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ENHANCING GASOLINE ENGINE OPERATION BY IMPROVING AIR-FUEL RATIO DISTRIBUTION

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U.S. Cl. 44—69 8 Claims

ABSTRACT OF THE DISCLOSURE

A mixture of a silicone and a trisubstituted phosphate ester having at least two aryl groups, when added in a minor proportion to a leaded gasoline, will improve the distribution of the air-fuel mixture in the induction system of an aspirated multicylinder gasoline engine run with that blend, thereby increasing operating efficiency.

REFERENCE TO RELATED APPLICATION

In commonly assigned copending application Ser. No. 199,303, filed on the same date as the present application, there is disclosed and claimed a nonleaded gasoline containing a silicone. The present invention differs from that invention in that it is directed to a gasoline that contains an alkyl lead antiknock agent rather than being lead free.

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., at atmospheric pressure. The mixture of gasoline and air that leaves the carburetor and passes to the various cylinders through the intake manifold tends to

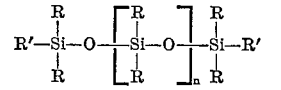
deposit some of the higher boiling fractions in the form of a liquid film on the walls of the intake manifold. This liquid film is the main factor in poor fuel distribution in the engine. Accordingly, it is desirable to have the gasoline present as a vapor or spray in the air/fuel mixture to ensure greater 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 leaded fuel fed to that engine a minor amount of a polysiloxane, also known as a silicone, along with a minor amount of a trisubstituted phosphate ester.

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 silicone 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 reentrained in the air stream passing through the manifold.

The silicones that are used in this invention can be further characterized as compounds of the formula:



wherein n is a whole number of at least 2 and wherein at least one R attached to each silicon atom is methyl and each remaining R is straight chain or branched chain, preferably straight chain, C_1 to C_{18} alkyl, or a straight chain or branched chain, preferably straight chain, C_1 to C_{18} alkyl group wherein at least two hydrogen atoms have been replaced by fluorine, thus providing at least one CF_3 or CF_2H group on the chain. The fluorinated alkyl group can be fully fluorinated, if desired, i.e., it can be a perfluoroalkyl group. R′ in the above formula can be any terminating group, as is known in the silicone art. Thus, one R′ could be hydrogen or methyl and the other one could be an OH group, a CH_3 group, or a CH_2OH group, for example. Very often in silicone designation the R′ groups are not definitely characterized, as impurities in the reaction mix can also act as terminating groups.

The viscosities of the silicones used in this invention will be within the range of about 5 to 8000 centistokes, preferably 20 to 5000 centistokes, measured at 25° C. Silicones of higher viscosity than about 8000 centistokes at 25° C. are not desirable because of their tendency to cause spark plug deposits as well as to form deposits on the undersides of the intake valves of an internal combustion engine.

It is known to add silicones to gasoline, as taught for example in U.S. Pat. 2,529,496, for the purpose of preventing an increase in the octane demand of an internal combustion engine on prolonged operation. The finding of the present invention is that when such silicones are added to a leaded gasoline along with small proportions of an alkyl diaryl phosphate or a triaryl phosphate, there is an improvement in the distribution of the air/fuel mixture to the various cylinders of the gasoline engine, thus improving the smoothness of operation. If the silicone is added to the leaded gasoline without also adding the phosphate additive, adverse results are obtained.

The silicone compounds of the present invention will be incorporated in leaded gasoline compositions in an amount ranging from about 2 to 50 pounds, or more usually from about 5 to 20 pounds, of the silicone per thousand barrels of gasoline, one barrel of gasoline containing

42 U.S. gallons. A concentration range of from 2 to 50 pounds per thousand barrels of gasoline is roughly equal to a weight percent concentration of from about 0.0008 to about 0.02 weight percent.

The substituted and unsubstituted silicones that will be used in this invention include dimethyl silicone, methyl n-decyl silicone, methyl isopropyl silicone, methyl octadecyl silicone, methyl perfluoropropyl silicone, and methyl trifluorotetradecyl silicone.

The trisubstituted phosphate ester employed in the present invention will be a monoalkyl diaryl phosphate or a triaryl phosphate in which the alkyl group will have from 1 to about 12 carbon atoms and the aryl groups will have from 6 to about 9 carbon atoms. Nonlimiting examples of such phosphates include methyl diphenyl phosphate, tricresyl phosphate, butyl diphenyl phosphate, cresyl diphenyl phosphate, isopropyl dixylyl phosphate, monodecyl dicresyl phosphate, and C_8 Oxo diphenyl phosphate. The term C_8 Oxo refers to a mixture of branched chain aliphatic alcohols averaging about 8 carbon atoms, the alcohols having been obtained by the well-known process in which olefins are reacted catalytically with hydrogen and carbon monoxide and the resulting aldehydes are converted to alcohols in a separate catalytic step.

The amount of monoalkyl diaryl phosphate or of triaryl phosphate, or of mixed phosphates, that will be used in this invention will be related to the amount of lead antiknock agent present, and will range from about 0.1 to about 0.6 theory based on the lead.

The method of expressing gasoline additive concentrations in terms of theories is well recognized by persons skilled in the art. Thus, one theory is the amount of a constituent that is stoichiometrically equivalent to the lead in the gasoline. In the case of a phosphate ester, one theory is the amount of ester that would react with the lead compounds to form $Pb_3(PO_4)_2$; thus, the ratio of phosphorus to lead would be 2/3 when one theory is present.

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 in the range of about 70 to 135° F. and a final boiling point 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 between about 70° F. and about 450° F., while aviation gasolines have narrower boiling ranges of between 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 are used in gasolines that contain 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 ethyl dichloride or ethylene dibromide.

Other additives such as those conventionally employed in gasolines may be used in practicing the present invention. These include corrosion inhibitors, rust inhibitors, anti-oxidants, solvent oils, antistatic agents, lead octane appreciators, e.g., t-butyl acetate, 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.

EXAMPLE 1

A gasoline blend was prepared using as the base a gasoline of 100 Research Octane rating that had the following inspection as shown in Table I.

TABLE I

Base gasoline inspections

ASTM distillation, Method D–86:	
Initial boiling point, ° F.	90
20% overhead, ° F.	144
50% overhead, ° F.	214
70% overhead, ° F.	255
90% overhead, ° F.	308
Final boiling point, ° F.	380
FIA analysis: [1]	
Vol. percent saturates	54
Vol. percent olefins	18
Vol. percent aromatics	28
Tetraethyl lead, cc./gal.	2.5

[1] Fluorescent indicator absorption analysis; ASTM 1319.

The blend was prepared by adding to the base gasoline by simple mixing, a dimethyl silicone at the concentration of 40 pounds per thousand barrels. The dimethyl silicone had a viscosity of 350 centistokes at 25° C. Both the base fuel and the blend also contained methyl diphenyl phosphate at a concentration equal to 0.2 theory based on the lead present in the fuel.

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 4000 pounds. In each test the engine was run at idle speed 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 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 r.p.m. 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 calculated spreads of air/fuel ratios at each testing

speed for each of the fuels are given in the following Table II.

TABLE II.—SPREAD OF AIR/FUEL RATIOS

Velocity	Base fuel	Base fuel plus silicone
Idle	1.95	1.14
50 m.p.h	1.90	0.93

The benefit of adding the dimethyl silicone is readily apparent from Table II.

EXAMPLE 2

Using the same type of engine tests and analysis procedures as described in Example 1 the same base fuel and a blend of that base fuel containing 10 pounds per thousand barrels of the silicone were compared for the effect of the additive treatment on the emission of hydrocarbons during the running of the engine. The results obtained are shown in the following Table III.

TABLE III.—EFFECT OF SILICONE ON HYDROCARBON EMISSION

	Hydrocarbons (p.p.m.)		
Speed	Base fuel	Base fuel plus silicone	Percent decrease
Idle	595	560	6.0
30 m.p.h	765	710	7.5
50 m.p.h	690	615	11.5

The effect of the dimethyl silicone in reducing hydrocarbon emissions as shown by the data in Table III is believed to be a result of improvements both in geometric distribution of the air/fuel mixtures and in distribution with respect to time.

EXAMPLE 3

Test blends similar to those of Example 1 were prepared wherein in one case the gasoline contained 20 pounds per thousand barrels of the silicone of 350 centistokes viscosity along with 0.2 theory of methyl diphenyl phosphate and in the other case the methyl diphenyl phosphate was omitted. Each gasoline blend contained 3 cc. of tetraethyl lead per gallon. Each of these blends was run separately in a 6-cylinder Ford engine mounted on a test stand for a total of 110 hours in a cyclic operation wherein for 1½ hours the engine was idled at a 13/1 air/fuel ratio and then for 4 hours the engine was run at 2000 r.p.m. with a 14/1 air/fuel ratio under a load of 105 ft. pounds. At the end of each test, after shutdown, while the engine was still warm, the compression pressures on each cylinder were measured using standard procedures. Then the exhaust valves were removed from the engine and inspected for evidence of channeling that would indicate blowby. The measured compression pressures are shown in Table IV.

TABLE IV.—COMPRESSION PRESSURES AT TERMINATION OF ENGINE TESTS

	Pressure (p.s.i.g.)					
Cylinder	1	2	3	4	5	6
Additive in fuel:						
Silicone alone	185	187	165	180	190	198
Silicone plus phosphate	198	198	195	198	193	197

Inspection of the exhaust valves revealed, in the case of the leaded fuel with silicone alone, two valves having clearly visible channels and indentations and four valves having light to moderate discoloration. There were no valves showing channeling in the engine run with the leaded fuel containing both the silicone and the phosphate and one valve showed no markings or discoloration whatever. The other valves had light to moderate discoloration. Thus, the compression figures and the valve conditions show that a blowby condition existed in at least two cylinders of the engine run with the fuel containing silicone but no phosphates.

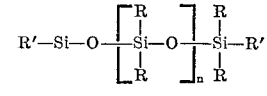
These test results show that use of the phosphate in conjunction with the silicone prevents the adverse effects on exhaust valves that occur when an engine is run with a leaded gasoline to which a silicone is added. This action of the phosphate in preventing problems of valve function is entirely unrelated to the previously known action of aryl phosphates in modifying engine deposits so as to reduce preignition, spark plug fouling, octane requirement increase, and the like as taught, for example, in U.S. Pat. 3,034,877.

There is no intention to limit this invention to the specific examples herein presented by way of illustration. The scope of the invention is to be determined by the appended claims.

What is claimed is:

1. A gasoline composition comprising a major proportion of a leaded gasoline into which have been incorporated from about 2 to 50 pounds, per thousand barrels of gasoline, of a silicone having a viscosity of from 5 to 8000 centistokes at 25° C., and from 0.1 to 0.6 theory, based on the alkyl lead content of the fuel, of a trisubstituted phosphate ester selected from the group consisting of a monoalkyl diaryl phosphate and a triaryl phosphate, the weight ratio of phosphate ester to silicone being within the range of about 1:1 to about 2.4:1,

said silicone being represented by the formula:



wherein n is a whole number of at least 2, at least one R attached to each Si is methyl, and each remaining R is C_1 to C_{18} alkyl, or C_1 to C_{18} alkyl wherein at least two hydrogen atoms have been replaced by fluorine, thus providing at least one CF_3 or CF_2H group on the chain, R′ being a terminating group.

2. Composition as defined by claim **1** wherein said phosphate ester is a triaryl phosphate wherein the aryl groups have from 6 to about 9 carbon atoms.

3. Composition as defined by claim **1** wherein said phosphate ester is a monoalkyl diaryl phosphate wherein the alkyl group has from 1 to about 12 carbon atoms and the aryl groups have from 6 to 9 carbon atoms.

4. Composition as defined by claim **1** wherein said phosphate ester is methyl diphenyl phosphate.

5. Composition as defined by claim **1** wherein said silicone is dimethyl silicone.

6. Composition as defined by claim **1** wherein said phosphate ester is cresyl diphenyl phosphate.

7. Composition as defined by claim **1** wherein said silicone is methyl perfluoropropyl silicone.

8. The method of improving the operation of an internal combustion engine which comprises running said engine with the gasoline composition of claim **1**.

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