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GASOLINE COMPOSITIONS

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The present invention relates to improved fuel compositions for carbureted internal combustion engines, particularly such fuels boiling in the gasoline boiling range.

During recent years, a problem of major concern to manufacturers of fuels for carbureted internal combustion engines has been the tendency of such engines to stall, especially at idling speeds and especially, in the case of automotive engines, before the engine has become completely warmed up after a cold start. This stalling is known to be caused by carburetor ice, particularly that which collects on the throttle plate and adjacent surfaces when moisture in the combustion air is cooled by the evaporation of the fuel in the carburetor. The problem has been aggravated by the present day trend to more volatile gasolines.

Heretofore this difficulty has sometimes been alleviated by incorporation in the fuel certain water-soluble freezing point depressants, such as alcohols, including glycols, or the like. However, such an expedient requires relatively large concentrations of the freezing point depressant, for example, from about 0.1% to as high as 2 or 3%. In many cases, this is so uneconomical as to preclude the commercial use of such additives.

Furthermore, in order to be effective, such additives must, of course, be substantially water-soluble and this results in a further difficulty. During normal handling during distribution and marketing, it is virtually impossible to avoid contact between the fuel and water, because storage tanks normally contain a separate phase of water on the bottom thereof. The contact of the fuel and water results in a "leaching" action, whereby at least some of the additive is lost to the water phase. After this, the fuel again tends to cause carburetor icing.

It is accordingly a principal object of the present invention to provide an improved fuel composition for carbureted internal combustion engines. It is a more particular object of the invention to provide such a fuel which has improved carburetion characteristics, especially such as to decrease stalling due to the formation or accumulation of ice in carburetors. It is a further object of the invention to provide a gasoline fuel composition with improved anti-carburetor-icing characteristics and which does not require as an ingredient thereof a relatively large concentration of an anti-icing additive. A still further object of the invention is to provide a fuel composition for carbureted internal combustion engines with improved anti-icing characteristics not appreciably affected by the normal contact thereof with water during commercial handling. Other objects will be apparent from the description of the invention.

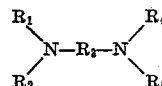
It has now been discovered that these objects and others are accomplished by the addition, to a fuel for carbureted internal combustion engines, of a substantially water-insoluble organic material of a particular class in extremely small concentrations, far below the effective concentrations of anti-icing additives heretofore known, namely a minor amount of an N-alkyl substituted alkylene diamine.

The additives of the present invention are particularly N-alkyl-substituted alkylene diamines, which contain at least two hydrogen atoms attached directly to nitrogen,

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at least one N-alkyl substituent of which diamine contains from 10 through 30 carbon atoms and the alkylene group of which diamine contains from 2 through 6 carbon atoms, the two free valences of which alkylene group (or the nitrogen atoms of the diamine) being separated through no more than 4 carbon atoms and preferably through only 3 carbon atoms.

The additives of the present invention thus may be represented by the formula:



wherein R_1 is an alkyl group containing from 10 through 30 carbon atoms; R_2 , R_4 and R_5 are hydrogen atoms or alkyl groups, at least two of which are hydrogen atoms; and R_3 is an alkylene group containing from 2 through 6 carbon atoms, the two free valences of which are separated through no more than 4 carbon atoms, and preferably through 3 carbon atoms only.

The requirement that at least one N-substituted alkyl group must contain at least 10 carbon atoms is essential to the invention. If the alkyl group is too short, the compound will not be sufficiently effective as an anti-icing agent and it will be inadequately resistant toward water leaching. It is preferred that the N-substituted alkyl groups contain a total of at least 12 carbon atoms. In general, the total number of carbon atoms in all N-substituted groups should be no greater than 30, and preferably no greater than 20. It is also preferred that the N-substituted alkyl groups and the alkylene group be hydrocarbyl groups. The alkyl groups can be either saturated or unsaturated and either straight chain or branched chain groups. It is also preferred that the alkylene group contain no more than 4 carbon atoms and especially no more than 3 carbon atoms.

An especially suitable class of the additives of the invention consists of the mono-N-substituted alkylene diamines, particularly such propylene diamines wherein the alkyl group is a straight hydrocarbyl chain containing from 12 through 18 carbon atoms. Mixtures of compounds within the broad class are effective, and particularly suitable mixtures are those obtained from fatty acids, for example, from coconut oil fatty acids, soya bean oil fatty acids or tallow oil fatty acids. Mixtures of mono-N-alkyl substituted alkylene diamines derived from such fatty acids can be readily prepared, for example, by reacting the mixture of fatty acids with ammonia to form the corresponding amides, reduction of the amides to the corresponding amines, reacting the amines with, for example, acrylonitrile, crotonitrile or methacrylonitrile, and reduction of this reaction product to the corresponding mono-N-alkyl substituted alkylene diamines.

It will be noted in this connection that when an alkyl group or radical is referred to herein as one derived from a fatty acid, what is meant is the alkyl radical which would be obtained by replacement of the double-bonded oxygen of the acyl radical of the fatty acid by two hydrogen atoms, regardless of the actual steps involved in the preparation of the compound containing the alkyl radical in question.

Such mixtures of commercial or technical grade mono-N-alkyl substituted propylenediamines wherein the alkyl groups are derived from natural fatty acids are available at about 80% diamine content under trade name, "Duomeens." "Duomeen C" is a mixture of mono-N-alkyl substituted 1,3-propylene-diamines wherein the alkyl groups are derived from coconut oil fatty acids. "Duomeen T," "Duomeen S" and "Duomeen 12" are such mixtures wherein the alkyl groups are derived from the fatty acids of tallow oil, the fatty acids from soya bean oil, and lauric acid, respectively.

Some examples of other compounds suitable for the practice of the invention either alone or in mixtures of such compounds are 3-laurylamino-1-butylamine, N,N'-dodecyl-1,3-propanediamine, N - octadecyl-1,3-propanediamine, N,N'-dioctyl-1,2-ethanediamine, N-hexadecyl-1,2-ethanediamine, N - oleyl-n'-dodecyl-1,3-propanediamine, N - hexadecyl-N'methyl-1,2-propanediamine and N-decyl-N'-secondarybutyl-1,3-propanediamine.

The effective concentrations of the additives of the invention are extremely low. Generally, a concentration no greater than 500 parts per million by weight (0.05% wt.) is sufficient under even the most severe conditions of temperature, humidity and gasoline volatility, but up to 1000 p.p.m. (wt.) can sometimes be used to advantage. Concentrations as low as 5 p.p.m. (wt.) (0.0005% wt.) are remarkably effective, although for the usual commercial application, it will be desirable to use at least 10 to 15 p.p.m. and preferably at least 20 p.p.m. Especially suitable concentrations are those above about 30, but usually no more than about 50 p.p.m. need be used. Under severe engine operating conditions or where intake manifold cleanliness is a critical problem, it will be generally desirable to use no more than 200 p.p.m. or preferably no more than 100 p.p.m.

The fuels in which the additives of the invention are advantageously incorporated are those used in carbureted internal combustion engines, that is, gasolines designed for use in, for example, automotive, marine, aviation and two cycle engines. Such gasolines have A.S.T.M. distillation 50% evaporated temperatures not exceeding 260° F. and especially no greater than 240° F. The invention is particularly advantageous in the case of gasolines having A.S.T.M. distillation 50% evaporated temperatures no greater than 220° F.

Besides the anti-icing additive, the gasoline compositions of the present invention can, and ordinarily will, contain the usual commercial additives, for example, anti-detonants such as tetraethyl lead, iron carbonyl, dicyclopentadienyl iron, xylidene and N-methyl aniline, scavengers such as ethylene dibromide and ethylene dichloride, dyes, spark plug anti-foulants such as tricresyl phosphate, combustion modifiers such as alkyl boronic acids and lower alkyl phosphates and phosphites, oxidation inhibitors such as N,N'-disecndarybutylphenylenediamine, N-n-butyl - p - aminophenol and 2,6-ditertiarybutyl-4-methylphenol, metal deactivators such as N,N'-disalicylal-1,2-propanediamine, and rust inhibitors such as polymerized linoleic acids.

The invention is illustrated in the following examples, which, however, should not be considered limitations thereof.

EXAMPLE I

A standard ASTM-CFR fuel research engine was fitted with a Chevrolet carburetor (Carter, Model No. WA-1-413S). Intake air for the engine was adjusted for the tests to a constant temperature and humidity at the air inlet to the carburetor of 41° F. and 75 percent relative humidity, respectively, a combination of atmospheric conditions which is known to lead to carburetor icing very frequently in practice. Since it is also well known that stalling due to carburetor icing in automobiles most frequently occurs soon after a cold start and at a time when the engine speed is reduced to idling, for example, as an automobile is stopped at a street intersection, these circumstances were simulated, and the test procedure standardized, by operating the test engine on the test gasoline with the throttle adjusted to 30° open position until the temperature of the body of the carburetor is reduced to 36° F. With the base gasoline selected for all of these tests, one having a 50% A.S.T.M. boiling point of 200° F. and containing the usual commercial additives, but no alcohol or other anti-icing agent, the time necessary to reduce the temperature of the body of the carburetor to 36° F. was uniformly about 3 minutes. At this time, the throttle valve was closed to

the idling position. The time interval then expiring until the engine stalled is the measure of the tendency of the test gasoline composition to prevent stalling due to carburetor icing and is called the "stall time" of the test gasoline composition. Compositions with greater "stall times" are, of course, superior to those with lesser "stall times."

To provide data which are more meaningful in respect to the value of the gasoline compositions of the invention, a large number of tests were made on the base gasoline alone and also on the base gasoline with 1% by volume of isopropyl alcohol (a well known freezing point depressant type of gasoline anti-icing additive). The stall time obtained with the base gasoline and an anti-icing additive was divided by the stall time obtained with the base gasoline alone, thus giving a "stall time ratio" which is a direct measure of magnitude of the anti-icing benefit of the additive.

The results are given in Table I.

Table I.—Average stall time ratios

STALL TIME WITH ANTI-ICING ADDITIVES/STALL TIME WITH BASE GASOLINE

Anti-Icing Additive	Concentration	Average Stall Time Ratio
Isopropyl alcohol.....	1% v.....	1.7
Duomeen T.....	20 p.p.m.....	2.2
Do.....	30 p.p.m.....	2.2
Do.....	50 p.p.m.....	1.8
Do.....	100 p.p.m.....	3.8
Duomeen C.....	20 p.p.m.....	1.3
Do.....	30 p.p.m.....	1.7
Do.....	50 p.p.m.....	1.7
Do.....	100 p.p.m.....	2.7
Do.....	200 p.p.m.....	4.2
N-Lauryl-1,3-propanediamine.....	50 p.p.m.....	1.7
Do.....	100 p.p.m.....	4.2
Do.....	200 p.p.m.....	6.3

These data show the extraordinary concentration effectiveness relationship of the additives of the present invention. For example, it should be especially noted that approximately 200 times as much isopropyl alcohol is required to match the anti-icing benefits of the anti-icing additives of the present invention.

EXAMPLE II

When precisely the same test as described in Example I is made on the same base gasoline but with 20, 50 and 100 p.p.m. (wt.) of N,N'-didecyl-1,2-ethanediamine similarly superior results are obtained.

EXAMPLE III

When precisely the same test as described in Example I is made on the same base gasoline but with 10, 30 and 200 p.p.m. (wt.) of N-dodecyl-N'-ethyl-1,3-propanediamine similarly superior results are obtained.

EXAMPLE IV

In order to prove the critical nature of the requirement that at least one N-substituted alkyl group must contain at least 10 carbon atoms, compounds not within this class were also tested in exact accordance with the procedure described in Example I. The results obtained, again in terms of stall time ratio, are given in Table II:

Table II.—Average stall time ratios

STALL TIME WITH ADDITIVE/STALL TIME WITH BASE GASOLINE

Additive	Concentration, p.p.m.	Average Stall Time Ratio
N,N'-bis(2-ethylhexyl)-1,3-propanediamine.....	50	0.8
N,N'-diethyl-1,3-propanediamine.....	50	1.2
2-methyl-1,3-propanediamine.....	50	0.8

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It can be readily seen that compounds outside of the class to which the invention is limited are essentially ineffective for the anti-icing purpose, even though they are lower molecular weight homologues thereof.

EXAMPLE V

In order further to prove the critical nature of the requirement that least one N-substituted alkyl group must contain at least 10 carbon atoms, compounds within this class and others not meeting the requirement were compared in water leaching tests. In each of these tests, 2 liters of iso-octane containing the diamine additive in question at a concentration of 100 parts per million by weight were vigorously shaken with 250 cc. of distilled water. Subsequently, and after settling, the amount of the diamine which had transferred to the aqueous phase was determined by electrometric titration. The following data, calculated by difference, are the concentrations of the diamine left in the iso-octane:

	P.p.m. (wt.) left in I.O.
N,N-dimethyl-1,3-propanediamine	40
N,N-diethyl-1,3-propanediamine	50
Duomeen C	80
Duomeen T	85

It will be noted from these data that most of each of the additives within the scope of the invention was retained in the hydrocarbon, whereas half or more of the lower alkyl diamines was lost to the water phase.

EXAMPLE VI

A series of 5000-mile road tests was undertaken using a commercial premium grade gasoline containing the usual commercial additives (but no alcohol or other known anti-icing agent) and in addition 30 parts per million by weight of a mixture of N-alkyl substituted 1,3-propanediamines wherein the alkyl groups are derived from, and contain the same carbon atoms as, coconut oil fatty acids, a preferred gasoline composition in accordance with the present invention. The test fleet consisted of 10 automobiles of recent models of several popular makes. For comparison purposes the entire fleet was first run for approximately two months (about 5000 miles per car) on the same base gasoline, but without the diamine anti-icing additive. At the end of this "base line" period, the engine of each car was dismantled, thoroughly inspected for intake manifold and carburetor deposits and other effects related to fuels, and then thoroughly cleaned. Each car was then switched to the gasoline containing the diamine anti-icing additive. No deleterious effects of this gasoline composition have been found and no carburetor icing difficulties have been encountered.

Together with the anti-icing additive of the present invention, it is also possible to incorporate into the gasoline composition with advantage minor amounts of certain synthetic lubricants, for example, mixtures of poly-oxa-hydrocarbons, such as the mono-alkyl ethers of polyoxy-1,2-propylene diols of U.S. 2,448,664, or the mono-hydroxy heterized oxyethylene oxy-1,2-propylene aliphatic ethers of U.S. 2,425,755, and the similar compounds described in U.S. 2,425,845, U.S. 2,520,611 and U.S. 2,520,612. These synthetic lubricants can be added in a volume or weight ratio of the anti-icing additives of the present invention of 0.25:1 up to as high as 250 or 500:1, about a 1:1 ratio being preferred in many cases.

We claim as our invention:

1. A gasoline fuel composition for carbureted internal combustion engines consisting essentially of gasoline having an A.S.T.M. distillation 50% evaporated temperature not exceeding 260° F. and containing from about 10 to about 100 parts per million by weight of an N-alkyl substituted alkylene diamine containing at least two hydrogen atoms attached directly to nitrogen, and having the two

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diamine nitrogen atoms separated by a chain of from 2 through 4 carbon atoms, at least one N-substituted alkyl group of which contains from 10 through 30 carbon atoms and the alkylene group of which contains from 2 through 6 carbon atoms.

2. A gasoline fuel composition in accordance with claim 1, wherein the N-alkyl substituted alkylene diamine is a mono-N-alkyl substituted alkylene diamine.

3. A gasoline fuel composition in accordance with claim 1, wherein the N-alkyl substituted alkylene diamine is an N,N-dialkyl substituted alkylene diamine.

4. A gasoline fuel composition in accordance with claim 1, wherein the N-alkyl substituted alkylene diamine is an N,N'-dialkyl substituted alkylene diamine.

5. A gasoline fuel composition in accordance with claim 1, wherein the alkylene group of the N-alkyl substituted alkylene diamine contains from 2 through 4 carbon atoms.

6. A gasoline fuel composition in accordance with claim 5, wherein the alkylene group of the N-alkyl substituted alkylene diamine is a propylene group.

7. A gasoline fuel composition in accordance with claim 6, wherein the propylene diamine is a mono-N-alkyl substituted propanediamine, the alkyl group of which contains from 12 through 18 carbon atoms.

8. A gasoline composition in accordance with claim 7, wherein the alkyl group of the mono-N-alkyl substituted propanediamine is derived from, and contains the same carbon atoms as, a natural fatty acid.

9. A gasoline composition for carbureted internal combustion engines consisting essentially of gasoline having an A.S.T.M. distillation 50% evaporated temperature not exceeding 260° F. and containing from 20 to 100 parts per million by weight of a mixture of mono-N-alkyl substituted 1,3-propanediamines, the alkyl groups of which are derived from, and contain the same carbon atoms as, coconut oil fatty acids.

10. A gasoline fuel composition for carbureted internal combustion engines consisting essentially of gasoline having an A.S.T.M. distillation 50% evaporated temperature not exceeding 260° F. and containing from about 10 to about 50 parts per million by weight of an N-alkyl substituted alkylene diamine containing at least two hydrogen atoms attached directly to nitrogen and having the two diamine nitrogen atoms separated by a chain of from 2 through 4 carbon atoms, at least one N-substituted alkyl group of which contains from 10 through 30 carbon atoms and the alkylene group of which contains from 2 through 6 carbon atoms.

11. A gasoline fuel in accordance with claim 10, wherein the N-alkyl substituted alkylene diamine is a mono-N-alkyl substituted alkylene diamine.

12. A gasoline fuel in accordance with claim 11, wherein the alkylene group of the mono-N-alkyl substituted alkylene diamine is a propylene group, and the alkyl group contains from 12 through 18 carbon atoms and is derived from, and contains the same carbon atoms as, a natural fatty acid.

13. A gasoline composition for carbureted internal combustion engines consisting essentially of gasoline having an A.S.T.M. distillation 50% evaporated temperature not exceeding 260° F. and containing from about 10 to about 50 parts per million by weight of a mixture of mono-N-alkyl substituted 1,3-propanediamines the alkyl groups of which are derived from, and contain the same carbon atoms as, coconut oil fatty acids.

References Cited in the file of this patent

UNITED STATES PATENTS

2,447,615	Jones	Aug. 24, 1948
2,706,677	Duncan et al.	Apr. 19, 1955
2,736,658	Pfohl et al.	Feb. 28, 1956