United States Patent Office 3,004,838 Patented Oct. 17, 1961

3,004,838

ANTIKNOCK COMPOSITIONS

Melvin L. Larson, Royal Oak, Mich., assignor to Ethyl Corporation, New York, N.Y., a corporation of Delaware

No Drawing. Filed Oct. 24, 1956, Ser. No. 617,926
6 Claims. (Cl. 44—69)

This invention relates to improved liquid fuel for spark ignition internal combusion engines and to composite additives for such fuel.

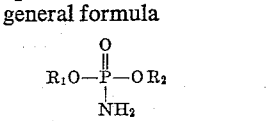
In recent years there has been a marked trend in the automotive industry of utilizing high compression, spark ignition engines in passenger cars and trucks. With such engines the accumulation of engine deposits results in a number of serious problems, including spark plug fouling and surface ignition (also known as deposit-induced autoignition or wild ping). Spark plug fouling results from the formation of conductive deposits on the firing end of spark plugs which provide a conductive surface for the electrical charge so that the decrease in resistance results in an insufficient potential across the spark plug electrodes. Under such circumstances the production of a spark at the spark gap is prevented. Surface ignition is erratic ignition produced by glowing engine deposits and manifests itself in reduced efficiency of operation, loss of power and of fuel economy and in increased wear of engine parts.

A critical limitation imposed upon any additive to be used in alleviating spark plug fouling or controlling surface ignition is that it must not destroy an appreciable amount of the alkyllead antiknock compounds which are employed in gasoline. Failure to meet this limitation causes, among other things, loss of gasoline octane quality, a property which is needed in these days of the high compression engine. Another adverse effect caused by an additive which destroys the antiknock effectiveness of alkyllead antiknock agents is the substantial economic waste caused thereby.

On object of this invention is to provide composite additives for gasoline capable of substantially reducing spark plug fouling and surface ignition without causing loss of antiknock effectiveness. Another object is to provide improved gasoline compositions having the above properties. Other objects of this invention will be apparent from the ensuing description.

The above and other objects are accomplished by providing a gasoline additive consisting essentially of an alkyllead antiknock agent, a scavenging amount of an organic halide scavenger capable of reacting with the lead during combustion in a spark ignition internal combustion engine to form relatively volatile lead halide, and a dialkyl phosphoramidate in which each alkyl group contains from 2 to 10 carbon atoms, the phosphoramidate being present in the additive in amount such that the phosphorus-to-lead atom ratio is from about 0.1:3 to about 1.6:3. Also provided by this invention is gasoline containing from about 0.02 to about 6.5 grams of lead per gallon as an alkyllead antiknock agent, a scavenging amount of organic halide scavenger capable of reacting with the lead during combustion in a spark ignition internal combustion engine to form relatively volatile lead halide and a dialkyl phosphoramidate as defined above which is present in amount such that the phosphorus-to-lead atom ratio is from about 0.1:3 to about 1.6:3.

The dialkyl phosphoramidates used according to this invention have the general formula



wherein R_1 and R_2 are alkyl groups containing from 2 to 10 carbon atoms. Preferred dialkyl phosphoramidates used in this invention are those in which the alkyl groups contain from 4 to 10 carbon atoms. These particular phosphoramidates are preferred because they possess ideal solubility characterisitcs; they are infinitely soluble in most present-day gasolines and have an exceptionally low solubility in water. Low water solubility is a very important feature of an additive for gasoline because gasoline normally comes in contact with or contains water and since the preferred dialkyl phosphoramidates have such low solubility in water, their continued presence in the gasoline is assured.

Particularly preferred dialkyl phosphoramidates are those in which the alkyl groups both contain the same number of carbon atoms and in which the total number of carbon atoms in the molucule is from 8 to 20. These are particularly preferred because not only do they have all of the efficacious attributes of the preferred type disclosed above, but they are very inexpensive and easily made from readily available starting materials.

The compositions of this invention are capable of (1) obviating ordinary knock, (2) substantially reducing surface ignition and (3) alleviating spark plug fouling because of the cooperation among the several ingredients. Moreover, these important benefits are obtained with virtually no loss in antiknock effectiveness of the alkyllead ingredient.

Among the features of this invention is that the dialkyl phosphoramidate ingredients have unusually great effectiveness in reducing surface ignition rate and alleviating spark plug fouling. In addition to this, these phosphoramidates cooperate with the alkyllead antiknock agent during engine combustion in some currently unexpected manner so that there is almost no loss in the antiknock effectiveness of the entire composition. In other words, the dialkyl phosphoramidates have the very unusual property of exhibiting very little destruction of or antagonism toward the antiknock effectiveness of the alkyllead antiknock agent. This represents a substantial advance in the art inasmuch as phosphorus compounds in general have heretofore been reported as being among the most serious antagonists for tetraalkyllead antiknock agents. Other important features of this invention are that the dialkyl phosphoramidates are easily made and have a high phosphorus content, the amount of phosphorus in the molecule ranging as high as over 20 percent by weight. Thus, the petroleum refiner is provided with not only an inexpensive, highly effective and eminently useful composition, but one in which only a small amount of the phosphoramidate ingredients need be added to achieve the desired phosphorus-to-lead atom ratio. This further reduces his costs and simplifies his handling, storage and blending operations. Thus, the present invention not only provides highly unexpected results but is an important contribution to the art.

To prepare the improved composite additives of this invention, the desired proportions of the ingredients are placed in a suitable container, such as a blending tank, and mixed. To insure homogeniety, use is made of conventional physical agitation, such as stirring, shaking or the like. The order of addition of the ingredients during formulation is not critical.

Representative alkyllead antiknock compositions of this invention—i.e., composition additives—are presented in Table I. The figures following the representative ingredients are parts by weight. The two figures following the dialkyl phosphoramidate ingredients show respectively the amounts which are used to obtain a composition having a phosphorus-to-lead atom ratio of 0.1:3 and 1.6:3. If the lower figure is doubled, the resulting composition will have a phosphorus-to-lead atom ratio of 0.2:3 whereas one-fourth of the second figure provides a

composition having a phosphorus-to-lead atom ratio of 0.4:3. For other phosphorus concentrations, the proper adjustments are evident.

Table I.—Antiknock fluid compositions

Antiknock agent	Scavenger	Dialkyl phosphoramidate
Tetramethyllead 267	Ethylene dibromide 226.	Diethyl phosphoramidate 5.1–81.6.
Do	Ethylene dibromide 94 and ethylene dichloride 99.	Dipropyl phosphoramidate 6.1–96.5.
Tetraethyllead 323	Ethylene dibromide 188.	Dibutyl phosphoramidate 7.0–111.5.
Do	Ethylene dibromide 94 and ethylene dichloride 99.	Diisobutyl phosphoramidate 7.0–111.5.
Do	Ethylene dibromide 113 and ethylene dichloride 99.	Di-2-amyl phosphoramidate 7.9–126.4.
Do	Mixed dibromotoluenes 200.	Dihexyl phosphoramidate 8.8–141.3.
Do	Mixed dibromotoluenes 125 and ethylene dichloride 99.	Di-2-ethylhexyl phosphoramidate 10.7–171.2.
Do	Mixed dibromotoluenes 150 and 1,2,4-trichlorobenzenes 175.	Didecyl phosphoramidate 12.6–201.1.
Do	Ethylene dibromide 94 and mixed trichlorobenzenes 146.	Butyl isobutyl phosphoramidate 7.0–111.5.
Do	1,4-dibromobutane 216.	Propyl isopropyl phosphoramidate 6.0–96.5.
Do	1,4-dibromobutane 108 and 1,4-dichlorobutane 127.	Propyl heptyl phosphoramidate 7.9–126.4.
Tetrapropyllead 379	Acetylene tetrabromide 346.	Diisopropyl phosphoramidate 6.0–96.5.
Dimethyldiethyllead 295.	β,β′-dibromodiethyl ether 232.	Dineopentyl phosphoramidate 7.9–126.4.
Methyltriethyllead 309.	β,β′-dibromodiisopropyl ether 130 and β,β′-dichlorodiethyl ether 143.	Dioctyl phosphoramidate 10.7–171.2.

The antiknock fluid compositions shown in Table I are presented for illustrative purposes only. Other antiknock fluid compositions will now be apparent to one skilled in the art.

Many blending procedures are available to prepare the improved fuel compositions of this invention. For example, a composite additive of this invention, such as described in Table I, can be blended in appropriate concentration with gasoline to provide a finished fuel of this invention containing from about 0.02 to about 6.5 grams of lead per gallon. Another method is to add an appropriate concentration of a dialkyl phosphoramidate separately to the fuel before, after or at the same time a conventional alkyllead antiknock fluid composition is blended with the fuel. Still another procedure is to blend with the fuel each of the ingredients of the above composite additives separately or in various combinations in any sequence.

Illustrative improved fuel compositions of this invention are shown in Table II. The two figures following each of the ingredients are weights in grams thereof. By blending each of the ingredients in the amounts of the respective lower figures with 10 gallons of gasoline, a fuel composition of this invention containing about 0.5 gram of lead per gallon as the leadalkyl antiknock agent is prepared. The respective higher figures following each ingredient show the amount in grams thereof which are blended with 10 gallons to provide a lead content of about 6.5 grams per gallon. These illustrative fuels have a phosphorus-to-lead atom ratio of 0.4:3. The characteristics of the base fuels represented in Table II as A, B, C and D are as follows:

Base Fuel A—A blend of straight-run, catalytically cracked and polymer stocks. Initial boiling point, 98° F.; endpoint, 402° F.

Base Fuel B—A 100% catalytically cracked gasoline having an initial boiling point of 105° F. and an endpoint of 425° F.

Base Fuel C—An aviation gasoline of grade 100/130 comprising isopentane, alkylate, aromatics and straight-run gasolines. Initial boiling point, 82° F.; endpoint, 330° F.

Base Fuel D—A blend of light catalytically cracked naphtha, polymer stock, catalytic reformate and light straight-run naphtha containing butane to the proper Reid vapor pressure. Initial boiling point, 90° F.; endpoint, 368° F.

Table II.—Antiknock fuel compositions

Base fuel	Antiknock agent	Scavenger	Dialkyl phosphoramidate
A	Tetramethyllead 6.4–83.8.	Ethylene dichloride 2.4–31.1.	Diethyl phosphoramidate 0.5–6.4.
A	Tetraethyllead 7.8–101.4	Ethylene dibromide 2.3–29.5 and ethylene dichloride 2.4–31.1.	Diisopropyl phosphoramidate 0.6–7.6.
B	do	Ethylene dibromide 2.7–35.4 and ethylene dichloride 2.4–31.1.	Dibutyl phosphoramidate 0.7–8.7.
B	do	Mixed dibromotoluenes 3.6–47.1.	Diamyl phosphoramidate 0.8–9.9.
C	do	1,3-dibromobutane 5.2–67.8.	Dioctyl phosphoramidate 1.0–13.4.
C	do	1,4-dibromobutane 5.2–67.8.	Didecyl phosphoramidate 1.2–15.8.
D	Tetrabutyllead 10.5–136.6.	Mixed dibromotoluenes 3.0–39.1 and 1,2,4-trichlorobenzene 2.9–37.9.	Butyl isobutyl phosphoramidate 0.7–8.8.
D	Trimethylethyllead 6.8–88.2.	1,3-dibromopropane 2.4–31.7 and β,β′-dichlorodiethyl ether 3.5–44.9.	Ethyl octyl phosphoramidate 0.8–9.9.

To illustrate the great effectiveness of the compositions of this invention in suppressing surface ignition, recourse was had to engine tests. A spark ignition internal combustion engine equipped with an electronic device which automatically recorded surface ignitions was used in the tests. This engine was operated on a commercially available gasoline containing 3 milliliters of tetraethyllead per gallon as a conventional antiknock mixture (tetraethyllead, about 0.5 theory of bromine as ethylene dibromide and about 1.0 theory of chlorine as ethylene dichloride). This established a baseline in terms of the number of surface ignitions which occurred per hour. Another portion of the same leaded fuel was then treated with a typical, preferred dialkyl phosphoramidate of this invention—di-2-ethylhexyl phosphoramidate—in amount such that the phosphorus-to-lead atom ratio was 0.4:3. The engine was then operated on this fuel and the effect of the presence of this phosphoramidate determined. It was found that the phosphorus-free, leaded gasoline produced 115 surface ignitions per hour of engine operation, whereas the gasoline composition of this invention only exhibited 26 surface ignitions per hour. In other words, the fuel composition of this invention resulted in a surface ignition rate which was only 23 percent of that of the untreated leaded fuel, a reduction in surface ignition rate of 77 percent having been achieved. These results are illustrative of the enhanced surface ignition suppression properties of the compositions of this invention. Equally good results are obtained with other such compositions, such as those shown in Tables I and II.

My compositions also effectively alleviate spark plug fouling by beneficially modifying the characteristics of deposits formed on spark plug electrodes and insulators. Since my dialkyl phosphoramidate additives are highly effective in reducing surface ignition and spark plug fouling, they may be used at lower concentrations than additives suggested heretofore to obtain the same degree of effectiveness. On the other hand, they may be used at the same or higher concentrations if still greater benefits regarding these problems are desired.

Another outstanding characteristic of my improved antiknock compositions is that in use there is no adverse effect on the antiknock effectiveness of the alkyllead antiknock agent during the cooperation of this agent and the

dialkyl phosphoramidate additives of this invention. This exceptional characteristic of my phosphoramidate additives was clearly demonstrated by conducting a series of comparative engine tests.

In the present tests the amount of tetraethyllead antagonism exhibited by typical dialkyl phosphoramidates of this invention—diethyl phosphoramidate, dibutyl phosphoramidate, diisoamyl phosphoramidate and di-2-ethylhexyl phosphoramidate—was determined by the standard ASTM Research Method, Test Procedure D908/51 (which can be found in the 1952 edition of "ASTM Manual of Engine Test Methods for Rating Fuels"). In these tests primary measurements were made of the percent of the tetraethyllead effectiveness destroyed, if any, caused by these dialkyl phosphoramidates. For comparative purposes, identical tests were run using triethyl phosphate and triisobutyl phosphate, additives described heretofore as being useful in leaded gasolines. The experiments consisted of blending with individual portions of a standard base fuel, 3.0 milliliters of tetraethyllead per gallon as an anti-knock fluid consisting essentially of tetraethyllead, 0.5 theory of bromine as ethylene dibromide and 1.0 theory of chlorine as ethylene dichloride. To each of these fuel portions was added an amount of the phosphorus additive under test such that the phosphorus-to-lead atom ratio was 0.4:3. The test fuel used had a volume percent composition as follows: diisobutylene, 20%; toluene, 20%; isooctane, 20%; n-heptane, 40%.

Table III—Effect of phosphorus additives on tetraethyllead antiknock effectiveness

Phosphorus additive:	Percent tetraethyllead effect destroyed
Additives of the invention—	
Diethyl phosphoramidate	2
Dibutyl phosphoramidate	1
Diisoamyl phosphoramidate	0
Di-2-ethylhexyl phosphoramidate	0
Additives not of the invention—	
Triethyl phosphate	8
Triisobutyl phosphate	7

The above data clearly show that the tetraethyllead antagonism, if any, of the additives of this invention is extremely low. In fact, the tetraethyllead antagonism of the prior art additives is at least over several times that of the additives of this invention. Thus, triethyl phosphate produced 400 percent as much tetraethyllead antagonism as diethyl phosphoramidate and triisobutyl phosphate produced 700 percent as much as dibutyl phosphoramidate. It will be noted that diisoamyl phosphoramidate and di-2-ethylhexyl phosphoramidate did not destroy any of the tetraethyllead antiknock effectiveness.

The preeminence of the diakyl phosphoramidates of this invention from the standpoint of their compatibility with alkyllead antiknock agents during engine combustion was further demonstrated by conducting another series of engine tests. In this instance the standard ASTM Motor Method, Test Procedure D357 (which can be found in the 1953 edition of "ASTM Manual of Engine Test Methods for Rating Fuels") was used. The gasoline used had a motor octane number clear—i.e., unleaded—of 71.4. For the present tests the gasoline samples each contained 3 milliliters of tetraethyllead per gallon, 0.5 theory of bromine as ethylene dibromide and 1.0 theory of chlorine as ethylene dichloride. A sample of this leaded gasoline was subjected to the above ASTM test method and the octane number of the fuel determined. Then, representative fuels of this invention were subjected to the same test procedure. These particular fuels contained diethyl phosphoramidate, dibutyl phosphoramidate or di-2-ethylhexyl phosphoramidate in amount such that the phosphorus-to-lead atom ratio was 1:3. For comparative purposes another series of leaded gasolines was prepared, these containing the same concentration of phosphorus as tributyl phosphite, triethyl phosphate or triisobutyl phosphate—additives suggested in the prior art—and were rated under the same conditions. The results of these tests are shown in Table IV.

Table IV.—Effect of phosphorus additives on tetraethyllead antiknock effectiveness

Phosphorus additive	Octane number	Change in octane number
None	84.0	
Additives of the invention:		
Diethyl phosphoramidate	83.8	−0.2
Dibutyl phosphoramidate	83.9	−0.1
Di-2-ethylhexyl phosphoramidate	83.6	−0.4
Additives not of the invention:		
Tributyl phosphite	82.8	−1.2
Triethyl phosphate	83.1	−0.9
Triisobutyl phosphate	82.7	−1.3

The data shown in Table IV establish that the dialkyl phosphoramidate additives of this invention exhibited practically no adverse effect upon the antiknock effectiveness of tetraethyllead, whereas somewhat closely related aliphatic phosphorus compounds suggested in the prior art caused a substantial amount of this adverse effect. Thus, the compositions of this invention result in the virtual elimination of deposit-induced engine problems without incurring any significant amount of alkyllead antagonism.

The alkyllead antiknock agents which are present in the compositions of this invention are represented by such compounds as tetramethyllead, tetraethyllead, tetrapropyllead, tetrabutyllead, diethyldimethyllead, triethylmethyllead, and the like, or mixtures thereof. Such compounds containing from 4 to about 16 carbon atoms, one atom of lead and a plurality of lead-to-carbon bonds, are capable of increasing the octane quality of gasoline when employed therein in antiknock quantities—about 0.02 to about 6.5 grams of lead per gallon. Of such compounds, tetraalkyllead compounds having 4 to about 12 carbon atoms have superior volatility characteristics from the standpoint of engine induction and are thus preferred. Halogen-containing alkyllead compounds, such as triethyllead bromide, may also be used in the compositions of this invention.

Typical dialkyl phosphoramidates useful in the practice of this invention include diethyl phosphoramidate, dipropyl phosphoramidate, diisopropyl phosphoramidate, ethylpropyl phosphoramidate, ethylisopropyl phosphoramidate, propylisopropyl phosphoramidate, ethylisoamyl phosphoramidate, propyl-3-hexyl phosphoramidate, ethyldecyl phosphoramidate, and the like. Preferred dialkyl phosphoramidates used according to this invention are typified by and include dibutyl phosphoramidate, diisobutyl phosphoramidate, di-sec-butyl phosphoramidate, ditert butyl phosphoramidate, di-sec-amyl phosphoramidate, dihexyl phosphoramidate, diheptyl phosphoramidate, dioctyl phosphoramidate, dinonyl phosphoramidate, didecyl phosphoramidate, butylamyl phosphoramidate, hexyloctyl phosphoramidate, and the like. Of these preferred dialkyl phosphoramidates, those in which both alkyl groups contain the same number of carbon atoms are especially preferred because of their low cost and ease of manufacture. Mixtures of these dialkyl phosphoramidates can also be used.

The dialkyl phosphoramidates used according to this invention can be prepared by known chemical methods which are reported in the literature. One such method is to react ammonia with a dialkyl phosphoryl chloride in which each alkyl group contains from 2 to 10 carbon atoms. The ammonia is added to the chloride in a 100 mole percent excess of the amount required to replace the phosphorus-bonded chlorine. In general, the above reaction is carried out at a temperature between about 0 and about 50° C. It is advantageous to carry this reaction

out in a suitable solvent such as diethyl ether, petroleum ether, or the like.

The dialkyl phosphoryl chlorides are obtainable by reacting phosphoryl chloride with the appropriate monohydric alcohol or mixture of monohydric alcohols under known reaction conditions. About two moles of the alcohol are reacted per mole of phosphoryl chloride using a Lewis acid catalyst and temperatures between about 80 and 140° C.

The organic halide scavengers used in the compositions of this invention are compounds which react with the lead during combustion in the engine to form relatively volatile lead halides. The halogen of these scavengers has an atomic weight between 35 and 80; that is, the active scavenging ingredient is chlorine and/or bromine. Such scavengers include ethylene dibromide; ethylene dichloride; carbon tetrachloride; propylene dibromide; 2-chloro-2,3 - dibromobutane; 1,2,3-tribromopropane; hexachloropropylene; mixed bromoxylenes; 1,4-dibromobutane; 1,4-dichloropentane; β,β'-dibromodiisopropyl ether; trichlorobenzene; dibromotoluenes; tert-butyl bromide; 2-methyl-2-bromobutane; 2,3,3-trimethyl-2-bromobutane; tert-butyl chloride; 2,3-dimethyl-2,3-dibromobutane; 2,3-dimethyl-2,5-dibromohexane; 2-methyl - 2,3 - dibromobutane; 2-methyl-2,3-dichloroheptane; 2-methyl-2,4-dibromohexane; 2,4-dibromopentane; 2,5-dichlorohexane; 3-methyl-2,4-dibromopentane; 1-phenyl - 1 - bromoethane; 1-phenyl-1-chloroethane; ethyl - α - bromoacetate; diethyl-dibromomalonate; propyl-α-chlorobutyrate; 1,1-dichloro-1-nitroethane; 1,1-dichloro-2-nitroethane; 1,1-dibromo-1-nitrobutane; 2-chloro - 4 - nitropentane; 2,4-dibromo-3-nitropentane; 1-chloro-2-hydroxyethane; 1-bromo-3-hydroxypropane; 1-bromo-3-hydroxybutane; 3-methyl-2-bromo-4-hydroxypentane; 3,4-dimethyl-2-bromo-4-hydroxypentane; and, in general, scavengers disclosed in U.S. Patents 1,592,954; 1,668,022; 2,364,921; 2,479,900; 2,479,901; 2,479,902; 2,479,903 and 2,496,983. In short, it is preferred to employ halogenated scavengers containing only carbon and elements selected from the group consisting of hydrogen, bromine, chlorine, nitrogen and oxygen. Particularly preferred scavengers are halohydrocarbons, that is, bromohydrocarbons, chlorohydrocabons, and bromochlorohydrocarbons having a vapor pressure from 0.1 to 250 millimeters of mercury at 50° C. The total amount of scavenger used is preferably from about 0.5 to about 2.0 theories, a theory being defined as the quantity required to react with the lead to form lead halide—i.e., 2 atoms of halogen per atom of lead. This amount can be in the form of a single compound or a mixture of compounds. However, when I use mixtures of bromine-containing and chlorine-containing scavengers, particularly bromo- and chlorohydrocarbons as the scavenger complement, I can employ a wider range of concentrations in the proportions described in U.S. Patent 2,398,281. Thus, the scavenger concentrations used are those which are sufficient to control the amount of deposits formed in the engine, particularly on the exhaust valves.

The compositions of this invention can contain other ingredients, such as dyes for identification purposes; metal deactivators, such as N,N' - disalicylidene-1,2-diaminopropane, etc.; anti-icing and anti-rust additives; upper cylinder lubricants; induction system cleanliness agents; antioxidants, such as N,N'-di-sec-butyl-p-phenylenediamine, p-alkylamino phenols, alkyl phenols, etc.; and the like.

My antiknock fluids may be used in a variety of hydrocarbon base stocks boiling within or throughout the gasoline boiling range. This range is from about 80 to about 420° F. for motor gasolines, while the endpoint of aviation fuels is in the order of about 310–335° F. Thus, the improvements can be made in fuels resulting from thermal and catalytic cracking processes, reforming, hydroforming and alkylating procedures; in straight-run gasolines; and in various blends of gasoline hydrocarbons.

This application is a continuation-in-part of my prior copending application Serial No. 526,317, filed August 3, 1955, now abandoned.

I claim:

1. Gasoline containing from about 0.02 to about 6.5 grams of lead per gallon as an alkyllead antiknock compound, a scavenging amount of an organic halide scavenger capable of reacting with the lead during combustion in a spark ignition internal combustion engine to form relatively volatile lead halide, and a dialkyl phosphoramidate ester in which each alkyl group contains from 2 to 10 carbon atoms, said phosphoramidate ester being present in amount such that the phosphorus-to-lead atom ratio is from about 0.1:3 to about 1.6:3.

2. Gasoline containing from about 0.02 to about 6.5 grams of lead per gallon as tetraethyllead, a bromohydrocarbon and chlorohydrocarbon scavenger complement present in amount sufficient to control the amount of deposits formed in the engine, and a dialkyl phosphoramidate ester in which each alkyl group contains from 4 to 10 carbon atoms said phosphoramdiate ester being present in amount such that the phosphorus-to-lead atom ratio is from about 0.1:3 to about 1.6:3.

3. An antiknock composition adapted for use as an additive for gasoline consisting essentially of an alkyllead antiknock compound, a scavenging amount of an organic halide scavenger capable of reacting with the lead during combustion in a spark ignition internal combustion engine to form relatively volatile lead halide, and a dialkyl phosphoramidate ester in which each alkyl group contains from 2 to 10 carbon atoms, said phosphoramidate ester being present in amount such that the phosphorus-to-lead atom ratio is from about 0.1:3 to about 1.6:3.

4. An antiknock composition adapted for use as an additive for gasoline consisting essentially of tetraethyllead, a scavenging amount of ethylene dibromide and ethylene dichloride capable of reacting with the lead during combustion to form relatively volatile lead halide, and a dialkyl phosphoramidate ester in which each alkyl group contains from 4 to 10 carbon atoms, said phosphoramidate ester being present in amount such that the phosphorus-to-lead atom ratio is from about 0.1:3 to about 1.6:3.

5. The gasoline composition of claim 1 in which said phosphoramidate is dibutyl phosphoramidate.

6. The antiknock composition of claim 3 in which said phosphoramidate is dibutyl phosphoramidate.

References Cited in the file of this patent

UNITED STATES PATENTS

2,405,560	Campbell	Aug. 13, 1946
2,765,220	Yust et al.	Oct. 2, 1956
2,794,717	Gilbert	June 4, 1957
2,797,153	Bereslavsky	June 25, 1957
2,828,195	Yust et al.	Mar. 25, 1958
2,863,743	Pellegrini et al.	Dec. 9, 1958
2,878,255	Toy et al.	Mar. 17, 1959
2,897,068	Pellegrini et al.	July 28, 1959

FOREIGN PATENTS

683,405	Great Britain	Nov. 26, 1952
708,006	Great Britain	Apr. 28, 1954
709,471	Great Britain	May 26, 1954
1,094,828	France	Dec. 15, 1954
1,100,185	France	Mar. 30, 1955

OTHER REFERENCES

Ind. and Eng. Chem. March 1948, vol. 40, No. 3, "Suitability of Gasolines as Fuel," by James and Morris, pp. 405–411.

Ind. and Eng. Chem. March 1951, vol. 43, No. 3, "Antiknock Antagonists," by Livingston, pages 663–670.