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SYNERGISTIC ANTI-ICING COMPOSITION

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ABSTRACT OF THE DISCLOSURE

Synergistic anti-icing composition of (1) polyhydroxy alcohol and (2) an N-alkylalkylenepolyamine or N-alkylpolyalkylenepolyamine in which said alkyl contains at least one aryl group.

BACKGROUND OF THE INVENTION

A serious problem in the operation of automobiles is stalling of the engine due to the formation of ice in the carburetor throttle body and on the throttle plate. As is well known, at temperatures ranging from about 30° to about 60° F. and at periods of relatively high humidities, such stalling has been encountered under idling or low load conditions. This is caused by the air-borne moisture undergoing freezing due to the refrigerating effect encountered in normal fuel vaporization within the carburetor. The ice formed on the throttle plate and adjacent carburetor walls restricts the narrow air openings and causes engine stalling.

The icing problem is of increasing importance because of the design of newer automobiles. For example, present cars do not have a manual throttle and therefore the operator of the car is no longer able to increase the idle speed during the warm up period to prevent such stalling. Furthermore, the increasing use of automatic transmissions adds to this problem because the idle speed must be kept low to avoid creeping and, accordingly, the idle speed is not sufficiently fast to avoid stalling due to icing. Still another development which appears to add to this problem is the increased volatility of commercial gasolines, because more frequent stalling is encountered with the more volatile fuels.

Various methods have been proposed to eliminate the stalling of automobile engines, including the use of additives. In one method, an alcohol is used but this has the objection of requiring large concentrations of the alcohol in order to obtain reasonably satisfactory anti-icing. In another method various salts have been proposed.

DESCRIPTION OF THE INVENTION

It now has been found that the use of certain substituted polyamines in admixture with polyhydroxy alcohol produces a synergistic composition of improved potency for use as an anti-icing additive.

In one embodiment the present invention relates to a synergistic anti-icing composition of (1) polyhydroxy alcohol and (2) an N-(aryl-containing alkyl)-alkylenediamine or N-(aryl-containing alkyl)-polyalkylenepolyamine.

In another embodiment the present invention relates to gasoline containing a stabilizing concentration of the synergistic composition herein set forth.

As hereinbefore set forth, one component of the synergistic composition is a particularly substituted alkylenediamine or polyalkylenepolyamine. The particular substitution is alkyl containing at least 1 aryl group. The N-(aryl-containing alkyl)-alkylenediamine contains from 4 to 50 carbon atoms in the alkyl group which, as hereinbefore set forth, contains at least 1 aryl group, including phenyl, naphthyl or anthracyl. The alkylene moiety contains from 2 to 6 carbon atoms and may be of straight

or branched chain arrangement, with the nitrogen atoms preferably being attached to different carbon atoms. In the N-(aryl-containing alkyl)-polyalkylenepolyamine, the alkyl group will be as defined above, each alkylene group will contain from 2 to 6 carbon atoms, which may be of straight or branched chain arrangement, and the nitrogen atoms are preferably attached to different carbon atoms. The polyamine moiety may contain from 3 to 6 nitrogen atoms.

The polyamine may be further illustrated by the following formula:

$$R-\underset{\displaystyle R'}{\underset{|}{N}}-(CH_2)_x-\underset{\displaystyle R'}{\underset{|}{N}}-[(CH_2)_x-\underset{\displaystyle R'}{\underset{|}{N}}-]_y-H_2$$

where R is alkyl of from 4 to 50 carbon atoms and contains at least 1 aryl group, R′ is independenty selected from the group consisting of hydrogen and alkyl of 4 to 50 carbon atoms, x is from 2 to 6 and y is from 0 to 4.

Illustrative polyamines for use in the present invention include

N-(phenylbutyl)-1,3-propylenediamine,
N-(phenylpentyl)-1,3-propylenediamine,
N-(phenylhexyl)-1,3-propylenediamine,
N-(phenylheptyl)-1,3-propylenediamine,
N-(phenyloctyl)-1,3-propylenediamine,
N-(phenylnonyl)-1,3-propylenediamine,
N-(phenyldecyl)-1,3-propylenediamine,
N-(phenylundecyl)-1,3-propylenediamine,
N-(phenyldodecyl)-1,3-propylenediamine,
N-(phenyltridecyl)-1,3-propylenediamine,
N-(phenyltetradecyl)-1,3-propylenediamine,
N-(phenylpentadecyl)-1,3-propylenediamine,
N-(phenylhexadecyl)-1,3-propylenediamine,
N-(phenylheptadecyl)-1,3-propylenediamine,
N-(phenyloctadecyl)-1,3-propylenediamine,
N-(phenylnonadecyl)-1,3-propylenediamine,
N-(phenyleicosyl)-1,3-propylenediamine,
N-(phenylheneicosyl)-1,3-propylenediamine,
N-(phenyldocosyl)-1,3-propylenediamine,
N-(phenyltricosyl)-1,3-propylenediamine,
N-(phenyltetracosyl)-1,3-propylenediamine,
N-(phenylpentacosyl)-1,3-propylenediamine,
N-(phenylhexacosyl)-1,3-propylenediamine,
N-(phenylheptacosyl)-1,3-propylenediamine,
N-(phenyloctacosyl)-1,3-propylenediamine,
N-(phenylnonacosyl)-1,3-propylenediamine,
N-(phenyltriacontyl)-1,3-propylenediamine, etc.
N-(diphenylalkyl)-1,3-propylenediamine,
N-(triphenylalkyl)-1,3-propylenediamine, etc.,

correspondingly substituted ethylenediamines,

1,2-propylenediamines,
1,2-butylenediamines,
1,3-butylenediamines,
1,4-butylenediamines,
1,2-pentylenediamines,
1,3-pentylenediamines,
1,4-pentylenediamines,
1,5-pentylenediamines,
1,2-hexylenediamines,
1,3-hexylenediamines,
1,4-hexylenediamines,
1,5-hexylenediamines,
1,6-hexylenediamines,

corresponding substituted dialkylenetriamines, trialkylenetetramines, tetraalkylenepentamines and pentalkylenehexamines, in which the alkyl and alkylene moieties are selected from those hereinbefore set forth.

A particularly preferred diamine for use in the present invention is N-(phenylstearyl)-1,3-propylenediamine. The phenyl substituent may be in the 9 or 10 position or mix-

tures thereof. This material is available commercially as "Duomeen L–PS" or it may be prepared in any suitable manner as, for example, by adding a phenyl substituent at the double bond of oleic acid and converting the acid to the corresponding amine, followed by reaction with acrylonitrile and reducing to the amine. Similarly N-(phenyllauryl)-1,3-propylenediamine is prepared by adding a phenyl group at the double bond in dodecylenic acid or N-(phenylpalmityl)-1,3-propylenediamine is prepared by adding a phenyl group at the double bond of palmitoleic acid and further reacting as set forth above. When two phenyl groups are desired in the alkyl substituent, two phenyl groups, for example, may be added at the double bonds of linoleic acid. Similarly when three phenyl groups are desired, linolenic acid is used. These examples illustrate one method of preparing the specifically substituted polyamine for use in the present invention and serves as a basis for preparing other suitable polyamines. However, it is understood that these polyamines may be prepared in any suitable manner and that the aryl group may be further substituted by alkyl, hydroxy, alkoxy, amino or other groups. Of particular advantage are the hydroxy substituted derivatives, the hydroxy group being in the ortho, meta or para position on the phenyl ring. Illustrative compounds in this embodiment include N-(p-hydroxyphenylstearyl) - 1,3 - propylenediamine, N-(o-hydroxyphenyllauryl)-1,3-propylenediamine, etc.

In a preferred embodiment the phenyl substituent is attached on the alkyl chain. In another embodiment the phenyl substituent may be in the alkyl chain or attached at the end of the alkyl chain. Illustrative compounds in this embodiment include

N-methylphenylbutyl)-1,3-propylenediamine,
N-(ethylphenylbutyl)-1,3-propylenediamine,
N-(propylphenylbutyl)-1,3-propylenediamine,
N-(butylphenylbutyl)-1,3-propylenediamine,
N-(ethylphenylhexyl)-1,3-propylenediamine,
N-(butylphenyloctyl)-1,3-propylenediamine,
N-(hexylphenyldecyl)-1,3-propylenediamine,

etc., as well as

N-(6-phenylhexyl)-1,3-propylenediamine,
N-(8-phenyloctyl)-1,3-propylenediamine,
N-(12-phenyldodecyl)-1,3-propylenediamine, etc.

It is understood that these specific compounds are illustrative only and that other phenylalkyl substituents may be used as well as the correspondingly substituted polyalkylenepolyamines. Also, it is understood that the specific polyamines are not necessarily equivalent in their synergistic effect with the polyhydroxy alcohol but all of them will exhibit beneficial results.

In another embodiment, a poly-(aryl-containing alkyl)-alkylenediamine or poly-(aryl-containing alkyl)-polyalkylenepolyamine may be used. In these compounds, the "H_2" in the formula hereinbefore set forth will be replaced by R and R', these having the same definition as hereinbefore set forth. Illustrative compounds in this embodiment include N,N'-di-(arylalkyl) - alkylenediamine and particularly N,N'-di-(phenylalkyl)-1,3-propylenediamine, N^1N^3-di-(arylalkyl)-diethylenetriamine and N^1N^3-di-(phenylalkyl) - di - (1,3-propylene)-diamine, N^1N^4-di-(arylalkyl)-trialkylenetetramine, etc. The aryl, alkyl and alkylene moieties will be selected from those hereinbefore set forth. These compounds may be prepared in any suitable manner.

As hereinbefore set forth, the specifically substituted polyamine is used in admixture with a polyhydroxy alcohol. A preferred polyhydroxy alcohol is the commercially available hexylene glycol which is 2,4-dihydroxy-2-methylpentane. Other polyhydroxy alcohols include ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, other hexylene glycols as, for example, 1,6-dihydroxyhexane, 2,6-dihydroxyhexane, etc., heptylene glycol, octylene glycol, etc., diethylene glycol, dipropylene glycol, dibutylene glycol, tributylene glycol, etc., dihydroxycyclohexane as, for example, 1,4-dihydroxycyclohexane, 1,3-dihydroxycyclohexane, 1,2-dihydroxycyclohexane, etc., glycerol, 1,2,3-butanetriol, pentanetriol, hexanetriol, heptanetriol, erythritol, etc. In a preferred embodiment the polyhydroxy alcohol is a dihydroxy alcohol containing from 2 to 8 carbon atoms and may be of straight or branched chain. However, it is understood that the polyhydroxy alcohol may contain 3 or 4 hydroxy groups, as well as being of aliphatic or cyclic configuration.

When desired, a mixture of polyhydroxy alcohols is employed. Illustrative mixtures include a mixture comprising from 85% to 95% by weight of hexylene glycol and 5% to 15% by weight of glycerol, a mixture of 75% to 95% by weight of ethylene glycol and 5% to 25% by weight of erythritol, etc. Also when desired, a mixture of the particularly substituted polyamines may be employed. These will be selected from those hereinbefore set forth.

The mixture of polyamine and polyhydroxy alcohol will be used in any suitable proportion, which may range from 5% to 95% and preferably from 10% to 90% by weight of the polyamine and from 95% to 5% and preferably from 90% to 10% by weight of the polyhydroxy alcohol.

The amount of total anti-icing composition to be added to the gasoline will be sufficient to effect improved deicing. For economic reasons, the concentration should be as low as practicable and may range from 0.0001% to 0.05% by weight and preferably within the range of from about 0.002% to about 0.01% by weight of the fuel, based on the mixed polyamine and polyhydroxy alcohol exclusive of solvent when employed. While each of the polyamine and the polyhydroxy alcohol may be added separately to the fuel, it generally is preferred to prepare a composition of the polyamine and polyhydroxy alcohol in the proper concentrations and to add this composition to the fuel in the desired amount. When desired, the mixture of polyamine and polyhydroxy alcohol may be prepared as a solution in a suitable solvent such as a paraffinic, aromatic and/or naphthenic naphtha or gasoline. When desired, the solvent may comprise an aromatic or paraffinic hydrocarbon, including benzene, toluene, xylene, ethylbenzene, etc., pentane, hexane, heptane, octane, etc. When a solvent is used, the polyamine and hexylene glycol will comprise from about 10% to about 90% and preferably from about 25% to about 75% of the solution.

The synergistic composition in the present invention may be used in any gasoline. Commercial gasolines generally comprise a mixture of two or more of cracked gasoline, hydrocracked gasoline, reformed gasoline, alkylate, isoparaffins, aromatics, etc., and in some cases may contain straight run gasoline, coker distillate, etc. It is understood that the synergistic composition of the present invention may be used along with other additives incorporated in gasoline. These include antioxidant, metal deactivator, tetra-alkyl lead, detergent, dye, etc. When desired, one or more of these additional additives may be admixed with the composition of the present invention and marketed and used in this manner.

The following examples are introduced to illustrate further the novelty and utility of the present invention but not with the intention of unduly limiting the same.

EXAMPLE I

The synergistic composition of this example comprises a mixture of N-(phenylstearyl)-1,3-propylenediamine, the phenyl substituent being in the 9 or 10 position, and hexylene glycol.

The anti-icing properties were determined in a carburetor icing demonstrating apparatus consisting of a vacuum pump equipped so that cool moisture-saturated air from an ice tower is drawn through a simulated carburetor. The gasoline sample passes from a fuel reservoir through a flow meter into the carburetor at a rate of 1.4 lb./hr.

The air from the ice tower is passed at a flow rate of 14.4 lb./hr. at a temperature of 40° F. The manifold vacuum is 9.5 in. Hg at the start and 12.5 in. Hg at the end of the test. Evaporation of the gasoline in the carburetor further cools the cold moist air, with resulting ice formation on the throttle plate. The time in seconds is measured until a drop of 3 in. Hg vacuum occurs, which indicates stalling conditions.

The fuel used in this example is a commercial gasoline which, without anti-icing additive, reached stalling conditions within 7.5 seconds.

Other samples of this gasoline containing 25, 50 or 200 parts per million of hexylene glycol all reached stalling conditions within 12.1 seconds. Thus the hexylene glycol by itself, even in a concentration as high as 200 parts per million, was only of minor benefit for this purpose.

When the N-(phenylstearyl)-diamine was used in concentration of 25 and 50 parts per million, the stalling conditions were 16.1 and 21.3 seconds respectively. It will be noted that this diamine was only of moderate benefit.

In contrast to the above, when the N-(phenylstearyl)-1,3-propylenediamine at a concentration of 25 parts per million was used in admixture with hexylene glycol in a concentration of 50 parts per million, an average stalling condition of over 100 seconds was obtained. This demonstrates the strong synergistic effect obtained when compared to the 16.1 and 12.1 seconds resulting from the use of each of these components alone. Normally it would be expected that the stalling conditions would be equal to the sum obtained from each of these components alone, which would be 28.2 seconds, but instead, the stalling conditions were above 100 seconds.

The synergistic effect is even further demonstrated by the use of a mixture of 25 parts per million of the N-(phenylstearyl)-1,3-propylenediamine and 200 parts per million of hexylene glycol. This mixture extended the stalling conditions to 299 seconds. It normally would be expected that the stalling conditions would be 16.1 plus 12.1 or 28.2 seconds, the sum obtained when each of these components is used alone.

EXAMPLE II

In this example the polyhydroxy alcohol was dipropylene glycol. When used in a concentration of 25, 50 and 200 parts per million, it increased the stalling condition from 7.8 seconds to 11.0, 12.6 and 15.7 seconds, respectively.

In contrast to the above, when a mixture of 25 parts per million of N-(phenylstearyl)-1,3-propylenediamine and 200 parts per million of dipropylene glycol was used, the stalling condition was increased to 118 seconds, again demonstrating the synergistic effect.

EXAMPLE III

The anti-icing composition of this example is a blend of 60% by weight of N-(p-hydroxyphenyllauryl)-1,2-ethylenediamine and 40% by weight of 1,6-dihydroxyhexane. The composition is incorporated into a commercial gasoline in a concentration of 75 parts per million and serves to prevent stalling.

EXAMPLE IV

The anti-icing composition of this example is a mixture of 50% by weight of N-(naphthylpalmityl)-triethylenetetramine and 50% by weight of dipropylene glycol. The mixture is incorporated in a concentration of 100 parts per million in commercial gasoline and serves to prevent stalling.

EXAMPLE V

The anti-icing composition of this example is a blend of 60% by weight of N-(9,12-diphenylstearyl)-1,3-propylenediamine and 40% by weight of ethylene glycol. The composition is incorporated in a concentration of 100 parts per million in commercial gasoline and serves to prevent stalling.

EXAMPLE VI

The anti-icing composition of this example is a blend of 50% by weight of N^1N^3-di-(phenylheptyl)-diethylenetriamine and 50% by weight of ethylene glycol. The composition is incorporated in a concentration of 115 parts per million in commercial gasoline and serves to prevent stalling.

I claim as my invention:

1. Synergistic anti-icing composition of from about 5% to about 95% by weight of (1) dihydroxy aliphatic alcohol containing from 2 to 8 carbon atoms and from about 5% to about 95% by weight of (2) N-(aryl-substituted alkyl)-alkylenediamine wherein the alkyl group contains 4 to 50 carbon atoms, the aryl group is phenyl, naphthyl or anthracyl and the alkylene group contains 2 to 6 carbon atoms.

2. The composition of claim 1 in which said dihydroxy alcohol is hexylene glycol.

3. The composition of claim 1 wherein said dihydroxy alcohol is dipropylene glycol.

4. The composition of claim 1 wherein said N-(aryl-substituted alkyl)-alkylenediamine is N-(phenylstearyl)-1,3-propylenediamine.

5. The composition of claim 1 wherein said N-(aryl-substituted alkyl)-alkylenediamine is N-(hydroxyphenylstearyl)-1,3-propylenediamine.

6. The composition of claim 1 wherein said N-(aryl-substituted alkyl)-alkylenediamine is N-(phenyllauryl)-1,3-propylenediamine.

7. The composition of claim 1 incorporated in gasoline to prevent stalling due to icing of an internal combustion engine.

8. The composition of claim 7 incorporated in a concentration of from about 0.0001% to about 0.05% by weight of the gasoline.

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