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3,375,092

ANTI-ICING GASOLINE

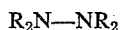
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ABSTRACT OF THE DISCLOSURE

This invention relates to an additive material and to a motor fuel composition containing same having anti-icing properties. The additive material is the reaction product of alkenyl succinic acid or anhydride in which the radical has from 8 to 24 carbon atoms and hydrazine having the formula R_2NNR_2 in which each R represents a member selected from the group consisting of hydrogen and an alkyl radical having from 1 to 4 carbon atoms.

This invention relates to a motor fuel composition for internal combustion engines having outstanding anti-icing, anti-stalling properties. This improvement is based on the use of an additive which is the reaction product of an alkylene succinic acid or anhydride with a hydrazine compound having the formula:



in which R is hydrogen or an aliphatic radical having from 1 to 4 carbon atoms.

Highly volatile winter gasoline blends are known to be prone to stalling during engine startup periods. This problem is most frequently encountered under atmospheric conditions of high humidity and relatively low temperatures ranging from about 30 to 50° F. In the operation of an internal combustion engine, a motor fuel is vaporized to a fuel-air mixture as it passes through the carburetor. This vaporization is accompanied by a sharp drop in the temperature of the mixture. During the starting period as a motor fuel is vaporized under cool, humid atmospheric conditions, the temperature of the fuel-air mixture drops to freezing temperatures resulting in the formation and deposition of ice particles on the throttle blade and walls of the carburetor. The ice in the carburetor partially or completely blocks the air passage between the carburetor throat and the throttle valve causing stalling of the engine.

Many anti-icing, anti-stalling additives or additive combinations are known or have been proposed for use in gasoline. While a goodly number are reasonably effective as anti-stalling agents, and aside from the question of costs, their use very often gives rise to entirely new and serious problems. As a general rule, the primary factors which will prevent the use of a gasoline additive include corrosiveness to the metal in the carburetor, or in storage tanks or other metal containers with which the fuel comes in contact or the development of insoluble precipitates and/or emulsions in the fuel itself which cause gas line filter plugging or plugging of the fine passages in the carburetor.

A recent development in the field of anti-stalling motor fuels is that disclosed in U.S. Patent No. 3,148,960. According to this discovery, an N-aminoethyl alkenyl succinic acid which is formed from ethylene diamine and an alkenyl succinic anhydride, is effective for improving the anti-stalling properties of gasoline. When the foregoing additive was employed in a gasoline containing some water, it was found that on mixing the gasoline became turbid as a result of the formation of an emulsion. An emulsion cannot be tolerated in gasoline because it will carry water present in fuel storage tanks into the fuel

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system of the motor vehicle promoting corrosion and instability of the additives in the fuel in addition to promoting both gas line fuel filter plugging as well as blockage of the fine jets of the carburetor.

An improved motor fuel additive has now been discovered which substantially improves the anti-stalling property of gasoline containing same. Moreover, this novel gasoline is remarkably free of filter plugging and corrosion side effects which so often prevent the use of otherwise effective additives.

In accordance with this invention, the improved motor fuel comprises gasoline containing from about 0.0005 to 0.5 weight percent of the product produced by reacting an alkenyl succinic acid or anhydride wherein the alkenyl radical has 8 to 24 carbon atoms with a hydrazine compound having the formula:



in which R is hydrogen or an alkyl radical having from 1 to 4 carbon atoms in a mole ratio of 2:1 to 1:4 respectively.

The reaction product of the invention may be prepared by contacting suitable quantities of the alkenyl succinic acid or anhydride and the hydrazine compound. This may be done either with or without a mutual solvent. Moderate heat may be employed to speed up formation of the reaction product.

The alkenyl succinic acid or anhydride component employed in making the reaction product comprises those in which the alkenyl radical has from 8 to about 24 carbon atoms. It is understood that mixtures of alkenyl succinic acids or anhydrides within the noted range may also be employed. It is preferable to employ those alkenyl succinic acids or anhydrides in which the alkenyl group has from about 8 to 16 carbon atoms with the particularly preferred material being tetrapropenyl succinic acid. This particular compound is prepared by alkylating maleic anhydride with propylene tetramer using as is or hydrolyzing the product to the acid. Specific effective compounds include octenyl succinic acid and anhydride, 2,3-dimethyl hexenyl succinic acid and its anhydride, 4-ethyl hexenyl succinic acid and its anhydride, undecenyl succinic acid and its anhydride, hexadecenyl succinic acid, and tetradecenyl succinic acid.

The hydrazine compound used to make the reaction product has the formula:



in which each R is hydrogen or an alkyl radical having from 1 to 4 carbon atoms. Thus hydrazine itself may be employed or alkyl derivatives thereof, such as the various mono-, di-, tri- and tetra-methyl, ethyl, propyl and butyl substituted hydrazines. Unsymmetrical dimethyl hydrazine is particularly preferred among the alkyl substituted hydrazines.

Equal mole proportions of the alkenyl succinic acid or anhydride and of the hydrazine compound may be employed in preparing the anti-icing reaction product of this invention. More broadly, however, the alkenyl succinic acid or anhydride and the hydrazine compound may be reacted within proportions ranging from about 2:1 to 1:4, respectively. The most effective reaction products were those in which substantially equal mole proportions of the two components were employed.

As an example of the preparation of the additive of the invention, 56.8 gm. (0.2 mole) of tetrapropenyl succinic acid in 300 ml. of benzene was reacted with 7 gm. (0.22 mole) of hydrazine added dropwise. The mixture was stirred for two hours and then refluxed overnight. The reaction product was stripped to a pot temperature of 150° C. to affect recovery of the adduct.

The following data illustrate the improvements brought

about by the anti-stalling, anti-icing additives of the invention. In these data, the invention is illustrated by additives prepared from reacting either tetrapropenyl succinic acid or tetrapropenyl succinic acid anhydride with either hydrazine or unsymmetrical dimethyl hydrazine.

The action of the anti-icing reaction product was evaluated for its anti-stalling, anti-icing effects in a carburetor icing demonstrator apparatus consisting of a vacuum pump equipped so that cool, moisture saturated air from an ice tower is drawn through a simple glass tube gasoline carburetor. The gasoline sample is placed in a sample bottle and is drawn into the glass carburetor through a 20 gauge hypodermic needle. Evaporation of the gasoline in the gas tube further cools the cold, moist air with resulting ice formation on the throttle plate. The formation of ice on the throttle plate causes an engine to stall and it has been found that this condition is equivalent to a pressure drop across the throttle plate of about 0.5 inch of mercury, and the time to reach this pressure drop is recorded. The vacuum pump is adjusted to give a vacuum of 1.8 inches mercury and the test is run until either a pressure of 2.3 inches mercury has been reached or it is run for 300 seconds. Since with most fuels this pressure drop is reached in 1 to 4 minutes, 300 seconds is the maximum time for a run. A recording of 300 seconds indicates no stalling within the test period. Each fuel is run four times in succession and the average is reported. If the difference between the runs is great, the glass tube carburetor and the test throttle are washed with alcohol, flushed out with gasoline and the runs repeated. An unleaded winter grade premium gasoline having a Reid vapor pressure of about 12 gives a stall in about 40 to 70 seconds in this test. Additives which raise the stalling time to over 200 seconds are regarded as effective anti-stalling, anti-icing additives.

The base fuel employed to evaluate the effectiveness of the additive reaction product of this invention, referred to as runs A and J below, was a winter grade premium gasoline having an ASTM Research Octane Rating of about 95.0. This gasoline had a 50% ASTM distillation point of 214° F. and a Reid vapor pressure of about 11.8 lbs. and was ideally suited for testing the effectiveness of the anti-icing reaction product. The fuels in runs B through I are the additive containing fuels derived from the same base fuel showing the components and the amounts employed in preparing the additive.

The results of the anti-icing tests are given in Table I below wherein the anti-icing performance of the base fuel is compared to the anti-icing property of the base gasoline minus the reaction product of this invention. The components of the reaction product and the mole ratios in which they were reacted to produce the specific products employed are also given. The anti-icing test runs were conducted with the reaction product being employed at a concentration of 14.8 lbs. per 1,000 barrels of gasoline. This corresponds to about 0.0055 weight percent for the anti-icing agent.

TABLE I.—ANTI-ICING TEST

Fuels with anti-icing reaction product:	Stalling time, seconds
A. Base fuel	44
B. + TPS ^a Acid (0.2) ^b hydrazine (0.22) ^b	300+
C. + TPS acid (0.2) hydrazine (0.11)	300+
D. + TPS acid (0.2) UDMH ^c (0.1)	300+
E. + TPS acid (0.2) UDMH (0.2)	300+
F. + TPS anhydride (0.2) hydrazine (0.2)	202
G. + TPS anhydride (0.2) hydrazine (0.4)	300+
H. + TPS anhydride (0.2) UDMH (0.2)	294
I. + TPS anhydride (0.2) UDMH (0.4)	300+
J. Base fuel	42

^a TPS is tetrapropenyl succinic.

^b Numbers in parentheses indicate moles employed in preparing the additive.

^c UDMH is unsymmetrical dimethyl hydrazine.

The foregoing data show that the additive of the invention is an outstanding anti-icing additive for gasoline. This additive is compatible with the other components normally used in gasoline including tetraalkyl lead octane improvers, metal deactivators, gum inhibitors, and the like.

Important features of the fuels containing the anti-icing additive of the invention are that it forms substantially no precipitates or insolubles or emulsions in gasoline during the normal handling and storage periods and is substantially non-corrosive with the result that the gasolines of the invention are free of corrosion and fuel filter plugging problems which have both been serious drawbacks to proposed anti-icing additives.

The base fuel blends noted above were compared as to their corrosion properties in a rust test. Polished strips of metal, steel strip and carburetor metal, were placed in sample bottles containing 90 ml. of the test fuel together with 10 ml. of distilled water. The bottles were stoppered and shaken for one minute. The percentage of rust on the metal strips for both the portion of the metal strip immersed in the gasoline and the part immersed in the water phase was taken over the indicated period of time as shown in Table II below. The additive containing fuels had a concentration of about 18 pounds per thousand barrels of gasoline in the additive.

TABLE II.—RUST TEST

	Steel Strip		Carburetor Metal		Time, days
	Gasoline, percent	Water Rust	Gasoline, percent	Water Rust	
A	50	2	50	2	3
B	11	—	—	—	6
D	25	—	—	—	6
E	—	—	—	—	6
F	10	10	—	—	2
G	—	—	—	—	2
H	—	—	—	—	6
I	3	—	—	—	6

¹ Spot.

² Rust.

NOTE.—Dashes indicate that no rust was present on the metal strip.

A gasoline representative of this invention was tested for its tendency to form an emulsion and/or a precipitate in comparison to a known anti-icing additive. A gasoline was prepared using a base fuel similar to that employed in Table I above containing 18 pounds per thousand barrels of the reaction product of tetrapropenyl succinic anhydride and hydrazine. This fuel was designated Blend A.

A similar fuel was prepared except that it contained 18 pounds per thousand barrels of N-aminoethyl tetrapropenyl succinamic acid. This was designated Blend B.

560 ml. of each fuel was stirred for an hour with 30 ml. of distilled water. At the end of this time, the stirring was stopped and the samples observed while standing.

Blend A separated in one minute leaving a clear gasoline. Blend B separated in two minutes leaving a turbid gasoline. The test shows that the gasoline of the invention forms no emulsion in contrast to a known gasoline blend.

The filterability of the fuel of the invention was determined in the Filter Index Test in comparison to a base fuel containing no anti-stalling additive and to a fuel containing a commercially employed anti-stalling additive. This test involves storing samples of the test fuels over 3 percent distilled water in terneplated one gallon cans. Each week before sampling for filter index test, the test gasolines were stirred in the cans for one minute and then allowed to settle for one minute. The filter index number is the logarithm of the relative amount of time it takes for the samples to go through a standard gasoline filter. A filter index of 2.0 means that the test fuel took 10 times longer to pass through the filter than the base fuel. In Table III below A is the base fuel containing no anti-stalling additive, B is the base fuel containing 20 pounds per thousand barrels of equal amounts of the reaction product of tetrapropenyl succinic anhydride and unsymmetrical dimethyl hydrazine in 1:1 mole ratio and

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a light distillate mineral lubricating oil having an SUS at 100° F. of 105, and C is the base fuel containing 20 pounds per thousand barrels of equal amounts of tetrapropenyl succinic acid and the same lubricating oil used in B above.

TABLE III.—FILTER INDEX

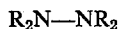
Test Fuel	Times, weeks			
	1	2	3	4
A-----	1.10	0.93	1.07	1.00
B-----	1.13	0.99	1.02	0.97
C-----	1.15	1.30	1.12	2.15

The filterability of the base fuel and the fuel of the invention are about equal while the filterability of the fuel representative of a commercial anti-stalling additive is far inferior to that of the other fuels.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and, therefore, only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A gasoline additive comprising the reaction product of a first component selected from the group consisting of alkenyl succinic acids and anhydrides in which said alkenyl radical has from 8 to about 24 carbon atoms and a hydrazine compound having the formula:



in which each R represents a member selected from the group consisting of hydrogen and an alkyl radical having from 1 to 4 carbon atoms, prepared by reacting said first component with said hydrazine compound at a mole ratio in the range of 2:1 to 1:4 respectively.

2. A gasoline additive according to claim 1 in which said reaction is conducted at mole ratios in the range of 1:1 to 1:2 respectively.

3. A gasoline additive according to claim 1 in which said alkenyl radical has from 10 to 16 carbon atoms.

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4. A gasoline additive according to claim 1 prepared by reacting tetrapropenyl succinic acid with hydrazine.

5. A gasoline having improved anti-stalling, anti-icing properties containing from about 0.0005 to 0.05 weight percent of the reaction product of a first component selected from the group consisting of alkenyl succinic acids and anhydrides in which said alkenyl radical has from 8 to about 24 carbon atoms and a hydrazine compound having the formula:



10 in which each R represents a member selected from the group consisting of hydrogen and an alkyl radical having from 1 to 4 carbon atoms, prepared by reacting said first component with said hydrazine compound at a mole ratio in the range of 2:1 to 1:4 respectively.

15 6. A gasoline composition according to claim 5 in which said reaction product is prepared by reacting said components at a mole ratio in the range of 1:1 to 1:2 respectively.

20 7. A gasoline composition according to claim 5 in which said alkenyl radical has from 10 to 16 carbon atoms.

8. A gasoline composition according to claim 5 in which said reaction product is prepared by reacting tetrapropenyl succinic acid with hydrazine.

25 9. A gasoline composition according to claim 5 in which said reaction product is prepared by reacting tetrapropenyl succinic acid with unsymmetrical dimethyl hydrazine.

30 10. A gasoline composition according to claim 5 in which said reaction product is prepared by reacting tetrapropenyl succinic acid with hydrazine.

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