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2,902,354

ANTI-STALL GASOLINE

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This invention relates to gasoline compositions for use in internal combustion engines and is particularly concerned with new gasoline compositions adapted to provide improved engine operation under cool and humid weather conditions.

A well known difficulty encountered in the operation of automobile engines in cool and humid weather is that of frequent stalling during the warm-up period. It has now been recognized that the cause of this stalling is ice formation in the carburetor. The trouble has become more prevalent in post-war cars since the use of automatic transmissions and automatic chokers and the elimination of the hand throttle give the driver less control over the engine during warm-up. In addition to the inconvenience of restarting, this type of stalling is a serious safety hazard. The stalling mechanism is generally agreed to be as follows: As the fuel evaporates, it removes heat from the surrounding metal parts thereby lowering their temperature. The temperature is quickly lowered below 32° F. if the ambient temperature is low enough and the fuel is sufficiently volatile. Moisture in the incoming air that comes in contact with these cold parts begins to form a coating of ice. The ice first appears on the throttle plate and carburetor barrel near it. If enough moisture is present in the incoming air, the ice continues to build up on the top and edges of the throttle plate. When the throttle plate is closed, as during idling, the ice chokes off the air flow through the small clearance between the plate and carburetor wall. This causes the engine to stall. The engine can usually be restarted since heat from the exhaust manifold melts the ice. However, stalling will continue until the engine is warmed up. This may require 10 to 20 minutes under severe conditions. Atmospheric conditions conducive to stalling are ambient temperatures of 30° F. to 60° F. and relative humidity above 65%. The most critical conditions are 35° F. to 40° F. ambient temperature at 100% relative humidity.

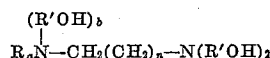
As is well known, a gasoline is a mixture of hydrocarbons having an initial boiling point falling between about 75° F. and about 135° F. and an end point falling between about 250° F. and about 450° F. and which boils substantially continuously therebetween.

It has been recognized in the prior art that the volatility characteristics of any given gasoline will affect its susceptibility to stalling to a certain extent. For example, it has been found that gasolines having relatively high mid-boiling points are generally less susceptible to stalling than gasolines having lower mid-boiling points. It will be appreciated, however, that control of stalling by means of fuel volatility alone is not feasible since other performance properties are involved. Thus, the relatively low volatility gasolines generally exhibit poorer starting and slower warm-up characteristics than those of higher volatility. Furthermore, even the lower volatility fuels are prone to produce stalling under stall-inducing conditions. Accordingly, it will be appreciated

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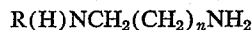
that some more practicable means of overcoming the stalling problem than volatility control would be highly desirable. Such a means is provided by the present invention which is predicated on the discovery that certain aliphatic hydroxy amines when added to the gasoline in small amounts will overcome stalling difficulties due to ice formation in the carburetor of an engine. It is, therefore, the primary object of this invention to provide gasoline compositions containing minor amounts of these aliphatic hydroxy amines. Other and further objects of the invention will become apparent from the following detailed description thereof.

The aliphatic hydroxy amines of the invention correspond to the general formula:



where R is an aliphatic radical having from 1 to about 20 carbon atoms; R' is selected from the radicals $-CH_2-CH_2-$ and $-CH_2-C(CH_3)_2H-$; a is an integer from 0 to 1 and b is an integer from 1 to 2, the sum of a and b always being 2; and n is an integer from 1 to 2. The aliphatic radical R may be straight-chained, branch-changed or cyclic in structure and it may be saturated or unsaturated.

The aliphatic hydroxy amines of the invention are formed by the reaction of either ethylene oxide or propylene oxide with a diamine of the formula



where R is either hydrogen or an aliphatic radical having from 1 up to 20 carbon atoms, as defined above and n is an integer from 1 to 2. Typical diamines are, for example, ethylene diamine (where R is hydrogen) and diamines where R is an aliphatic radical, such as the following:

N-methyl-1,3-trimethylene diamine
N-tertiary butyl-1,3-trimethylene diamine
N-cyclohexyl-1,3-trimethylene diamine
N-octyl-1,3-trimethylene diamine
N-decyl-1,3-trimethylene diamine
N-dodecyl-1,3-trimethylene diamine
N-tetradecyl-1,3-trimethylene diamine
N-hexadecyl-1,3-trimethylene diamine
N-octadecyl-1,3-trimethylene diamine
N-octadecenyl-1,3-trimethylene diamine
N-dehydroabietyl-1,3-trimethylene diamine

Mixtures of diamines can also be employed in the invention. One such mixture, for example, is composed of diamines in approximately the following proportions:

8% N-octyl-1,3-trimethylene diamine
9% N-decyl-1,3-trimethylene diamine
47% N-dodecyl-1,3-trimethylene diamine
18% N-tetradecyl-1,3-trimethylene diamine
8% N-hexadecyl-1,3-trimethylene diamine
5% N-octadecyl-1,3-trimethylene diamine
5% N-octadecenyl-1,3-trimethylene diamine

For convenience, this mixture of diamines is designated hereinafter as "Diamine Mixture A."

Another highly suitable mixture of diamines is one having the following approximate composition:

2% N-tetradecyl-1,3-trimethylene diamine
24% N-hexadecyl-1,3-trimethylene diamine
28% N-octadecyl-1,3-trimethylene diamine
46% N-octadecenyl-1,3-trimethylene diamine

For convenience, this mixture of diamines is designated hereinafter as "Diamine Mixture B."

The reaction between the ethylene oxide or propylene oxide and the diamine can be readily effected by meth-

ods well known to the art. For example, the reaction may be carried out by adding the alkylene oxide to the diamine in the presence of a small amount, i.e., from about 0.02% to about 0.1%, of finely divided sodium and heating the mixture to about 150° C. to 175° C. for a period of from about three to about six hours. The amount of alkylene oxide used in the reaction will be governed by the number of amino hydrogen atoms present in the amine. Thus, where the amine contains four such hydrogens, as in the case of ethylene diamine, four mole proportions of the alkylene oxide are reacted with one mole proportion of the amine. Correspondingly, where the amine contains three amino hydrogens, i.e., where R in the formula $R(H)NCH_2(CH_2)_nNH_2$ is an aliphatic radical, three mole proportions of the alkylene oxide per mole proportion of the diamine is used.

The aliphatic hydroxy amines may also be readily formed by reaction of the diamine with an excess of the alkylene oxide in the absence of a catalyst. The excess alkylene oxide insures complete reaction of all the amino hydrogens without any significant reaction of hydroxy alkyl groups with alkylene oxide to form polyether products.

Specific examples of aliphatic hydroxy diamines contemplated by the invention are the following:

- (1) N,N,N',N' tetrakis-2-hydroxypropyl ethylene diamine;
- (2) N-methyl N,N',N' tris-2-hydroxyethyl-1,3-trimethylene diamine;
- (3) N-butyl N,N',N' tris-2-hydroxypropyl-1,3-trimethylene diamine;
- (4) N-hexyl N,N',N' tris-2-hydroxyethyl-1,3-trimethylene diamine;
- (5) N-octyl N,N',N' tris-2-hydroxyethyl-1,3-trimethylene diamine;
- (6) N-octyl N,N',N' tris-2-hydroxypropyl-1,3-trimethylene diamine;
- (7) N-decyl N,N',N' tris-2-hydroxyethyl-1,3-trimethylene diamine;
- (8) N-dodecyl N,N',N' tris-2-hydroxyethyl-1,3-trimethylene diamine;
- (9) N-tetradecyl N,N',N' tris-2-hydroxyethyl-1,3-trimethylene diamine;
- (10) N-hexadecyl N,N',N' tris-2-hydroxyethyl-1,3-trimethylene diamine;
- (11) N-octadecyl N,N',N' tris-2-hydroxyethyl-1,3-trimethylene diamine;
- (12) N-octadecenyl N,N',N' tris-2-hydroxyethyl-1,3-trimethylene diamine;
- (13) N-octadecyl N,N',N' tris-2-hydroxypropyl-1,3-trimethylene diamine;
- (14) N-mixed R,N,N',N' tris-2-hydroxyethyl-1,3-trimethylene diamine (prepared from "Diamine Mixture A") in which R is composed of aliphatic radicals in about the following proportions: 8% octyl, 9% decyl, 47% dodecyl, 18% tetradecyl, 8% hexadecyl, 5% octadecyl and 5% octadecenyl; and
- (15) N-mixed R,N,N',N' tris-2-hydroxyethyl-1,3-trimethylene diamine (prepared from "Diamine Mixture B") in which R is composed of aliphatic radicals in about the following proportions: 2% tetradecyl, 24% hexadecyl, 28% octadecyl and 46% octadecenyl.
- (16) N-dehydroabietyl N,N',N' tris-2-hydroxyethyl-1,3-trimethylene diamine.

ANTI-STALLING EFFECTIVENESS

The ability of representative examples of the aliphatic hydroxy diamines of the invention to prevent engine stalling under conditions conducive to carburetor icing have been demonstrated by means of a series of tests conducted as follows.

(a) Description of test

A standard Chevrolet engine, equipped with a Holley single downdraft carburetor, was mounted in a "cold"

room refrigerated to 50° F. A Holley carburetor was used since it has been shown to be very susceptible to icing. A thermocouple was attached to the throttle plate shaft to record the plate temperature. A ½-inch insulating gasket was placed between the carburetor and manifold to prevent heat conduction. An asbestos sheet covered the entire manifold system to shield the carburetor from convection and radiation. A spray chamber was used to saturate the incoming air with moisture before entering an ice tower which cooled the air to about 35° F.

In conducting a test, the engine was first run for about 10 minutes at 2000 r.p.m. to bring the engine temperature to equilibrium. The engine was then shut off. When the throttle shaft temperature rose to 40° F., the engine was restarted with the idle speed set at 400 to 500 r.p.m. so that the base fuel stalled at idle in 10 seconds or less after a run-time of 20 to 40 seconds. Run-time means the time that the engine was run at 2000 r.p.m. before returning to idle.

All runs were started when the throttle shaft reached 40° F. At the instant of starting, the throttle arm was moved to the 2000 r.p.m. position and a stop watch started. At the end of the selected run-time, the throttle arm was moved to the idle position. The time required stall was recorded. Several tests were made at each run-time and averaged.

In evaluating an additive, the base fuel was first tested followed by several concentrations of the additive. The system was flushed between tests with the fuel to be run next. Any improvement caused by the additive was reflected in a longer run-time (as compared to the base fuel) to cause stalling in 10 seconds or less when the engine was idled. The more effective the additive, the longer the run-time.

(b) Test results

Tests were run in three different base gasolines described in Table I. Test results illustrating the effect of the additives in reducing stalling are shown in Table II.

TABLE I

Fuel	Components	Boiling Range, °F.	Mid-Boiling Point, °F.
A	73% Catalytically Cracked 25% Natural Gasoline 2% Butane	89-375	176
B	70% Catalytically Cracked 30% Natural Gasoline	76-373	180
C	70% Catalytically Cracked 30% Natural Gasoline	98-387	194

It will be seen from Table II that the products of the invention show substantial ability as anti-stalling agents, the N-mixed R,N,N',N' tris-2-hydroxyethyl-1,3-trimethylene diamine prepared from "Diamine Mixture B" (Example 15) being especially effective.

TABLE II.—ANTI-STALLING TESTS

[Initial throttle plate temp. = 35° F.]

Test No.	Compound Added	Fuel	Run-Time to 10 Sec. Stall-Time (Sec.)		
			0.0 Wt. Percent	0.01 Wt. Percent	0.05 Wt. Percent
1	None	A	40		
2	Example 15	A		105	140
3	None	B	20		
4	Example 15	B		80	
5	None	C	20		
6	Example 14	C		50	
7	Example 1	C		30	

The amount of hydroxy aliphatic amine to be added to the gasoline will vary depending upon the particular amine and the particular gasoline being treated, as well as upon the conditions of use for which the gasoline is

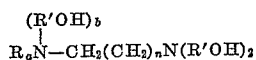
designed. In general, the additives may be added in amounts of from 0.0004% up to about 1.0%, by weight, the usual amount being from about 0.002% to about 0.1%.

The anti-stall additives of the invention may be used in the gasoline along with other anti-stall addition agents or other additives designed to impart other improved properties thereto. Thus, anti-knock agents, pre-ignition inhibitors, anti-rust agents, metal-deactivators, dyes, anti-oxidants, detergents, etc., may be present in the gasoline. Also, the gasoline may contain a small amount, from about 0.01% to about 1%, by weight, of a solvent oil or upperlube. Suitable oils, for example, include coastal and mid-continent distillate oils having viscosities within the range of from about 50 to about 500 S.U.S. at 100° F. Synthetic oils, such as diester oils, polyalkylene glycols, silicones, phosphate esters, polypropylenes, polybutylenes and the like, may also be used.

Although the present invention has been illustrated herein by means of specific examples and embodiments thereof, it is not intended that the scope of the invention be limited in any way thereby, but only as indicated in the following claims.

What is claimed is:

1. A gasoline containing a minor proportion, sufficient to improve the anti-stalling characteristics thereof, of a compound of the formula:



wherein R is an aliphatic radical having from 1 to about 20 carbon atoms; R' is a radical selected from the group consisting of $-CH_2-CH_2-$ and $-CH_2-C(CH_3)_2H-$ radicals; a is an integer from 0 to 1 and b is an integer from 1 to 2, the sum of a and b always being 2; and n is an integer from 1 to 2.

2. A gasoline containing a minor proportion, sufficient

to improve the anti-stalling characteristics thereof, of N,N,N',N' tetrakis-2-hydroxypropyl ethylene diamine.

3. A gasoline containing a minor proportion, sufficient to improve the anti-stalling characteristics thereof, of N-octyl - N,N',N' tris - 2 - hydroxyethyl-1,3-trimethylene diamine.

4. A gasoline containing a minor proportion, sufficient to improve the anti-stalling characteristics thereof, of N-R,N,N',N' tris-2-hydroxyethyl-1,3-trimethylene diamine, wherein R is composed of aliphatic radicals in about the following proportions, 2% tetradecyl, 24% hexadecyl, 28% octadecyl and 46% octadecenyl radicals.

5. A gasoline containing a minor proportion, sufficient to improve the anti-stalling characteristics thereof, of N-octadecyl N,N',N' tris-2-hydroxyethyl-1,3-trimethylene diamine.

6. A gasoline containing a minor proportion, sufficient to improve the anti-stalling characteristics thereof, of N-R,N,N',N' tris - 2 - hydroxyethyl - 1,3 - trimethylene diamine, wherein R is composed of aliphatic radicals in about the following proportions, 8% octyl, 9% decyl, 47% dodecyl, 18% tetradecyl, 8% hexadecyl, 5% octadecyl and 5% octadecenyl.

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