(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 149 486**
A2

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **85100316.0**

(22) Date of filing: **14.01.85**

(51) Int. Cl.[4]: **C 10 L 1/22**
C 10 L 1/14

(30) Priority: **17.01.84 US 571624**

(43) Date of publication of application:
24.07.85 Bulletin 85/30

(84) Designated Contracting States:
DE FR GB NL

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(54) **Detergent composition and gasoline composition containing same.**

(57) Combinations of certain amides and hydrocarbon soluble components are compositions useful as carburetor detergents, and gasoline compositions containing said compositions.

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This invention relates to an improved motor fuel composition for an internal combustion engine. More particularly, the invention relates to a motor fuel composition effective to inhibit the formation of harmful deposits, for example, on the carburetor of an internal combustion engine.

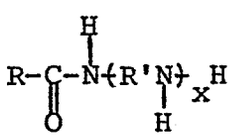
It is well known that internal combustion engine fuels such as gasoline tend to deposit sludge and varnish in the carburetor and engine. Heretofore, there has been continuing interest in developing improved detergents which inhibit the formation of such deposits.

Gasoline fuels containing oxygenates have recently become more prevalent and these gasoline fuels can require new compositions as carburetor detergents to obtain optimum results.

The present invention, is aimed at providing compositions especially useful as carburetor detergents for gasoline fuels containing oxygenates and especially to provide gasoline fuel compositions containing oxygenates with a decreased tendency to form deposits in carburetors.

The present invention therefore provides a detergent composition characterized by including:

(a) an amide having the formula



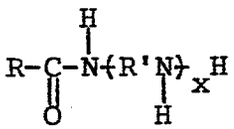
wherein R is a C_6 - C_{22} alkyl, R' is a C_2 to C_6 alkyl or branched alkyl, and x = 1 to 10; and

(b) at least one hydrocarbon-soluble carboxylic dispersant characterized by the presence within its molecular structure of: a substantially saturated hydrocarbon based radical containing at least about 30 aliphatic carbon atoms, attached to at least one acyl or acyloxy radical, which is also attached through nitrogen to a polar group.

Further features and advantages of the invention will be apparent from the following detailed description of preferred embodiments of the invention taken together with the accompanying examples.

In its broad aspect, this invention provides a detergent composition comprising two essential components wherein:

Component A is an amide having the formula

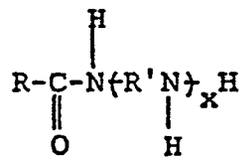


and polycondensation products thereof; and Component B is a hydrocarbon-soluble "carboxylic dispersant".

As used herein, the term "carboxylic dispersant" means known hydrocarbon-soluble dispersants whose molecular structure is highlighted by the presence of a substantially saturated hydrocarbon-based radical containing at least about 30 aliphatic carbon atoms and at least 1 acyl or acyloxy attached to said hydrocarbon-based radical and also through nitrogen to a polar group. The carboxylic dispersants are the reaction products of carboxylic acids or derivatives thereof with polar reagents,

including organic nitrogen-containing compounds having at least one >NH group such as polyamines.

Component A employed in the compositions of this invention are known amides having the formula:



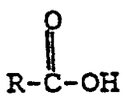
wherein R is a C_6 - C_{22} alkyl;

R' is a C_2 to C_6 alkyl or branched alkyl; and

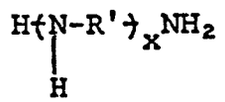
x = 1 to 10, and preferably 1 to 6.

and polycondensation products thereof.

As is well known, these amides are formed by reacting fatty acids having the formula:



wherein R is a C_6 - C_{22} alkyl and polyamines having the formula:



wherein R' is a C_2 to C_6 alkyl or branched alkyl; and

x = 1 to 10, and preferably 1 to 6.

Component B employed in the compositions of this invention is a hydrocarbon-soluble "carboxylic dispersant". As used herein, the term "carboxylic dispersant" means known hydrocarbon-soluble dispersants whose molecular structure is characterized by the presence of a substantially saturated hydrocarbon-based radical containing at least about 30 aliphatic carbon atoms and at least 1 acyl or acyloxy attached to said hydrocarbon-based radical and also through nitrogen to a polar group. The carboxylic dispersants are the reaction products of carboxylic acids or derivatives thereof with polar reagents, including organic nitrogen-containing compounds having at least one >NH group such as polyamines. The following U. S. patents are incorporated by reference herein for their disclosure of examples of Component B.

3,163,603	3,351,552	3,541,012
3,184,474	3,381,022	3,542,678
3,215,707	3,399,141	3,542,680
3,219,666	3,415,750	3,567,637
3,271,310	3,433,744	3,574,101
3,272,746	3,444,170	3,576,743
3,281,357	3,448,048	3,630,904
3,306,908	3,448,049	3,632,510
3,311,558	3,451,933	3,632,511
3,316,177	3,454,607	3,697,428
3,340,281	3,467,668	3,725,441
3,341,542	3,501,405	4,234,435
3,346,493	3,522,179	Re 26,433

The preferred carboxylic dispersants for use as Component B are those in which the acidic moiety is a substituted succinic acid. Dispersants of this type are most often prepared by the reaction of one of the above-identified polar reagents with the appropriate substituted succinic acylating agent. Suitable acylating agents include the acids, anhydrides, esters and acyl hadlides, with the acids and anhydrides being preferred.

The substituted succinic acylating agent may be prepared by the alkylation of maleic acid, fumaric acid, maleic anhydride or the like with a source of the desired hydrocarbon-based radical, which is a known reaction described in the patents incorporated by reference hereinabove. As used herein, the term "hydrocarbon-based radical" 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 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, 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; examples are halo (especially chloro and bromo), hydroxy, alkoxy, nitro, carbalkoxy and alkylthio.

(3) Hetero radicals; that is, radicals which, while predominantly hydrocarbon in character within the context of this invention, contain atoms other than carbon present in a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms will be apparent to those skilled in the art and include, for example, nitrogen, oxygen and sulfur.

In general, no more than about three substituents or hetero atoms, and preferably no more than one, will be present for each ten carbon atoms in the hydrocarbon-based radical.

Preferably, the hydrocarbon-based radicals in Component B are free from acetylenic unsaturation and have about 30 to about 5000 carbon atoms, desirably about 50 to about 300 carbon atoms. The radicals are usually hydrocarbon or chloro-substituted hydrocarbon.

The source of the hydrocarbon-based radical is generally a homopolymer or interpolymer of polymerizable olefin monomers containing about two to sixteen and usually about two to six carbon atoms. Illustrative monomers of this type are ethylene, propylene, 1-butene, 2-butene, isobutene, 1-octene and 1-decene. The polymer may also contain units derived from polyenes, including conjugated dienes such as 1,3-butadiene and isoprene; nonconjugated dienes such as 1,4-hexadiene, 1,4-cyclohexadiene, 5-ethylidene-2-norbornene and 1,6-octadiene; and trienes such as 1-isopropylidene-3a,4,7,7a-tetrahydroindene, 1-isopropylidenecyclopentadiene and 2-(2-methylene-4-methyl-3-pentenyl)[2.2.1]bicyclo-5-heptene.

A first preferred class of polymers comprises those of terminal olefins such as propylene, 1-butene, isobutene and 1-hexene. Especially preferred within this class are polybutenes comprising predominantly isobutene units. A second preferred class comprises terpolymers of ethylene, a C_{3-8} a-monoolefin and a polyene selected from the group consisting of nonconjugated dienes (which are especially preferred) and trienes. Illustrative of these terpolymers is "Ortholeum 2052" manufactured by E. I. duPont de Nemours & Company, which is a terpolymer containing about 48 mole percent ethylene groups, 48 mole percent propylene groups, and 4 mole percent 1,4-hexadiene groups, and having an inherent viscosity of 1.35 (8.2 grams of polymer in 100 ml. of carbon tetrachloride at 30°C.).

The source of the hydrocarbon-based radical contains at least about 30 and preferably at least about 50 carbon atoms. Among the olefin polymers, those having a number average molecular weight (as determined by gel permeation chromatography) of about 700-5000 are preferred, although higher polymers having number average molecular weights from about 10,000 to about 100,000 or higher may sometimes be used.

In the alkylation reaction, at least one mole of unsaturated acid or acid derivative is normally used per mole of hydrocarbon-based radical source. Particularly when said source contains a substantial number of olefinic bonds, more than one mole of unsaturated acid or acid derivative may be used per mole thereof. The hydrocarbon-based radical in the resulting acylating agent should be substantially saturated; that is, at least about 95% of the carbon-carbon bonds therein should be single bonds.

The carboxylic dispersant is prepared by reacting the substituted succinic acid, anhydride or other acrylating agent with at least one of the above-identified polar reagents. Suitable nitrogen compounds are those characterized by a radical of the structure >NH wherein the two remaining valences of nitrogen are satisfied by hydrogen, in particular, polyamines.

The polyamines for preparing Component B are alkylene polyamines (and mixtures thereof), including those having the formula:

$$A\text{-}N\left(\begin{array}{c}A\\|\end{array}\right)\left(R^2\text{-}N\left(\begin{array}{c}A\\|\end{array}\right)\right)_n H$$

wherein n is an integer between about 1 and 10, preferably between 2 and 8; each A is independently hydrogen or a hydrocarbon or hydroxy-substituted hydrocarbon radical having up to about 30 atoms; and R^2 is a divalent hydrocarbon radical

having about 1-18 carbons. Preferably, A is an aliphatic radical of up to about 10 carbon atoms which may be substituted with one or two hydroxy groups, and R^2 is a lower alkylene radical having 1-10, preferably 2-6, carbon atoms. Especially preferred are the alkylene polyamines where each A is hydrogen. Such alkylene polyamines include methylene polyamines, ethylene polyamines, butylene polyamines, propylene polyamines, pentylene polyamines, hexylene polyamines and heptylene polyamines. The higher homologs of such amines and related aminoalkyl-substituted piperazines are also included. Specific examples of such polyamines include ethylene diamine, triethylene tetramine, tris(2-aminoethyl)amine, propylene diamine, trimethylene diamine, hexamethylene diamine, decamethylene diamine, octamethylene diamine, di(heptamethylene)triamine, tripropylene tetramine, tetraethylene pentamine, trimethylene diamine, pentaethylene hexamine, di(trimethylene)trimine, 2-heptyl-3-(2-aminopropyl)imidazoline, 1,3-bis(2-aminoethyl)imidazoline, 1-(2aminopropyl)piperazine, 1,4-bis(2-aminoethyl)piperazine and 2-methyl-1-(2-aminobutyl)piperazine. Higher homologs, obtained by condensing two or more of the above-illustrated alkylene amines, are also useful.

The ethylene polyamines, examples of which are mentioned above, are especially useful for reasons of cost and effectiveness. Such polyamines are described in detail under the heading "Diamines and Higher Amines, Aliphatic" in Kirk-Othmer, Encyclopedia of Chemical Technology, Third Edition, Vol. 7, pp. 580-602. They are prepared most conveniently by the reaction of an alkylene chloride with ammonia or by reaction of an ethylene imine with a ring-opening reagent such as ammonia. These reactions result in the production of the somewhat complex mixtures of alkylene polyamines, including cyclic condensation products such as piperazines. Because of their availability, these mixtures are particularly useful in preparing the compositions of this invention. Satisfactory products can also be obtained by the use of pure alkylene polyamines.

Hydroxy polyamines, e.g., alkylene polyamines having one or more hydroxyalkyl substituents on the nitrogen atoms, are also useful in preparing Component B. Preferred hydroxyalkyl-substituted alkylene polyamines are those in which the hydroxyalkyl group has less than about 10 carbon atoms. Especially of such hydroxyalkyl-substituted polyamines include N-(2-hydroxyethyl)ethylene diamine, N,N'-bis(2-hydroxyethyl)ethylene diamine, 1-(2-hydroxyethyl)-piperazine, monohydroxypropyldiethylene trimine, dihydroxy-propyltetraethylene pentamine and N-(3-hydroxybutyl)tetramethylene diamine. Higher homologs obtained by condensation of the above-illustrated hydroxyalkyl-substituted alkylene amines through amino radicals or through hydroxy radicals are likewise useful.

In the reaction of the acylating agent with the polar compound, it is frequently preferred to employ a substantially inert, normally liquid organic diluent such as benzene, toluene, xylene or naphtha.

Typical carboxylic dispersants suitable for use as Component B are listed in Table I by reactants and diluent.

TABLE I

Example	(I) Acylating agent	(II) Polar compound	Ratio of equivalents, I:II	Reaction temperature, °C.	Diluent
1	Polybutenyl (mol. wt. about 900) succinic anhydride prepared from chlorinated polybutene containing predominantly isobutene units	Polyethylene amine mixture containing about 3-7 amino groups per molecule	0.91	140	Xylene
2	Same as Example 1	Pentaethylene hexamine	0.41	140	Xylene
3	Like Example 1 except polybutene mol. wt. is about 1050	Pentaethylene hexamine	0.61	140	Xylene
4	Like Example 1, except polybutene mol. wt. is about 850	Diethylene triamine	1.0	140	Xylene
5	Same as Example 4	Ethylene diamine	1.0	140	Xylene
6	Same as Example 4	N—(2-hydroxyethyl)-	1.06	140	Xylene

The detergent compositions of this invention generally contain equal parts by weight of Component A and Component B. Most often, the weight ratio of Component A to Component B is between about 0.2:1 and about 5:1, and preferably between about 1:1 and about 3:1.

As previously mentioned, the compositions of this invention are principally useful as carburetor detergent additives for gasoline fuel compositions, especially gasoline fuel compositions containing from about 1 volume percent to about 15 volume percent, preferably from about 2 volume percent to about 10 volume percent, oxygenate additives such as alcohols, ethers, and the like, e.g., methanol, ethanol, tertiary butyl alcohol, diethyl ether, methyl ethyl ether, and mixtures thereof.

Generally, these fuel compositions contain an amount of the composition of this invention sufficient to provide carburetor and engine detergency; usually, this amount is about 10-1000 parts by weight, preferably about 25-250 parts, of the composition of this invention per million parts of fuel.

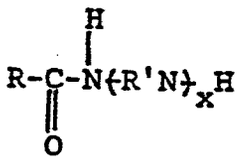
The fuel compositions can contain, in addition to the compositions of this invention, other additives which are well known to those of skill in the art. These include antiknock agents such as tetraethyl lead, dyes, antioxidants such as 2,6-di-tertiary-butyl-4-methylphenol, rust inhibitors such as alkylated succinic acids and anhydrides, bacteriostatic agents, gum inhibitors, metal deactivators, demulsifiers, upper cylinder lubricants and anti-icing agents.

The compositions of this invention can be added directly to the fuel, or they can be diluted with a substantially inert, normally liquid organic diluent such as naphtha, benzene, toluene, xylene or a normally liquid fuel as described above, to form an additive concentrate. These concentrates generally contain about 20-90% by weight of the composition of this invention and may contain, in addition, one or more other conventional additives known in the art or described hereinabove.

An illustrative detergent composition of this invention is present in Example I below.

EXAMPLE I

In this Example I, Component A is



wherein R is a C_{22} alkyl;

R' is a C_4 alkyl or branched alkyl;

and

x is 6; and

Component B is the product of Example II from Table I.

An example of the detergent compositions of this invention is a mixture of equal parts by weight of Component A and Component B.

EXAMPLE II

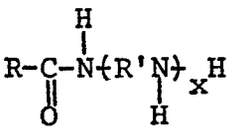
An example of a gasoline composition of this invention is unleaded base gasoline containing 5 volume percent methanol, 5 volume percent tertiary butyl alcohol, and 250 ppm of the detergent composition of Example I.

The combination of Component A and Component B, as illustrated in Example I, can provide improved inhibition to deposit formation as opposed to compositions which contain only Component A or Component B.

CLAIMS

1. A detergent composition characterized by including:

(a) an amide having the formula



wherein R is a C_6 - C_{22} alkyl, R' is a C_2 to C_6 alkyl or branched alkyl, and x= 1 to 10; and

(b) at least one hydrocarbon-soluble carboxylic dispersant characterized by the presence within its molecular structure of: a substantially saturated hydrocarbon based radical containing at least about 30 aliphatic carbon atoms, attached to at least one acyl or acyloxy radical, which is also attached through nitrogen to a polar group.

2. A composition according to claim 1, characterized in that the weight ratio of Component A to Component B is from about 0.2:1 to about 5:1.

3. A composition according to claim 1 or 2, characterized in that Component B is prepared by the reaction of a substituted succinic acid acylating agent with at least one polar reagent.

4. A composition according to claim 3, characterized in that the substituent on the substituted succinic acid acylating agent is derived from a homopolymer or interpolymer of polymerizable olefin monomers containing about 2-6 carbon atoms and has a molecular weight of about 700-5000.

5. A composition according to claim 4, characterized in that said substituent is derived from a polybutene comprising predominantly isobutene units.

6. A composition according to any of the preceding claims, characterized in that the weight of Component A to Component B is from about 1:1 to about 3:1.

7. A composition according to any of the preceding claims, characterized in that the polar reagent is at least one organic nitrogen-containing compound having at least one >NH group.

8. A composition according to claim 7, characterized in that the nitrogen-containing compound is at least one alkylene polyamine.

9. A composition according to claim 8, characterized in that the alkylene polyamine is an ethylene polyamine.

10. A composition according to any of the preceding claims, characterized in that x equals 1 to 6.

11. A gasoline composition comprising a major amount of gasoline, from about 1 volume percent to about 15 volume percent oxygenate additive, and about 10 to 1000 parts by weight, per million parts of said gasoline composition, of a composition according to any of the preceding claims.

12. The gasoline composition of claim 11, characterized in that the oxygenate additive is selected from the group consisting of methanol, ethanol, tertiary butyl alcohol, and mixtures thereof.