United States Patent Office 3,055,746 Patented Sept. 25, 1962

3,055,746

ADDUCTS OF ALIPHATIC MONOCARBOXYLIC ACIDS AND ALIPHATIC AMINES IN GASOLINE

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No Drawing. Filed May 7, 1959, Ser. No. 811,535
9 Claims. (Cl. 44—66)

This invention relates to a volatile gasoline composition of improved anti-stalling properties containing an adduct of a monocarboxylic acid and a high base strength amine of prescribed composition. More particularly, it involves the discovery that adducts of monocarboxylic acids and high base strength amines are effective anti-stalling additives for gasoline.

In a commonly-assigned copending application, Serial No. 803,385, filed April 1, 1959, it is disclosed that adducts of a high base strength amine and a C_2 to C_{12} hydrocarbyl monocarboxylic acid in a concentration between about 0.2 and 5.0 weight percent act as octane appreciators for leaded gasoline having a prescribed aromatic and/or olefin content. The subject invention involves the discovery that adducts of hydrocarbyl monocarboxylic acids and high base strength amines of prescribed chain length are effective anti-stalling and anti-icing additives for volatile gasolines in substantially lower concentrations than are required for their actions as octane appreciators.

The gasoline fuel composition of this invention comprises a substantial concentration of volatile components, and 0.001 to 0.1 weight percent of an adduct of a C_2 to C_{18} alkyl amine having a pka between 8 and 11.5 and a hydrocarbyl monocarboxylic acid containing 2 to 18 carbon atoms, said adduct containing a total of 8 to 20 carbon atoms. The presence of amine-acid adducts of prescribed composition and in prescribed concentration imparts outstanding anti-icing and anti-stalling properties to the resulting gasoline composition.

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-acid adducts 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 additive of the invention is particularly useful in winter gasolines employed in northern portions of the country since they have Reid vapor pressures between about 9 and 13.5, depending on the area.

A preferred class of effective amine-acid adducts have the general formula: $RNH_2 \cdot R'COOH$ wherein R is an aliphatic hydrocarbyl radical containing 2–18 carbon atoms and R' is an aliphatic hydrocarbyl radical containing 1–17 carbon atoms, the total number of carbon atoms in said adduct being between 8 and 20.

Amine-monocarboxylic acid adducts are usually solids and are simply prepared by mixing equi-molar portions of a C_2 to C_{18} aliphatic hydrocarbyl monocarboxylic acid with an aliphatic amine containing 2–18 carbon atoms

and having a pka between 8 and 11.5. Aliphatic hydrocarbyl amines containing 2–18 carbon atoms have high base strengths as measured by a pka between 8 and 11.5 so that they readily form stable adducts with aliphatic hydrocarbyl monocarboxylic acids containing 2–18 carbon atoms. In Physical Chemistry, by Daniels and Alberti, published in 1955 by John Wiley & Sons, pages 466–471, pka is defined as the negative log of the acid ionization constant. A pka of 7 and particularly a pka of 8 and above, indicates a high base strength, whereas a pka below 7 indicates low base strength.

It is necessary for the amine-acid adduct to have a total of 8 to 20 carbon atoms to be effective as an anti-stalling, anti-icing additive. As will be shown later, adducts containing either below 8 or above 20 carbon atoms are relatively ineffective as anti-stalling, anti-icing additives.

Examples of effective anti-stalling, anti-icing amine-acid adducts are the following: ethylamine-lauric acid adduct, ethylamine-2-ethylhexanoic acid adduct, isopropylamine-2-ethylhexanoic acid adduct, isopropylamine-myristic acid adduct, hexylamine-propionic acid adduct, nonylamine-acetic acid adduct, nonylamine-2-ethylhexanoic acid adduct, laurylamine-propionic acid adduct, laurylamine-hexanoic acid adduct and laurylamine-butyric acid adduct.

The amine-acid adducts are effective as anti-stalling, anti-icing additives in concentrations of 0.001 to 0.05 weight percent of the total fuel. Adduct concentrations as high as 0.1 weight percent can be employed but lower concentrations falling within the preferred 0.001 to 0.02 weight percent concentration range are just as effective from the standpoint of imparting anti-stalling, anti-icing properties to gasoline. Concentrations of the order of 4 and 16 lbs. of adduct per 1000 bbls. of gasoline equivalent to concentrations of 0.0015 and 0.006 weight percent, respectively, have proven particularly effective in forming fuels of excellent anti-stalling properties.

The action of the adducts as anti-stalling, anti-icing additives was evaluated in carburetor icing demonstrator apparatus consisting of a single cylinder Briggs and Stratton engine equipped so that cooled, moisture-saturated air from an ice "tower" is drawn through a simple glass tube gasoline carburetor and fed into the engine. 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 the engine to stall and the time required for the engine to stall due to ice formation is recorded and serves as a measure of the icing and stalling properties of the fuel being tested. The engine is run at 3500 r.p.m. because this engine speed has been found to be best for differentiating between the icing and stalling properties of different fuels. Since most fuels stall 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 45–55 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 effectivenesses of amine-monocarboxylic acid adducts of prescribed composition as anti-stalling anti-icing additives for gasoline

was a winter grade premium gasoline having an octane rating of about 100 and containing 3 cc. of TEL per gallon. This winter grade gasoline, which had a 50% ASTM distillation point of 210 and a Reid vapor pressure of about 13 lbs., was ideally suited for testing the stalling characteristics of the additives because of its high vapor pressure. This base fuel had an average stalling time of 47 seconds in the afore-described stalling test.

In Table I there is shown the effect of individual acids and amines on the stalling properties of this base fuel.

TABLE I

Base fuel + 16 lbs. additive per 1000 bbls.:	Stalling time, secs.
Isopentanoic acid	76
Propionic acid	60
Isooctane soluble fraction of a wax oxidate	60
t-Butyl amine	46
Primene 81R (a t-C_{12}–C_{15} alkyl primary amine)	61
Primene JMT (a t-C_{18}–C_{24} alkyl amine)	46

The data in the foregoing table demonstrate that the hydrocarbyl monocarboxylic acids and high base strength amines in concentrations of 16 lbs./1000 bbls. of fuel equivalent to a concentration of 0.006 weight percent, have substantially no effect on the anti-stalling, anti-icing properties of the base fuel.

In Table II there is shown the action of various amine-acid adducts as anti-stalling, anti-icing additives in the same base fuel employed in Table I.

TABLE II

Action of Amine-Acid Adducts as Anti-Icing Additives

Additive	Concentration, Weight Percent	Stalling Time, secs.
Adducts containing 8–20 carbon atoms:		
t-butylamine: 2-ethylhexanoic acid	0.006	300+
Do	0.003	258+
Do	0.0015	248
Primene 81R:isopentanoic acid (av. of 18 c. atoms)	0.006	241
Primene 81R:propionic acid (av. 16 c. atoms)	0.006	300+
t-butylamine:isopentanoic acid	0.006	279+
t-butylamine:isooctane soluble fraction of wax oxidate (est. av. of 20 c. atoms)	0.006	200
Do	0.0015	203
t-butylamine:isooctane soluble fraction of oxidized SAE 8 paraffin distillate oil (est. av. of 18 c. atoms)	0.006	243
n-butylamine:2-ethylhexanoic acid	0.006	271
Adducts Containing less than 8 Carbon Atoms—t-butylamine:propionic acid	0.006	85
Adducts Containing more than 20 Carbon Atoms:		
Primene JMT:2-ethylhexanoic acid (est. av. of 28 c. atoms)	0.006	85
Do	0.0015	72
Primene JMT:isopentanoic acid (est. av. of 25 c. atoms)	0.006	87
Primene JMT:propionic acid (est. av. of 23 c. atoms)	0.006	118
Primene JMT:isooctane soluble wax oxidate fraction (est. av. of 36 c. atoms)	0.006	74
Primene JMT:isooctane soluble fraction of oxidized SAE 8 paraffin base distillate (est. av. of 34 c. atoms)	0.006	111
Primene 81R:2-ethylhexanoic acid (est. av. of 21 c. atoms)	0.006	61
Primene 81R: isooctane soluble fraction of oxidized SAE 8 paraffin base distillate (est. av. of 27 c. atoms)	0.006	131

The data in the foregoing table prove conclusively the outstanding superiority of acid-amine adducts containing 8–20 carbon atoms as anti-stalling, anti-icing additives in comparison with adducts containing both a smaller and higher number of carbon atoms in the molecule. Amine-acid adducts of the prescribed number of carbon atoms in the molecule all significantly improve the anti-stalling properties of the base fuel from a level of 47 seconds to over 200 seconds for the first stall. In contrast, amine-acid adducts containing less than 8 or more than 20 carbon atoms only slightly improve the anti-stalling properties of the base fuel. As has been indicated previously, a good anti-icing, anti-stalling additive should improve the properties of the base fuel to such an extent that no stall is noted in 200 seconds.

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 adduct having the general formula $RNH_2 \cdot R'COOH$ wherein R is an aliphatic hydrocarbyl radical containing 2–18 carbon atoms and R' is an aliphatic hydrocarbyl radical containing 1–17 carbon atoms, said adduct containing a total of 8–20 carbon atoms and imparting improved anti-stalling, anti-icing properties to said gasoline.

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

3. The gasoline according to claim 1 in which said amine-acid adducts are present in a concentration between 0.001 and 0.05 weight percent.

4. A gasoline motor fuel having a Reid vapor pressure above 9 and containing 0.001 to 0.05 weight percent of an amine-acid adduct having the general formula:

$$RNH_2 \cdot R'COOH$$

wherein R is an aliphatic hydrocarbyl radical containing 2–18 carbon atoms and R' is an aliphatic hydrocarbyl radical containing 1–17 carbon atoms, said adduct containing a total of 8–20 carbon atoms and imparting improved anti-stalling, anti-icing properties to said motor fuel.

5. The gasoline motor fuel according to claim 4 in which said adduct is a t-butylamine:2-ethylhexanoic acid adduct.

6. The gasoline motor fuel according to claim 4 in which said adduct is t-butylamine:isopentanoic acid adduct.

7. The gasoline motor fuel according to claim 4 in which said adduct is an n-butylamine:2-ethylhexanoic acid adduct.

8. The gasoline motor fuel according to claim 4 in which said adduct is a t-C_{12} to C_{15} alkyl primary amine: propionic acid adduct.

9. The gasoline motor fuel according to claim 4 in which said adduct is a t-C_{12} to C_{15} alkyl primary amine: isopentanoic acid adduct.

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