) is a straight-chain
4 or branched-chain alkyl or alkenyl radical containing from
5 about 3 to about 100 carbon atoms.

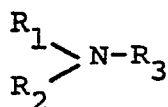
1 27. The fuel compositions of Claim 25 wherein the
2 aliphatic hydrocarbon based substituent on the succinic
3 anhydride or acid acylating agent (B)(i) is a straight-chain
4 or branched-chain alkyl or alkenyl radical containing from
5 about 8 to about 30 carbon atoms.

1 28. The fuel compositions of Claim 25 wherein the
2 aliphatic hydrocarbon based substituent on the succinic
3 anhydride or acid acylating agent (B)(i) is a straight-chain
4 or branched-chain alkyl or alkenyl radical containing from
5 about 9 to about 15 carbon atoms.

1 29. The fuel compositions of Claims 26, 27 or 28
2 wherein the aliphatic hydrocarbon based substituent on the
3 succinic anhydride or acid acylating agent (B)(i) is a
4 straight-chain or branched-chain alkenyl radical.

1 30. The fuel compositions of Claim 29 wherein the
2 aliphatic hydrocarbon based substituent on the succinic
3 anhydride or acid acylating agent (B)(i) is polypropenyl
4 radical containing 12 carbon atoms.

1 31. The fuel compositions of Claims 24, 25, 26,
2 27 or 28 wherein (B)(ii) is an amine having the formula



4 wherein R_1 is a hydrocarbon based radical containing from 1
5 to about 24 carbon atoms and R_2 and R_3 are independently
6 hydrogen or hydrocarbon based radicals containing from about
7 1 to about 24 carbon atoms with the proviso that when R_2 and
8 R_3 are both hydrogen R_1 is a hydrocarbon based radical
9 selected from the group consisting of tertiary alkyl rad-
10 icals, containing from about 4 to about 24 carbon atoms,
11 cycloalkyl radicals containing from about 5 to about 7
12 carbon atoms, aryl radicals containing from about 6 to about
13 14 carbon atoms and alkaryl and aralkyl radicals containing
14 from about 7 to about 20 carbon atoms.

1 32. The fuel compositions of Claim 31 wherein R_2

2 is a hydrocarbon based radical and R_3 is hydrogen.

1 33. The fuel compositions of Claim 31 wherein the
2 hydrocarbon radical R_1 is selected from the group consisting
3 of straight-chain or branched-chain alkyl radicals contain-
4 ing from 1 to about 24 carbon atoms, cycloalkyl radicals
5 containing from about 5 to about 7 carbon atoms, aryl rad-
6 icals containing from about 6 to about 14 carbon atoms and
7 alkaryl and aralkyl radicals containing from about 7 to
8 about 20 carbon atoms and R_2 and R_3 are independently hy-
9 drogen or hydrocarbon radicals selected from the group
10 consisting of straight-chain or branched-chain alkyl rad-
11 icals containing from about 1 to about 24 carbon atoms,
12 cycloalkyl radicals containing from about 5 to about 7
13 carbon atoms, aryl radicals containing from about 6 to about
14 14 carbon atoms and alkaryl and aralkyl radicals containing
15 from about 7 to about 20 carbon atoms.

1 34. The fuel compositions of Claim 33 wherein R_2
2 is a hydrocarbon based radical selected from the group con-
3 sisting of straight-chain or branched-chain alkyl radicals
4 containing from 1 to about 24 carbon atoms, cycloalkyl
5 radicals containing from about 5 to about 7 carbon atoms,
6 aryl radicals containing from about 6 to about 14 carbon
7 atoms and alkaryl and aralkyl radicals containing from
8 about 7 to about 20 carbon atoms and R_3 is hydrogen.

1 35. The fuel compositions of Claim 34 wherein R_1
2 and R_2 are cycloalkyl radicals having from about 5 to about
3 7 carbon atoms.

1 36. The fuel compositions of Claim 35 wherein R_1
2 and R_2 are cyclohexyl radicals.

1 37. Fuel compositions for use in an internal
2 combustion engine comprising, (A) a major proportion of a
3 fuel containing (i) from about 10 to 100 percent by volume
4 of methanol or ethanol and (ii) from about 90 to 0 percent
5 by volume of a normally liquid hydrocarbonaceous petroleum
6 distillate fuel and (B) a minor portion of a corrosion
7 inhibiting reaction product of (i) at least one straight-
8 chain or branched-chain alkenyl substituted succinic anhy-

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9 dride or acid acylating agent and (ii) at least one amine of
10 the formula



12 wherein R_1 is a hydrocarbon based radical and R_2 and R_3 are
13 independently hydrogen or hydrocarbon based radicals with
14 the proviso that when R_2 and R_3 are both hydrogen R_1 is a
15 hydrocarbon based radical selected from the group consisting
16 of tertiary alkyl, cycloalkyl, aryl, alkaryl and aralkyl
17 radicals.

1 38. The fuel compositions of Claim 37 wherein R_2
2 is a hydrocarbon based radical and R_3 is hydrogen.

1 39. The fuel compositions of Claim 37 wherein the
2 hydrocarbon based radical R_1 is selected from the group
3 consisting of straight-chain or branched-chain alkyl radi-
4 cals containing from 1 to about 24 carbon atoms, cycloalkyl
5 radicals containing from about 5 to about 7 carbon atoms,
6 aryl radicals containing from about 6 to about 14 carbon
7 atoms, and alkaryl and aralkyl radicals containing from
8 about 7 to about 20 carbon atoms and R_2 and R_3 are inde-
9 pendently hydrogen or hydrocarbon radicals selected from the
10 group consisting of straight-chain or branched-chain alkyl
11 radicals containing from about 1 to about 24 carbon atoms,
12 cycloalkyl radicals containing from about 5 to about 7
13 carbon atoms, aryl radicals containing from about 6 to about
14 14 carbon atoms and alkaryl and aralkyl radicals containing
15 from about 7 to about 20 carbon atoms.

1 40. The fuel compositions of Claim 39 wherein R_2
2 is a hydrocarbon based radical selected from the group con-
3 sisting of straight-chain or branched-chain alkyl radicals
4 containing from 1 to about 24 carbon atoms, cycloalkyl
5 radicals containing from about 5 to about 7 carbon atoms,
6 aryl radicals containing from about 6 to about 14 carbon
7 atoms and alkaryl and aralkyl radicals containing from about
8 7 to about 20 carbon atoms and R_3 is hydrogen.

1 41. The fuel compositions of Claim 40 wherein R_1
2 and R_2 are cycloalkyl radicals containing from about 5 to
3 about 7 carbon atoms.

1 42. The fuel compositions of Claim 41 wherein R_1
2 and R_2 are cyclohexyl radicals.

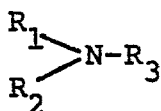
1 43. The fuel compositions of Claims 37, 38, 39,
2 40, 41 or 42 wherein the straight-chain or branched-chain
3 alkenyl substituent on the succinic anhydride or acid
4 acylating agent (B) (i) contains from about 3 to about 100
5 carbon atoms.

1 44. The fuel compositions of Claim 43 wherein the
2 straight-chain or branched-chain alkenyl substituent on the
3 succinic anhydride or acid acylating agent (B) (i) contains
4 from about 8 to about 30 carbon atoms.

1 45. The fuel compositions of Claim 43 wherein the
2 straight-chain or branched-chain alkenyl substituent on the
3 succinic anhydride or acid acylating agent (B) (i) contains
4 from about 9 to about 15 carbon atoms.

1 46. The fuel compositions of Claim 43 wherein the
2 straight-chain or branched-chain alkenyl substituent on the
3 succinic anhydride or acid acylating agent (B) (i) is poly-
4 propenyl radical containing 12 carbon atoms.

1 47. Fuel compositions for use in an internal
2 combustion engine comprising (A) a major portion of a fuel
3 containing (i) from about 20 to 100 percent by volume of
4 ethanol and (ii) from about 80 to 0 percent by weight of a
5 normally liquid hydrocarbonaceous petroleum distillate fuel
6 and (B) a minor portion of a corrosion inhibiting reaction
7 product of (i) at least one straight-chain or branched-chain
8 alkenyl substituted succinic anhydride or acid acylating
9 agent wherein said alkenyl substituent contains from about
10 9 to about 15 carbon atoms and (ii) at least one amine of
11 the formula



13 wherein R_1 and R_2 are cycloalkyl radicals containing from

14 about 5 to about 7 carbon atoms and R_3 is hydrogen.

1 48. The fuel compositions of Claim 47 wherein the
2 normally liquid hydrocarbonaceous distillate fuel (A)(ii) is
3 gasoline and the corrosion inhibiting reaction product (B)
4 is the reaction product of (i) a straight-chain or branched-
5 chain alkenyl substituted succinic anhydride or acid acylat-
6 ing agent wherein said alkenyl substituent is polypropenyl
7 radical containing 12 carbon atoms and (ii) dicyclohexyl-
8 amine.



European Patent
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EUROPEAN SEARCH REPORT

0086049

Application number

EP 83 30 0294

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X, Y	FR-A-2 050 049 (ESSO) * Claims 1,2,3,6,8-12 *	1-46	C 10 L 1/02 C 10 L 1/22 C 10 L 1/14
Y	US-A-3 893 825 (L.A. GOELLER) * Column 1, line 65 - column 3, line 8; column 3, lines 67-68 *	1,2,8- 19,24, 25,31- 42,47, 48	
D, Y	US-A-4 282 007 (R.L. SUNG) * Claims 1-10,14-19 *	1-6,20 -22,24 -29,43 -48	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 10 L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 11-05-1983	Examiner RO TSAERT L.D.C.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	