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3,705,024

FUEL DISTRIBUTION IN A GASOLINE ENGINE
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5 Claims

ABSTRACT OF THE DISCLOSURE

A tertiary diamine having one long aliphatic hydrocarbon group and one short alkyl group attached to each nitrogen atom of the diamine, when added in minor proportion to a gasoline, will improve the distribution of the air/fuel mixture in the intake manifold of a multicylinder gasoline engine that is run with the resulting blend thereby increasing operating efficiency. A representative diamine is dimethyl dioctadecyl ethylene diamine.

BACKGROUND OF THE INVENTION

This invention concerns an improved motor fuel composition and an improved method of operating an internal combustion engine. More particularly, the invention concerns incorporating into a motor fuel, such as gasoline, an additive composition that will modify the induction tract surfaces of an aspirated multicylinder internal combustion engine in such a way as to improve the geometric and time distribution of the fuel in the induction system of that engine.

In operating a gasoline engine, it is necessary to supply to the cylinders a mixture of gasoline and air in proper proportions. In most instances, this is accomplished by the use of a carburetor wherein the fuel is aspirated into a stream of moving air. In an aspirated multicylinder engine the mixture of air and fuel is distributed to the various cylinders through an intake manifold. One problem that arises in such a system is that the air/fuel ratio tends to vary from cylinder to cylinder, i.e. there is a geometric variation, some cylinders receiving a relatively rich mixture and others a relatively lean mixture. Similarly, variations in air/fuel ratio in particular cylinders of a multicylinder engine can vary with respect to time. Such variations cause an engine to accelerate and decelerate as frequently as once per second, even though an attempt is made to hold the vehicle under steady cruise conditions with a fixed position of the throttle. If the variation in air/fuel ratio with time becomes sufficiently severe, it feels to the automobile driver as if his car is being buffeted by winds.

Both the geometric variation in air/fuel ratio distribution and the variation with respect to time result in reduced operating efficiency, which shows up in at least two ways, one being a loss in fuel economy and another being uneven and reduced power. Accordingly, it is desirable to reduce such variations.

Gasolines used as motor fuels comprise a mixture of hydrocarbons of various boiling points. Thus a gasoline can have an initial boiling point in the range of about 70° to 135° F. and a final boiling point in the range of about 250° to 450° F. The mixture of gasoline and air that leaves the carburetor and passes to the various cylinders through the intake manifold tends to deposit some of the higher boiling fractions in the form of a liquid film on the walls of the intake manifold. This liquid film is the main factor in poor fuel distributor in the engine. Accordingly, it is desirable to have the gasoline present as a vapor or spray in the air/fuel mixture to ensure greater engine operating efficiency.

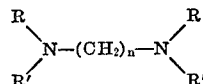
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DESCRIPTION OF THE INVENTION

In accordance with the present invention it has been found that the distribution of the air/fuel mixture to the various cylinders of an aspirated multicylinder internal combustion engine can be improved by incorporating in the fuel that is fed to that engine a minor amount of a tertiary diamine having attached to each nitrogen atom thereof one long straight chain aliphatic hydrocarbon group of from about 12 to 24 carbon atoms and a methyl group or an ethyl group.

It is believed that the improvement in air/fuel ratio distribution obtained when practicing this invention results from a phenomenon wherein at least a portion of the additive becomes adsorbed on the walls of the intake system of the engine to create a surface which is not easily wetted by liquid drops of gasoline. Thus any drops of gasoline that fall out of the mixture of gasoline and air in the intake system do not spread into a film but remain as discrete drops so that they are more easily entrained in the air stream passing through the manifold.

The tertiary diamines that are used in the present invention are represented by the formula:



wherein R is a C₁₂ to C₂₄ straight chain aliphatic hydrocarbon group, R' is a C₁ to C₂ alkyl group, and n is 2 to 4. Preferably, n is 2. As a specific example R can be C₁₈ alkyl, R' a methyl group, and n is 2, i.e. dimethyl dioctadecyl ethylene diamine. Other specific examples include diethyl didodecyl propylene diamine, dimethyl ditetradecyl ethylene diamine, dimethyl ditetradecyl propylene diamine, and dimethyl dihexadecyl butylene diamine.

While it has previously been taught, e.g. in copending application Ser. No. 20,083, filed Mar. 16, 1970, to employ certain aliphatic amines in gasoline to improve the air/fuel distribution in the intake system of an aspirated multicylinder engine, some of these amines have the disadvantage of tending to react with the small amounts of carbonyl compounds that may be present in the fuel, and thereby be partially lost, thus reducing the effectiveness of the amines. The tertiary diamines employed in the present invention have no tendency to react with carbonyls that may be present in the fuel.

The amines of this invention will be used in gasoline in a total concentration within the range of from about 5 to about 80 pounds of the amine mixture per 1000 barrels of gasoline, a barrel containing 42 U.S. gallons. The preferred concentration range is from about 10 to about 40 pounds of total amines per 1000 barrels of gasoline. The concentration range of from 10 to 40 pounds per 1000 barrels is roughly equal to a weight percent concentration of from about 0.004 to about 0.016 weight percent.

The gasolines in which the additives of this invention are employed are conventional petroleum distillate fuels boiling in the gasoline range and intended for internal combustion engines, preferably spark ignition engines. Gasoline is defined as a mixture of liquid hydrocarbons having an initial boiling pt. somewhere in the range of about 70 to 135° F. and a final boiling point somewhere in the range of about 250 to 450° F. Gasolines are supplied in a number of different grades, depending upon the type of service for which they are intended. The additives of the invention are particularly useful in motor and aviation gasolines. Motor gasolines include those defined by ASTM specification D-439-58T, Types A, B and C, and are composed of a mixture of various types of hydrocarbons, including aromatics, olefins, paraffins, isoparaffins, naphthenes, and occasionally, diolefins. Not

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all of these types of hydrocarbons will necessarily be present in any particular gasoline. These fuels are derived from petroleum crude oil by various refining processes, including fractional distillation, catalytic cracking, hydro-forming alkylation, isomerization, polymerization and solvent extraction. Motor gasolines normally have boiling ranges within the limits of about 70° F. and about 450° F., while aviation gasolines have narrower boiling ranges, within the limits of about 100° F. and 330° F. The vapor pressures of gasoline as determined by ASTM Method D-323 vary between about 5 and about 18 p.s.i. at 100° F. The properties of aviation gasolines are set forth in U.S. Military Specification MIL-F-5572 and ASTM Specification D-910-57T.

The additives employed in accordance with this invention can be used in gasolines with other additive agents conventionally used in such fuels. It is common practice to employ from about 0.5 to about 4.0 cc./gal. of alkyl lead antiknock agents, such as tetraethyl lead, tetramethyl lead, dimethyl diethyl lead, or a similar alkyl lead antiknock agent or olefinic lead antiknock agent such as tetra-vinyl lead, triethyl vinyl lead, and the like, or a combination thereof, in motor gasolines and in aviation gasolines, e.g. 1.0 to 3.0 cc. of a tetraethyl-lead-tetramethyl-lead combination. The lead compounds are customarily employed in conjunction with a scavenging agent such as ethylene dichloride or ethylene dibromide. Antiknock agents that can be used also include other organometallic additives containing lead, iron, nickel, lithium, manganese and the like. The effectiveness of the tertiary diamines of this invention does not depend on the presence of these or other antiknock agents, however. Other additives conventionally employed in gasolines may be used in practicing the present invention. These include corrosion inhibitors, rust inhibitors, antioxidants, solvent oils, anti-static agents, octane appreciators, e.g., t-butyl acetate, auxiliary scavengers like tri-B-chloroethyl phosphate, dyes, anti-icing agents, e.g. isopropanol, hexylene glycol, and the like. There may also be included certain oil-soluble dispersants and detergents to provide significant improvement in overall engine cleanliness. This is taught, for example, by Calvino et al. in U.S. Pat. 3,223,495.

The nature of this invention and the advantages accruing from the practice thereof will be better understood when reference is made to the following examples, which include a preferred embodiment.

EXAMPLES

A gasoline blend was prepared using as the base an unleaded gasoline of 97 research octane rating that had an initial boiling point of 97° F., a 50% boiling point of 230° F., and a final boiling point of 386° F., by ASTM distillation method D-86. The gasoline blend was prepared by adding to the gasoline, by simple mixing, dimethyl ethylene diamine at a concentration of 20 pounds per thousand barrels of gasoline. The gasoline blend was then used as the fuel to operate a one-cylinder Wisconsin gasoline engine which was run at 1800 r.p.m. for 14 hours. The Wisconsin engine is an L-head engine in which the fuel is mixed with air in a carburetor. The engine was equipped with a removable intake manifold. During the test the temperature of the air/fuel mixture in the manifold and the temperature of the intake air were controlled at 115° F. and 125° F. respectively so as to simulate typical intake conditions. From previous experience it was found that a 14-hour test period was sufficient to enable the additive in the gasoline to reach equilibrium adsorption levels on the surfaces of the intake manifold. At the end of the test, the intake manifold was removed from the engine and tested for non-wetting properties. The test consisted in placing six separate drops of gasoline on a single spot on the manifold surface and then measuring the average diameter of the area over which the gasoline spread on the surface. A similar test was run on an intake manifold from the Wisconsin engine

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test in which no additive had been incorporated in the base gasoline. In each instance the diameter was measured to the nearest one-quarter inch. The results were as follows:

TABLE I

	Diameter spread, inches
No additive	2
20 p.t.b. of diamine	¾

It will be seen that in the case of the test wherein the engine had been run with the gasoline containing the tertiary diamine, the intake manifold surfaces had been rendered more resistant to wetting by gasoline than had the manifold surfaces of the engine run with the gasoline containing no added diamine. Based on a large number of tests, it has been determined that there is a good correlation between the results of the above-described Wisconsin engine test and a tendency for car hesitation on acceleration under actual driving conditions. When there is a wide spread between the air/fuel ratios reaching the several cylinders of an automotive engine and/or when there is a wide variation of air/fuel ratio with respect to time for particular cylinders, there will be a tendency for hesitation or even actual stalling when attempting to accelerate from a standing position, as for example when attempting to enter a stream of fast-moving traffic from a side street. The effect of various amines in reducing this hesitation is shown by the results of the following test.

A 1970 Chevrolet 8-cylinder automobile was chosen for the test. The car was first run until it had warmed up to normal operating temperatures. It was then accelerated from a standing position to high driving speed as rapidly as possible and any tendency for hesitation was noted. In all of the test runs the same driver was used accompanied by two additional observers, who were always the same persons. The car was tested with a commercial premium gasoline of about 100 to 101 octane rating and known to contain no additives with non-wetting properties. The car was also tested with gasoline blends prepared by adding to separate portions of that same gasoline various amines at the concentration of 20 pounds per thousand barrels.

The tendency for hesitation on acceleration was noted by the driver and the two other observers and rated on a scale of 0 to 5, zero being assigned to a case where hesitation was very bad or actual stalling occurred, and 5 was assigned to cases where acceleration was perfectly smooth. A rating of 1 was assigned to bad hesitation, 2 and 3 to moderate and slight hesitation, and 4 to very slight hesitation. Each test was repeated a minimum of 5 times. If the same results were obtained in each of the 5 times, this was considered sufficient; if there was some variation the test was run as many as 10 times and the most consistent ratings were chosen.

The correlation between the Wisconsin engine test results and the hesitation test results with various amines is shown in Table II which follows:

TABLE II.—EFFECT OF VARIOUS AMINES ON RESULTS OF WISCONSIN ENGINE MANIFOLD WETTING TESTS AND CHEVROLET ACCELERATION HESITATION TESTS

Added amine	Wetting test diameter spread, inches	Hesitation merit rating
None	2	0-1
(a) Hydrogenated tallow plus amine	¾	4
(b) Dimethyl hydrogenated tallow amine ¹		
(c) Mixed beta amines		
plus	¾	4
(b) Dimethyl hydrogenated tallow amine ¹		

¹ One part (a) plus 3 parts (b) by weight.

² One part (c) plus 3 parts (b) by weight.

NOTE.—Total amines in each case 20 pounds per 1,000 barrels.

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In the above tests hydrogenated tallow amine is a commercial material obtained by hydrogenation of tallow amine, the latter being a mixture of saturated and unsaturated primary aliphatic amines, predominantly C₁₆ and C₁₈ amines. Hydrogenation serves to remove substantially all of the unsaturation. Dimethyl hydrogenated tallow amine is a commercially available mixed amine containing approximately 60 weight percent of dimethyl n-octadecyl amine, about 30 weight percent of dimethyl n-hexadecyl amine, and about 10 weight percent of other closely related amines.

The mixed beta amines (c) in the above tests was a commercial mixture of 2-amino alkanes known as Armeen L-15, which is a mixture of beta amines of from 15 to 20 carbon atoms.

As an additional example, a gasoline blend coming within the scope of this invention can also be prepared by adding to a low-lead (0.5 cc. TEL/gallon) base gasoline of about 96 to octane number, having an initial ASTM boiling point of about 80° F. and a final boiling point of about 390° F., diethyl didodecyl propylene diamine in a concentration of about 30 pounds per thousand barrels of gasoline.

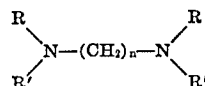
As a second additional example dimethyl dihexadecyl butylene diamine is blended at the rate of 25 pounds per thousand barrels into an unleaded gasoline of 97 octane rating having an initial ASTM boiling point of 97° F. and a final boiling point of 386° F.

We claim:

1. A gasoline composition comprising a major portion of gasoline into which has been incorporated

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from about 5 to 80 pounds, per thousand barrels of gasoline, of an aliphatic tertiary diamine of the formula:



wherein R is a C₁₂ to C₂₄ straight chain aliphatic hydrocarbon radical, R' is C₁ to C₂ alkyl and n is 2 to 4.

2. A gasoline composition as defined by claim 1 wherein said tertiary diamine is dimethyl dioctadecyl ethylene diamine.

3. A gasoline composition as defined by claim 1 wherein said tertiary diamine is diethyl didodecyl propylene diamine.

4. A gasoline composition as defined by claim 1 wherein said diamine is dimethyl dihexadecyl butylene diamine.

5. The method of improving the operation of an internal combustion engine which comprises running said engine with a gasoline composition as defined by claim 1.

References Cited

UNITED STATES PATENTS

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3,031,278	4/1962	Buckmann et al.	44-72
2,684,292	7/1954	Caron et al.	44-72

DANIEL E. WYMAN, Primary Examiner

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,705,024 Dated December 5, 1972

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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In column 1, line 69, change "distributor" to
--distribution--

In column 3, line 55, after "methyl" insert
--dioctadecyl--.

Signed and sealed this 12th day of February 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents