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FUEL COMPOSITION

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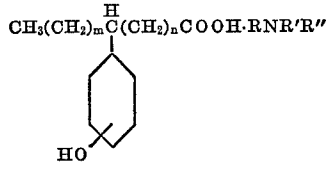
ABSTRACT OF THE DISCLOSURE

A volatile gasoline composition of improved anti-stalling and corrosion inhibiting properties containing a salt of an aliphatic amine and a hydroxyphenyl stearic acid.

This invention relates to a volatile gasoline composition of improved anti-stalling and corrosion inhibiting properties containing a salt of an aliphatic amine and a hydroxyphenyl stearic acid. More particularly, it involves the discovery that specific amine-hydroxyphenyl stearic acid salts are effective anti-stalling, anti-icing additives and corrosion inhibiting additives in gasoline.

The gasoline fuel composition of this invention comprises a substantial concentration of volatile components and 0.001 to 0.1 weight percent of an aliphatic amine-hydroxyphenyl stearic acid salt having the general formula:



in which m has the value of 7 or 8 and the sum of m and n is 15, R is an aliphatic hydrocarbyl radical containing from 2 to 24 carbon atoms, and R′ and R″ each represent hydrogen or a hydrocarbyl radical having from 1 to 8 carbon atoms. The presence of the amine-hydroxyphenyl stearic acid salt in prescribed concentration imparts outstanding anti-icing and anti-stalling properties and an unexpected level of corrosion resistance to volatile gasoline compositions.

When internal combustion engines are operated on a gasoline fuel having the desired volatility characteristics for cold weather driving, a stalling problem is encountered during the warm up period, particularly under cool, humid atmospheric conditions. It has been generally recognized that the cause of repeated engine stalling in cool, humid weather is the formation of ice in the carburetor. Gasoline evaporating in the carburetor has a sufficient refrigerating effect to condense and freeze moisture present in the air. Ice particles deposit on the metal surfaces of the carburetor and partially or completely block the air passage between the carburetor throat and the carburetor throttle valve with resulting stalling, particularly when the engine is idling.

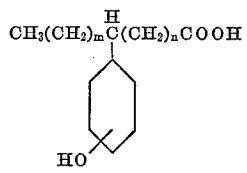
The amine-hydroxyphenyl stearic acid salts of this invention are particularly useful in highly volatile fuels having a Reid vapor pressure above about 9 which are particularly prone to engine stalling due to ice formation under cool, humid conditions. Stated another way, the additives of the invention are particularly useful in winter gasoline employed in northern portions of the country since they have Reid vapor pressures between about 9 and 13.5, depending on the area.

A surprising feature of the additives of the invention are their outstanding effectiveness as corrosion inhibitors in gasoline. The structure of the amine-hydroxyphenyl stearic acid salts appears to be critical in this regard since very similar amine salts are ineffective as corrosion inhibitors in gasoline rendering them unsuitable for a commercial product.

The amine-hydroxyphenyl stearic acid salts are semi-solid and are simply prepared by mixing equimolar portions of a C_2—C_{24} aliphatic amine with a hypdroxyphenyl stearic acid. The resulting salts are readily soluble in gasoline.

The aliphatic amines employed in forming effective anti-stalling and corrosion inhibiting additives are represented by the general formula RNR′R″ in which R is an aliphatic hydrocarbyl radical containing from 2–24 carbon atoms, and R′ and R″ each represent hydrogen or a hydrocarbyl radical having from 1 to 8 carbon atoms. Effective amines are ethylamine, n-butylamine, t-butylamine isoamylamine, 2-ethylhexylamine, t-octylamine, laurylamine, n-decylamine, isononylamine and mixtures of tertiary alkyl primary amines. A mixture of tertiary alkyl primary amines containing 11–14 carbon atoms sold under the trade name Primene 81–R and a mixture of tertiary alkyl primary amines containing 18–24 carbon atoms sold under the trade name Primene JMT are preferred amines for forming effective anti-stalling salts. Although branched primary amines are preferred, secondary amines and tertiary amines can also be used to make the amine salts of hydroxyphenyl stearic acid for application as gasoline additives.

The hydroxyphenyl stearic acids used in preparing the effective anti-stalling and corrosion inhibiting agents are represented by the formula:



in which m has a value of 7 or 8 and the sum of m and n is 15. Examples of specific effective hydroxyphenyl stearic acids include 9-(or 10-)-(4-hydroxyphenyl)octadecanoic acid, 9-(or 10-)-(2-hydroxyphenyl)octadecanoic acid, 9-(or 10-)-(4-hydroxy-2-methylphenyl)octadecanoic acid, and 9-(or 10-)-(2-hydroxy-4-ethylphenyl)octadecanoic acid.

Typical amine-hydroxyphenyl stearic acid salts effective as anti-staling, anti-icing additives and as corrosion inhibitors in gasoline include the following: tertiary butylamine salt of p-hydroxyphenyl stearic acid, t-ocylamine salt of 9-(or 10-)-(p-hydroxyphenyl) stearic acid, Primene 81–R salt 9-(or 10-)-(p-hydroxyphenyl) stearic acid, Primene JM-T salt of 9-(or 10-)-(p-hydroxyphenyl) stearic acid, tertiary-butylamine salt of 9-(or 10-)-(2-hydroxyphenyl) octadecanoic acid, stearylamine salt of 9-(or 10-)-(2-nonyl - 4 - hydroxyphenyl) octadecanoic acid.

It will be appreciated that the hydroxyphenyl derivatives of stearic acid prepared from oleic acid will have the hydroxyphenyl substituent on either the 9th or 10th carbon atom as indicated. The reaction produces a mixture of the two compounds which can be used without separating the individual compounds.

Amine-hydroxyphenyl stearic acid salts having the prescribed formula are effective anti-stalling and corrosion inhibiting additives when employed in concentrations of 0.001 to 0.1 weight percent of the gasoline. The preferred salt concentration falls in the range of 0.001 to 0.02 weight percent. Concentrations of the order of 3–36 pounds of amine-hydroxyphenyl stearic acid salt per thousand barrels of gasoline equivalent to concentrations of 0.001 to 0.12 weight percent have proven particularly

effective in forming fuels of excellent anti-stalling and corrosion inhibiting properties.

The action of the amine-hydroxyphenyl stearic acid salts as anti-stalling, anti-icing additives was evaluated in a carburetor icing demonstrator apparatus consisting of a vacuum pump equipped so that cooled, 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 hypodermic needle which is usually of 20 gauge. Evaporation of the gasoline in the glass 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 a pressure of 2.3 inches mercury has been reached or is run for 300 seconds. Since with most fuels this pressure drop is reached in 1–4 minutes, 300 seconds is the maximum time for a run. A recording of 300 seconds indicates no stall within the test period. Each fuel is run three times in succession and the average is reported. A leaded winter grade premium gasoline having a Reid vapor pressure of about 13 gives a stall in about 56–65 seconds in this test. Additives which raise the stalling time to over 200 seconds are regarded as effective preferred anti-stalling, anti-icing additives.

The base fuel employed to evaluate the effectiveness of amine-hydroxyphenyl stearic acid salts as anti-stalling, anti-icing additives was a winter grade premium gasoline having an octane rating of about 100 and containing 3 cc. of TEL per gallon. The base fuel which had a 50% ASTM distillation point of 230 and a Reid vapor pressure of about 11 pounds was ideally suited for testing the effect of additives on the stalling characteristics of the fuel because of its high vapor pressure. This base fuel had an average stalling time of 46 seconds in the afore-described stalling test.

In the following table there is shown the effectiveness of amine-hydroxyphenyl stearic acid salts of prescribed formula as anti-stalling, anti-icing additives.

ACTION OF AMINE-HYDROXYPHENYL STEARIC ACID SALTS AS ANTI-STALLING ADDITIVES

Run	Additive	Lbs. per 1,000 barrels	Stalling time, Sec.
1	None		46
2	t-Octylamine salt of 9-(or 10-)-(p-hydroxyphenyl) stearic acid.	3	75
3	do	5	300+
4	do	10	300+
5	t-Butylamine salt of 9-(or 10-)-(p-hydroxyphenyl) stearic acid.	3	259
6	do	10	300+
7	do	15	300+
8	Primene 81-R salt of 9-(or 10-)- (p-hydroxyphenyl) stearic acid.	3	63
9	do	10	300+
10	do	15	300+

The effectiveness of the amine-hydroxyphenyl stearic acid salts as corrosion inhibiting additives in gasoline was determined in the below described corrosion test. This test is conducted by adding 90 cc. of the test fuel and 20 cc. of water to a 4 ounce tall-form bottle. A clean cold-rolled steel strip measuring 5" x ½" x 1/16" is placed in the fluids in the bottle which is then stoppered. The bottle is shaken for 15 seconds and then kept standing at room temperature for 24 hours. The percentage of the metal surface covered by rust is then determined by visual examination. In all cases, the additive under test was employed in a concentration of 10 lbs. of additive per 1000 barrels of gasoline.

CORROSION TEST

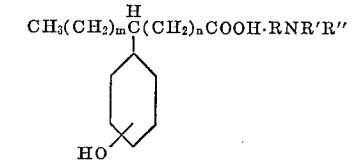
Run	Additive	Percent rust
1	None	90
2	t-butylamine salt of 9-(or 10-)-phenylstearic acid	80
3	t-Primene 81–R salt of 9-(or 10)-phenylstearic acid.	60
4	Morpholine salt of 9-(or 10)-phenylstearic acid	80
5	t-Butylamine salt of 9-(or 10)-(p-hydroxyphenyl) stearic acid.	5
6	t-Octylamine salt of 9-(or 10-)-(p-hydroxyphenyl) stearic acid.	5
7	Primene 81-R salt of 9-(or 10-)-(p-hydroxyphenyl) stearic acid.	5

The foregoing tests show that the amine salts of hydroxyphenyl stearic acid (runs 5 to 7) are outstandingly effective as corrosion inhibitors in gasoline while the similar amine salts of phenylstearic acid are quite ineffective for this purpose.

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 containing 0.001 to 0.1 weight percent of an amine-hydroxyphenyl stearic acid salt having the general formula:



in which m has the value of 7 or 8 and the sum of m plus n is 15, R is an aliphatic hydrocarbyl radical containing 2 to 24 carbon atoms, and R' and R" each represent hydrogen or a hydrocarbyl radical having from 1 to 8 carbon atoms.

2. A gasoline according to claim 1 having a Reid vapor pressure above about 9.

3. A gasoline according to claim 1 in which said salt is present in a concentration between 0.001 and 0.02 weight percent.

4. A gasoline according to claim 1 in which said salt is t-butylamine - 9-(or 10-)-(p-hydroxyphenyl) stearic acid salt.

5. A gasoline according to claim 1 in which said salt is t-C_{11-14} alkylamine-9(or 10-) - (p-hydroxyphenyl) stearic acid.

6. A gasoline according to claim 1 in which said salt is t-ocylamine-9(or 10-)-(-hydroxyphenyl) stearic acid.

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