United States Patent Office 3,106,461 Patented Oct. 8, 1963



3,106,461

# ANTI-STALLING MOTOR FUEL

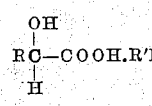
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No Drawing. Filed Mar. 3, 1961, Ser. No. 93,030
8 Claims. (Cl. 44—66)

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

In a commonly assigned, copending application Serial No. 811,535, filed May 7, 1959, now U.S. Patent No. 3,055,746, it is disclosed that salts of hydrocarbyl monocarboxylic acids and aliphatic primary amines of prescribed chain length are effective anti-stalling, anti-icing additives for gasoline. In another commonly assigned, copending application Serial No. 68,626, filed November 14, 1960, it is disclosed that amine salts of specific ether acids, namely, aryloxy-substituted aliphatic monocarboxylic acids for effective anti-stalling, anti-icing gasoline additives. The subject invention involves the discovery that specific salts of aliphatic primary amines and alpha-hydroxy monocarboxylic acids impart anti-stalling properties to volatile gasolines.

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 primary amine-alpha-hydroxy aliphatic monocarboxylic acid salt containing a total of 12 to 40 carbon atoms and having the general formula



wherein R is an aliphatic hydrocarbyl radical containing 1–18 carbon atoms and R′ is an aliphatic hydrocarbyl radical containing 2–24 carbon atoms. The presence of the amine-alpha-hydroxy monocarboxylic acid salt in prescribed concentration imparts outstanding anti-icing and anti-stalling properties 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-alpha-hydroxy 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.

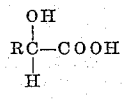
The amine-alpha-hydroxy monocarboxylic acid salts



employed as anti-stalling gasoline additives are usually solids and are simply prepared by mixing equimolar portions of a $C_2$–$C_{24}$ aliphatic primary amine with an alpha-hydroxy monocarboxylic acid containing 3 to 21 carbon atoms. The resulting salts are stable and gasoline-soluble.

The aliphatic primary amines employed in forming effective anti-stalling additives are represented by the general formula $R'NH_2$ in which R′ is an aliphatic hydrocarbyl radical containing 2–24 carbon atoms. Effective primary amines are ethylamine, n-butylamine, isoamylamine, 2-ethyl-hexylamine, 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 tradename Primene 81R and a mixture of tertiary alkyl primary amines containing 18–24 carbon atoms and sold under the tradename Primene JMT are preferred amines for forming effective anti-stalling salts.

The alpha-hydroxy aliphatic monocarboxylic acids used in preparing the effective anti-stalling agents are represented by the formula



wherein R is an aliphatic hydrocarbyl radical containing 1–18 carbon atoms. Examples of alpha-hydroxy monocarboxylic acids used in preparing the amine salts are the following: lactic acid, alpha-hydroxy valeric acid, alpha-hydroxy capric acid, alpha-hydroxy caprylic acid, alpha-hydroxy decanoic acid, alpha-hydroxy lauric acid, alpha-hydroxy oleic acid and alpha-hydroxy stearic acid.

It is necessary that the amine-alpha hydroxy monocarboxylic acid salts contain a minimum of 12 carbon atoms in order to be effective anti-stalling additives. Salts of amines and alpha-hydroxy fatty acids containing less than 12 carbon atoms are ineffective in enhancing the anti-stalling properties of the gasoline fuel. The amine-alpha hydroxy monocarboxylic acid salts advantageously contain 14–32 carbon atoms with the upper limit for effective salts being set at a total of 40 carbon atoms.

One of the features of this invention is that anti-stalling effectiveness is specific to amine salts of alpha-hydroxy aliphatic monocarboxylic acids. Amine salts of hydroxy-substituted aromatic monocarboxylic acids and amine salts of hydroxy fatty acids wherein the hydroxyl radical is attached to a carbon atom other than the alpha carbon atom are ineffective anti-stalling, anti-icing additives. For example, amine salts of ricinoleic acid are ineffective anti-stalling agents. Similarly, amine salts of hydroxy aromatic acids such as salicylic acid and 3-hydroxy naphthoic acid are also completely ineffective anti-stalling agents.

The amine-alpha-hydroxy fatty acid salts effective as anti-stalling, anti-icing additives in volatile gasoline are represented by the following: the n-butylamine salt of alpha-hydroxy decanoic acid, the t-octylamine salt of alpha-hydroxy stearic acid, the t-octylamine salt of alpha-hydroxy palmitic acid, the n-butylamine salt of alpha-hydroxy oleic acid, the t-$C_{11}$–$C_{14}$ alkylamine salt of alpha-hydroxy lauric acid, the n-butylamine salt of alpha-hydroxy lauric acid, the isopropylamine salt of alpha-hydroxy stearic acid, the isononylamine salt of alpha-hydroxy decanoic acid and the t-$C_{81}$–$C_{24}$ alkylamine salt of lactic acid and the t-$C_{11}$–$C_{14}$ alkylamine salt of alpha-hydroxy valeric acid.

Amine-alpha-hydroxy aliphatic monocarboxylic acid salts having the prescribed formula are effective anti-stalling additives when employed in concentrations of 0.001 to 0.1 weight percent of the gasoline. The preferred salt concentration forms in the range of 0.001 to 0.2 weight percent. Concentrations of the order of 4–32 pounds of amine-alpha-hydroxy fatty acid salt per thousand barrels of gasoline equivalent to concentrations of 0.0015 to 0.012 weight percent have proven particularly effective in forming fuels of excellent anti-stalling properties.

The action of the amine-alpha-hydroxy acid salts as anti-stalling, anti-icing additives was evaluated in 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 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 four times in succession and the average is reported. If the differences between runs are great, the glass tube carburetor and test throttle are washed with alcohol and the runs repeated. A leaded winter grade premium gasoline having a Reid vapor pressure of about 13 gives a stall in about 45–65 seconds in this test. Additives which raise the stalling time to over 150 seconds and preferably over 200 seconds are regarded as effective anti-stalling, anti-icing additives.

The base fuel employed to evaluate the effectiveness of amine-alpha-hydroxy monocarboxylic 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 210 and a Reid vapor pressure of about 13 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 60 seconds in the afore-described stalling test.

In the above-described test, aliphatic primary amines containing 2–16 carbon atoms were ineffective in improving the anti-stalling, anti-icing properties of the base fuel. For example, the addition of 16 pounds per thousand barrels (0.006 weight percent) of a t-$C_{11}$–$C_{14}$ alkyl primary amine mixture (Primene 81R) gave a gasoline having an average stalling time of about 61 seconds, essentially the same value obtained with the base fuel.

The addition of alpha-hydroxy fatty acids to the above base fuel slightly degraded the anti-stalling properties of the base fuel. For example, the addition of 16 pounds per thousand barrels (0.006 weight percent) of alpha-hydroxy decanoic acid to the above base fuel gave a gasoline having an average stalling time of 40 seconds which is somewhat poorer than the 60 seconds' average stalling time obtained with the base fuel. Lower hydroxy fatty acids such as lactic acid are too gasoline-insoluble to obtain a representative value in the anti-stalling test.

In the following table there is shown the effectiveness of amine-alpha-hydroxy aliphatic monocarboxylic acid salts of prescribed formula as anti-stalling, anti-icing additives.



*Action of Amine-Hydroxy Acid Salts as Anti-Stalling Additives*

| | Concentration, weight percent | Stalling time, sec. |
|---|---|---|
| n-Butylamine-alpha-hydroxy decanoic acid | 0.006 | 238 |
| Primene 81R-alpha-hydroxy decanoic acid | 0.006 | 236 |
| Primene JMT-alpha-hydroxy decanoic acid | 0.003 | 234 |
| Do | 0.006 | 210 |
| Primene 81R-lactic acid | 0.003 | 300 |
| Do | 0.006 | 300 |
| Primene JMT-lactic acid | 0.006 | 300 |
| n-Butylamine-lactic acid | 0.006 | 40 |
| t-Octylamine-lactic acid | 0.006 | 34 |
| t-Octylamine-ricinoleic acid | 0.006 | 57 |
| Primene 81R-ricinoleic acid | 0.006 | 53 |
| Primene JMT-ricinoleic acid | 0.006 | 52 |
| Primene 81R-salicylic acid | 0.006 | 39 |
| t-Octylamine-3-hydroxy naphthoic acid | 0.006 | 61 |
| Primene 81R,3,hydroxy naphthoic acid | 0.006 | 51 |
| Primene JMT-3-hydroxy naphthoic acid | 0.006 | 45 |
| Primene 81R-2-hydroxy-4-pentadecyl benzoic acid | 0.006 | 62 |

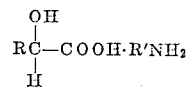
The data in the foregoing table show both the outstanding effectiveness of amine-alpha-hydroxy fatty acids of prescribed formula as anti-stalling, anti-icing gasoline additives and the highly specific nature of this property. The necessity of the salt containing a minimum of 12 carbon atoms is shown by the ineffectiveness of the n-butylamine and the t-octylamine salts of lactic acid. The ineffectiveness of the t-octylamine salt of lactic acid containing a total of 11 carbon atoms is in striking contrast to the effectiveness of the Primene 81R-lactic acid salt containing an average of about 15 carbon atoms.

The ineffectiveness of amine salts of hydroxy fatty acids containing the hydroxy radical on a carbon atom other than the alpha-hydroxy carbon atom further proves the highly specific action of the amine-alpha-hydroxy fatty acid salts of prescribed formula. The ineffectiveness of amine salts of hydroxy-substituted aromatic acids such as amine salts of salicylic and 3-hydroxy naphthoic acid is also significant in establishing the specificity of anti-stalling action to amine-alpha hydroxy fatty acid salts.

In addition to the above-demonstrated anti-icing property, amine-alpha-hydroxy aliphatic monocarboxylic acid salts improve the anti-corrosive properties of the gasoline fuel.

I claim:

1. A gasoline containing 0.001 to 0.1 weight percent of an amine-alpha-hydroxy aliphatic monocarboxylic acid salt having the general formula



wherein R is an aliphatic hydrocarbyl radical containing 1–18 carbon atoms and R' is an aliphatic hydrocarbyl radical containing 2–24 carbon atoms, said salt containing 12–40 carbon atoms and imparting improved anti-stalling, anti-icing properties to said gasoline.

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 n-butylamine-alpha-hydroxy decanoic acid salt.

5. A gasoline according to claim 1 in which said salt is t-$C_{11}$–$C_{14}$ alkylamine-alpha-hydroxy decanoic acid salt.

6. A gasoline according to claim 1 in which said salt is t-$C_{18}$–$C_{24}$ alkylamine-alpha-hydroxy decanoic acid salt.

7. A gasoline according to claim 1 in which said salt is t-$C_{11}$–$C_{14}$ alkylamine-lactic acid salt.

8. A gasoline according to claim 1 in which said salt is t-$C_{18}$–$C_{24}$ alkylamine-lactic acid salt.

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