United States Patent [19]

Zimmerman et al.

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[45] **Jan. 9, 1973**

[54] **GASOLINE COMPOSITION PROVIDING ENHANCED ENGINE OPERATION**

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[73] Assignee: **Esso Research and Engineering Company**

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[21] Appl. No.: **158,509**

[52] **U.S. Cl.** **44/72**

[51] **Int. Cl.** **C10l 1/22**

[58] **Field of Search** ..... 44/72; 260/583 R

[56] **References Cited**

UNITED STATES PATENTS

2,684,292	7/1954	Caron et al.	44/72
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3,342,570	9/1967	Kautsky	44/72
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Assistant Examiner—Mrs. Y. H. Smith

Attorney—Pearlman, Schlager & Slabey and Byron O. Dimmick

[57] **ABSTRACT**

A mixture of a beta-primary amine and a tertiary amine, each of which has a long aliphatic hydrocarbon group, 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, run with the resulting blend, thereby increasing operating efficiency. A representative mixture comprises 2-amino octadecane and dimethyl hydrogenated tallow amine.

8 Claims, No Drawings

GASOLINE COMPOSITION PROVIDING ENHANCED ENGINE OPERATION

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 combination 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.

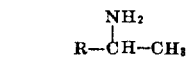
Gasolines used as motor fuels comprise a mixture of hydrocarbons of various boiling points. Thus a gasoline can have an initial boiling point in the range of about 70° to 135°F. and a final boiling point in the range of about 250° to 450°F. The mixture of gasoline and air that leaves the carburetor and 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 distribution 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.

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 long chain beta-amine, otherwise referred to as a 2-amino alkane, together with a minor amount of a tertiary amine having one long straight aliphatic chain and two short alkyl chains of no more than three carbon atoms.

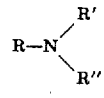
It is believed that the improvement in air/fuel ratio distribution obtained when practicing this invention results from a phenomenon wherein at least a portion of the additive becomes adsorbed on the walls of the intake system of the engine to create a surface which is not easily wetted by liquid drops 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 re-entrained in the air stream passing through the manifold.

The beta-amine used in the additive mixture of this invention can be represented by the formula:

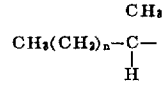


where R is a straight chain aliphatic hydrocarbon radical of from 10 to 22 carbon atoms. Thus the beta-amine has a total of from about 12 to 24 carbon atoms. Preferably R is about 14 to 18 carbon atoms. Mixed beta-amines can be used.

The tertiary amine can be represented by the formula:



wherein R is a straight chain aliphatic hydrocarbon radical of from about 12 to 24 carbon atoms, preferably C_{16} to C_{18}, and R′ and R″ are C_1 to C_3 alkyl, e.g., propyl or isopropyl, methyl, or ethyl, preferably C_1 to C_2, and most preferably methyl. R in this formula can also be straight chain aliphatic with a single methyl group attached to the carbon atom to which N is attached; i.e., R can be



where *n* will be a number from about 9 to about 21, thus making the total number of carbon atoms in R about 12 to about 24. Stated in other words, the tertiary amine can be a beta-amine derivative.

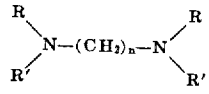
While the straight chains in the above formulas can be either saturated or unsaturated aliphatic hydrocarbon groups, the saturated hydrocarbon groups are preferred.

The beta-amines used in this invention include 2-amino dodecane, 2-amino hexadecane, 2-amino octadecene, 2-amino octadecane, and 2-amino eicosane. A representative mixture of beta-amines is that known as Armeen L-15, which is a mixture of beta-amines of from 15 to 20 carbon atoms.

The tertiary amines used in this invention include, for example, dimethyl octadecyl amine, diethyl dodecyl amine, methyl ethyl tetradecyl amine, and diisopropyl hexadecyl amine. Tertiary amines derived from beta-amines include 2-(dimethyl amino) octadecane and 2-(diethyl amino) dodecane. Mixed tertiary amines can also be used, as for example a commercial mixture of

tertiary amines identified as dimethyl hydrogenated tallow amine, wherein the long straight chain hydrocarbon groups of the tallow moiety are principally C_{16} and C_{18}. Another example is a mixture of tertiary amines known as Armeen DML-15 wherein the hydrogen atoms of the amino groups of Armeen L-15 mixed beta-amines have been replaced with methyl groups.

In place of or in addition to the tertiary amines mentioned above, tertiary diamines can also be used. The tertiary diamines are represented by the formula:



wherein R is a C_{12} to C_{24} straight chain aliphatic hydrocarbon group, R′ is a C_1 to C_2 alkyl group, and *n* is 2 to 4. Preferably, *n* is 2. As a specific example R can be C_{18} alkyl, R′ can be a methyl group, and *n* can be 2, i.e., dimethyl dioctadecyl ethylene diamine. Other specific examples include diethyl didodecyl propylene diamine and dimethyl dihexadecyl butylene diamine.

It has previously been taught in copending application Ser. No. 20,083, filed Mar. 16, 1970, to employ a mixture of a straight chain primary aliphatic amine and a tertiary aliphatic amine in gasoline to improve the air/fuel distribution in the intake system of an aspirated multicylinder engine. It was found, however, that one disadvantage in the use of a straight chain primary amine is that it tends 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 mixture to some extent. Although this reduction in effectiveness did not prevent the commercial use of the mixture of straight chain primary amine and tertiary amine, it was nevertheless considered desirable to minimize this disadvantage.

It has now been found that if a beta-amine is employed in place of the primary amine this tendency for loss by reaction with carbonyls is reduced. However, a tertiary amine is still necessary in the mixture to ensure a constant level of activity in improving the air/fuel mixture distribution. This is because the substitution of beta-amine for primary amine does not completely eliminate the tendency for loss of amine by reaction with carbonyls, although such reaction tendency is greatly reduced. Furthermore, since the beta-amine is more soluble in organic solvents, e.g., in an aromatic hydrocarbon, than is the straight chain primary amine, the substitution of beta-amine greatly facilitates handling of the amines as a liquid concentrate for gasoline blending purposes.

In the mixture of amines used in this invention the proportion of amines can range from about 75 percent beta-amine and 25 percent tertiary up to about 90 percent tertiary and 10 percent beta-amine, by weight. Preferably the amount of beta-amine in the mixture of beta-amine plus tertiary amine will be in the range of about 15 to 30 percent by weight.

The mixture of 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 1,000 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 1,000 barrels of gasoline. The concentration range of from 10 to 40 pounds per thousand 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 point 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 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, hydroforming, 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 psi 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 tetravinyl 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 hydrocarbyl amines 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, antistatic 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. No. 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

Gasoline blends were prepared using as the base an unleaded gasoline of 97 Research octane rating that had the inspections shown in Table I:

TABLE I

BASE GASOLINE INSPECTIONS

ASTM Distillation, Method D-86	
Initial Boiling Point, °F.	97
50% Overhead °F.	230
Final Boiling Point, °F.	386
FIA Analysis(*)	
Vol. % Saturates	61
Vol. % Olefins	11
Vol. % Aromatics	28
*Fluorescent Indicator Absorption Analysis; ASTM 1319	

Each blend was prepared by adding to the base gasoline by a simple mixing procedure a mixture of amines at the concentration of 20 pounds per thousand barrels of the gasoline. This mixture consisted of 1 part of 2-amino octadecane and 3 parts of dimethyl hydrogenated tallow amine, by weight.

The base fuel and the blend were run separately in a 1967, 6-cylinder, 175 cu. inch Valiant engine equipped with exhaust emission controls meeting the requirements of the State of California for 1967. The Valiant car was operated on a Clayton dynamometer with acceleration weights equivalent to 4,000 pounds. In each test the engine was run at idle speed, at 30 miles an hour, and at 50 miles an hour and the air/fuel ratio reaching each cylinder was determined. In order to accomplish this, sampling lines were extended into the individual exhaust valve ports of the engine, so as to permit the analysis of the combustion products from each of the six cylinders separately. The exhaust gas was filtered and cooled prior to analysis to remove solid particles and most of the water produced by the combustion of the gasoline. The exhaust gas was then analyzed for hydrocarbons, carbon monoxide, carbon dioxide, nitrogen oxide and oxygen. The car was held at a constant engine rpm and dynamometer speed for the period of each of the measurements, approximately 15 minutes at each speed condition. Air/fuel ratios were calculated by a material balance of the exhaust gas by well known procedures (see Lamont Eltinge, "Fuel/Air Ratio and Distribution from Exhaust Gas Compositions" SAE Paper 680114, January 1968; and R. S. Spindt "Air Fuel Ratios from Exhaust Gas Analysis" SAE Paper 650507, May 1965). The spread between the highest and the lowest calculated air/fuel ratio at each of the testing speeds for each of the fuels is given in Table II which follows. The air/fuel ratios were in the range of about 13/1 to about 15/1 at idle, and in the range of about 14.5/1 to about 17/1 at 30 miles per hour and at 50 miles per hour.

TABLE II

SPREAD OF AIR/FUEL RATIOS

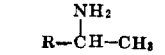
Velocity	Base Fuel	Base Fuel + Amine Mixture
Idle	1.02	1.18
30 mph	1.17	0.74
50 mph	2.48	1.8

It is to be noted that at both 30 mph and 50 mph there was a significant reduction in the spread of air/fuel ratios. The difference between 1.02 and 1.18 at idle is within the range of experimental error.

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 octane number, having an initial ASTM boiling point of about 80°F. and a final boiling point of about 390°F., a mixture of 2 parts by weight of dimethyl dioctadecyl ethylene diamine and 1 part by weight of 2-amino hexadecane. The mixture of amines is incorporated into the gasoline at a concentration of 30 pounds per thousand barrels of the gasoline.

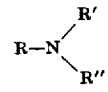
We claim:

1. A gasoline composition comprising a major proportion of gasoline into which has been incorporated from about 5 to about 80 pounds, per thousand barrels of gasoline, of a mixture of aliphatic amines, one of said amines being a beta-amine of the formula:

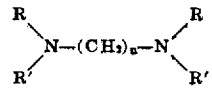


wherein R is a straight chain aliphatic hydrocarbon group of from about 10 to about 22 carbon atoms,

the second amine being an aliphatic tertiary amine selected from the group consisting of an amine of the formula:



wherein R is a straight chain aliphatic or single branched chain aliphatic hydrocarbon group wherein a single methyl group is attached to the carbon atom to which N is attached, R having a total of from about 12 to about 24 carbon atoms, and R′ and R″ are C_1 to C_3 alkyl; and



wherein R is a C_{12} to C_{24} straight chain aliphatic hydrocarbon radical, R′ is C_1 to C_2 alkyl and n is 2 to 4.

2. A gasoline composition as defined by claim 1 wherein the mixture of beta-amine plus tertiary amine contains from 75 to 10 weight percent of beta-amine and from 25 to 90 weight percent of tertiary amine.

3. A gasoline composition as defined by claim 1 wherein the amount of beta-amine in the mixture of beta-amine plus tertiary amine is within the range of about 15 to 30 percent by weight.

4. A gasoline composition as defined by claim 1 wherein said beta-amine is 2-amino octadecane.

5. A gasoline composition as defined by claim 1 wherein said tertiary amine is dimethyl hydrogenated tallow amine.

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

7. A gasoline composition as defined by claim 1 wherein said tertiary amine is 2-(dimethyl amino) octadecane.

8. 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.

* * * * *

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,709,668 Dated January 9, 1973

Inventor(s) Abraham A. Zimmerman, Louis E. Furlong and Mohan Vadekar

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

On the front page, first column, under data element identifier [75], the name of the inventor "Vadekar Mohan" should read -- Mohan Vadekar --.

Signed and sealed this 15th day of January 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents