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ANTIKNOCK COMPOSITIONS

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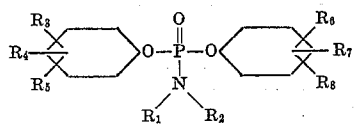
This invention relates to improved liquid fuel for spark ignition internal combustion engines and to composite additives for such fuel.

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 provides 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.

An object of this invention is to provide composite additives for spark ignition internal combustion engine fuels capable of substantially reducing surface ignition without causing loss of antiknock effectiveness. Another object is to provide improved liquid fuel for spark ignition internal combustion engines 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 an antiknock composition adapted for use an an additive for spark ignition internal combustion engine fuel comprising an alkyllead antiknock compound and, in amount sufficient to reduce surface ignition, a phosphoramidate having the general formula



where R_1 and R_2 are selected from the group consisting of hydrogen and alkyl radicals containing from 1 to 2 carbon atoms, and R_3, R_4, R_5, R_6, R_7 and R_8 are selected from the group consisting of hydrogen and alkyl radicals containing from 1 to 3 carbon atoms. Preferred phosphoramidates for the compositions of this invention are those in which R_1 and R_2 are both hydrogen and in

which both of the phenyl groups of the above general formula are substituted with at least one alkyl group containing from 1 to 3 carbon atoms, i.e., at least one of R_3, R_4 and R_5 and at least one of R_6, R_7 and R_8 of the above formula is an alkyl radical containing from 1 to 3 carbon atoms. These latter phosphoramidates are preferred because of their very high gasoline solubility, ease of manufacture and low cost. The foregoing antiknock compositions preferably contain a scavenger complement, although this is not essential to the present invention since my scavenger-free leaded fuels may be used in special applications, such as in break-in schedules of engines and in experimental studies of engine behavior. In all such special applications, the normal deterimental surface ignition rate is virtually eliminated by my scavenger-free fuels. Furthermore, the combination of an alkyllead antiknock agent and a phosphoramidate as defined above is very useful in blending operations because it permits great flexibility in the selection of the scavenger complement which may be used therewith in formulating finished gasolines for various general purposes.

The superior fuels of this invention are provided when the above alkyllead antiknock compositions are blended in antiknock quantities with liquid hydrocarbon fuel of the gasoline boiling range. Amounts of lead from about 0.02 to about 6.5 grams of lead per gallon can be used. Higher concentrations of alkyllead compounds may be used, such as in the preparation of gasoline-type fuels for the above special applications and in the preparation of concentrated leaded gasoline solutions which are diluted during blending operations to prepare finished fuels of this invention.

The amount of the above phosphoramidates used in the compositions of this invention is from about 0.05 to about 0.8 theory of phosphorus, a theory of phosphorus being the quantity required to react with the lead to form lead orthophosphate, i.e., 2 atoms of phosphorus per each 3 atoms of lead. In other words, the amount of phosphoramidates so used is such that the phosphorus-to-lead atom ratio is from about 0.1:3 to about 1.6:3. Greater or lesser amounts of the phosphoramidates may be employed depending upon such factors as the type of engine operation to be incurred, the octane quality of the fuel used, and the like. Best over-all results are achieved from compositions of this invention which contain the above-defined phosphoramidates in amounts such that the phosphorus-to-lead atom ratio is from about 0.4:3 to about 1:3. Such amounts are preferred.

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 between the alkyllead and phosphoramidate ingredients. Moreover, these improved benefits are obtained with virtually no loss in antiknock effectiveness of the alkyllead ingredient.

A striking feature of the phosphoramidates employed according to this invention is that for some unknown reason they do not interfere with the antiknock effectiveness of alkyllead antiknock agents. Thus, during engine combustion the phosphoramidate ingredient exerts its highly beneficial functions yet does not exhibit any antagonism toward the alkyllead antiknock agent. This is a very unexpected feature of the present phosphoramidates because phosphorus compounds in general have heretofore been reported as being among the most serious antagonists for tetraethyllead antiknock agents. Thus, the present invention not only provides highly unexpected results, but is an important contribution in 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 homogeneity, use is made of conventional methods of physical agitation, such as stirring, shaking, or the like. The order of addition of the ingredients during formulation is not critical. Thus, an alkyllead compound may be added to a phosphoramidate, a phosphoramidate may be added to an alkyllead compound, or these ingredients may be introduced into the blending apparatus concurrently. When a scavenger complement is employed, is can be added to an alkyllead-phosphoramidate blend which has been preformed as described above or the scavenger complement can be introduced into the blender concurrently with the other ingredients. However, it is desirable to take advantage of the enhanced solubility of some of the above phosphoramidates in or in the presence of scavengers and thereby reduce the time of the blending operation. This can be done by dissolving the phosphoramidate in the scavenger and blending this solution with an alkyllead compound, or by blending the phosphoramidate to a preformed mixture of an alkyllead compound and scavenger. The same blending procedures can be used when other ingredients are to be incorporated into the composite additives of this invention.

Representative alkyllead antiknock compositions of this invention—i.e., composite additives—are represented in Table I. The figures following the representative ingredients are parts by weight. The two figures following the phosphoramidate ingredient 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	Phosphoramidate
Tetramethyllead 267	None	Di-(3,5-dimethylphenyl-phosphoramidate 10.2–162.7.
Do	Ethylene dibromide 226.	Di(phenyl)-N-methyl-phosphoramidate 8.8–140.3.
Do	Ethylene dibromide 94 and ethylene dichloride 99.	Di-(4-n-propylphenyl)-phosphoramidate 12.3–196.8.
Tetraethyllead 323	None	Di-(3-ethylphenyl)-N-ethylphosphoramidate 11.1–177.6.
Do	Ethylene dibromide 188.	Di-(3-methylphenyl)-phosphoramidate 9.2–147.7.
Do	Ethylene dibromide 94 and ethylene dichloride 99.	Di-(2-methylphenyl)-phosphoramidate 9.2–147.7.
Do	Ethylene dibromide 113 and ethylene dichloride 99.	Di-(3-methylphenyl)-phosphoramidate 9.2–147.7.
Do	Mixed dibromotoluenes 200.	(Phenyl)(4-isopropyl-phenyl) phosphoramidate 10.9–174.4.
Do	Mixed dibromotoluenes 125 and ethylene dichloride 99.	Di-(phenyl)N,N-diethylphosphoramidate 10.2–162.7.
Do	Mixed dibromotoluenes 150 and 1,2,4-trichlorobenzenes 175.	Di-(3-methyl-4-ethylphenyl) phosphoramidate 11.1–177.6.
Do	Ethylene dibromide 94 and mixed trichlorobenzenes 146.	Di-(3,4,5-tri-n-propylphenyl)-N-methylphosphoramidate 17.2–274.7.
Do	1,4-dibromobutane 216.	Di-(phenyl)phosphoramidate 8.3–132.8.
Do	1,4-dibromobutane 108 and 1,4-dichlorobutane 127.	Di-(3,4,5-triisopropylphenyl)-N,N-diethylphosphoramidate 18.6–297.1.
Tetrapropyllead 379	Acetylene tetrabromide 346.	(2-methylphenyl)-(3,5-diethylphenyl)-phosphoramidate 10.6–170.1.
Dimethyldiethyllead 295.	β,β′-Dibromodiethylether 232.	Di-(4-methylphenyl)-N-methylphosphoramidate 9.7–155.2.
Methyltriethyllead 309.	β,β′-Dibromodiisopropyl ether 130 and β,β′-dichlorodiethyl ether 143.	Di-(4-ethylphenyl)-N,N-dimethylphosphoramidate 11.1–177.6.

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.

A variety of 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 a gasoline-type fuel 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 phosphoramidate separately to the fuel before, after or at the same time an alkyllead antiknock agent or 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 subcombinations 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 ten gallons of gasoline, a fuel composition of this invention containing 0.5 gram of lead per gallon as the lead alkyl antiknock agent is prepared. The respective higher figures following each ingredient show the amount in grams thereof which are blended with ten gallons to provide a lead content of 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.; end point, 402° F.

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

Base Fuel C: An aviation gasoline of grade 100/300 comprising isopentane, alkylate, aromatics and straight-run gasolines. Initial boiling point, 82° F.; end point, 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.; end point 368° F.

Table II.—Antiknock fuel compositions

Base Fuel	Antiknock Agent	Scavenger	Phosphoramidate
A	Tetramethyllead 6.4–83.8.	Ethylene dichloride 2.4–31.1.	Di-(4-isopropylphenyl)phosphoramidate 1.2–15.4.
A	Tetraethyllead 7.8–101.4.	Ethylene dibromide 2.3–29.5 and ethylene dichloride 2.4–31.1.	Di-(3-methylphenyl)-phosphoramidate 0.9–11.6.
B	do	Ethylene dibromide 2.7–35.4 and ethylene dichloride 2.4–31.1.	Di-(4-methylphenyl)-phosphoramidate 0.9–11.6.
B	do	Mixed dibromotoluenes 3.6–47.1 and ethylene dichloride 2.9–37.3.	Di-(3-ethylphenyl) N-methylphosphoramidate 1.0–13.4.
C	do	None	Di-(phenyl)-N,N-diethylphosphoramidate 1.0–12.8.
C	do	1,4-dibromobutane 5.2–67.8.	(Phenyl)(4-ethylphenyl)-phosphoramidate 0.9–11.6.
D	Tetrabutyllead 10.5–136.6.	Mixed dibromotoluenes 3.0–39.1 and 1,2,4-trichlorobenzene 2.9–37.9.	Di-(phenyl)phosphoramidate 0.8–10.4
D	Trimethylethyllead 6.8–88.2.	1,3-dibromopropane 2.4–31.7 and β,β′-dichlorodiethyl ether 3.5–44.9.	Di-(2-methylphenyl) N-methylphosphoramidate 0.9–12.2.

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 test. This engine was operated on a commercially available gasoline containing about 3.2 grams of lead 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. Individual portions of the same leaded fuel were then treated with typical phosphoramidates of this invention in amount such that the phosphorus-to-lead atom ratio was about 0.4:3. The engine was then operated on these fuels and the effect of the presence of these phosphoramidates determined. For comparative purposes, tricresylphosphate was blended in another portion of the same leaded fuel at a phosphorus-to-lead atom ratio of about 0.4:3 and the test repeated. The results of these experiments are shown in Table III.

Table III.—Effect of phosphorus additives on surface ignition rate

Phosphorus Additive	Surface Ignitions, No./Hr.	Reduction in Surface Ignition Rate, Percent
None	115	
Di-(3-methylphenyl)phosphoramidate	9	92
Di-(3-methylphenyl)-N-ethyl-phosphoramidate	7	94
Tricresylphosphate	37	68

It is obvious from the data in Table III that the typical phosphoramidates of this invention reduced the surface ignition rate well about 90 percent. In contrast, tricresylphosphate reduced surface ignition rate by only 68 percent. Thus, the number of surface ignitions which occurred during any given period of engine operation using typical phosphoramidates of this invention was less than one-fourth of the rate which occurred when using tricresylphosphate.

The results shown above are illustrative of the enhanced surface ignition suppressing 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 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 alkyl antiknock agent during the cooperation of this agents and the phosphoramidate additives of this invention. This exceptional characteristic of my phosphoramidate additives was clearly demonstrated by conducting a series of comparative engine tests.

Individual portions of a representative motor gasoline containing about 3.2 grams of lead per gallon as tetraethyllead as an antiknock fluid comprising tetraethyllead, 0.5 theory of bromine as ethylene dibromide and 1.0 theory of chlorine as ethylene dichloride—each portion containing a given concentration of phosphorus—were subjected to the standard ASTM Motor Method, Test Procedure D–357 (which can be found in the 1953 edition of "ASTM Manual of Engine Test Methods for Rating Fuels"). In these tests typical additives of this invention were tested at phosphorus-to-lead atom ratios of 0.4:3 and 1:3. As a comparison, tributylphosphite, an additive suggested heretofore, was tested under identical conditions at the same phosphorus-to-lead atom ratios. The results of these engine tests are shown in Table IV.

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

Phosphorus Additive	Tetraethyllead Effectiveness Destroyed, Percent	
	P:Pb=0.4:3	P:Pb=1:3
Di-(methylphenyl)-phosphoramidate [1]	0	0
Do.[2]	0	0
Do.[3]	0	0
Dicresyl phosphoramidate [4]	0	0
Dixylyl phosphoramidate [5]	0	0
Di-(3-methylphenyl)-N-methyl phosphoramidate	0	0
Tributyl phosphite	5	24

[1] A mixture of 3- and 4-methylphenyl isomers.
[2] Made from U.S.P. grade coal tar cresol.
[3] Made from coal tar cresol.
[4] Made from petroleum cresylic acid which contains cresols and xylenols.
[5] Mixed xylenol isomers.

It is clear from the data in Table IV that the phosphoramidates of this invention did not interfere with the antiknock effectiveness of tetraethyllead even when used at the relatively high concentration of a phosphorus:lead atom ratio of 1:3. Tributyl phosphite destroyed substantial amounts of tetraethyllead effectiveness.

The pre-eminence of the 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 Research Method, Test Procedure D–908 (which can be found in the 1953 edition of "ASTM Manual of Engine Test Methods for Rating Fuels") was used. The gasoline contained 3.2 grams of lead per gallon as tetraethyllead, 0.5 theory of bromine as ethylene dibromide and 1.0 theory of chlorine as ethylene dichloride. In the present tests the representative additives of this invention used were mixed di-(methylphenyl)-phosphoramidates, di-(3-methylphenyl)-N-methyl phosphoramidate, di-(3-methylphenyl)-N-ethyl phosphoramidate and dixylyl phosphoramidate. Tricresyl phosphate and triethyl phosphate were also tested under the same conditions. The results of these tests are shown in Table V.

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

Phosphorus Additive	Tetraethyllead Effectiveness Destroyed, Percent	
	P:Pb=0.4:3	P:Pb=1:3
Di-(methylphenyl)-phosphoramidate [1]	0	0
Di-(3-methylphenyl)-N-methylphosphoramidate	0	0
Di-(3-methylphenyl)-N-ethylphosphoramidate	0	0
Dixylyl phosphoramidate [2]	0	0
Tricresyl phosphate	3	3
Triethyl phosphate	8	17

[1] A mixture of 3- and 4-methylphenyl isomers.
[2] Mixed xylenol isomers.

Again the phosphoramidate additives of this invention exhibited no adverse effect upon the antiknock effectiveness of tetraethyllead, whereas tricresyl phosphate and triethyl phosphate caused a significant amount of this adverse effect. Thus, the phosphoramidate additives of this invention virtually eliminate deposit-induced engine problems without incurring alkyllead antagonism. As shown by the data in Tables III, IV and V, additives suggested heretofore not only are less effective in controlling

deposit-induced engine problems, but exhibit a substantial degree of alkyllead antagonism.

The exceptional characteristic of the phosphoramidate additives of this invention in not interfering with the antiknock effectiveness of the alkyllead antiknock agents during engine combustion is still further shown by the results of another series of engine tests. In these tests two commercially available high octane quality gasolines were used. To one of these—Fuel A—which contained 3 milliliters of tetraethyllead per gallon, ethylene dibromide and ethylene dichloride, was added varying amounts of dixylyl phosphoramidate so that a series of five fuels of this invention was provided. These fuels differed to the extent that they contained dixylyl phosphoramidate in amount such that the phosphorus-to-lead atom ratios were 0.2:3, 0.4:3, 0.6:3, 0.8:3 and 1:3, respectively. Each of these fuels was then subjected to the standard ASTM Research Method of the octane number of the fuel determined. The research octane number of the leaded, phosphorus-free gasoline was also measured. The same procedure was then repeated with the other base gasoline—Fuel B—which also contained 3 milliliters of tetraethyllead per gallon. In addition, still other samples of leaded Fuel B were treated with dicresyl phosphoramidate to provide a similar series of five different phosphorus-to-lead atom ratios. The results of this extensive series of engine tests are shown in Table VI.

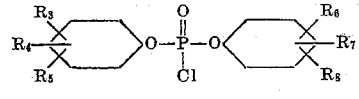
Table VI.—Effect of phosphoramidate additives on tetraethyllead antiknock effectiveness

Fuel	Phosphoramidate	Atom Ratio, P:Pb	Octane Number
A	None	P-free	98.6
A	Dixylyl phosphoramidate	0.2:3	98.6
A	do	0.4:3	98.7
A	do	0.6:3	98.7
A	do	0.8:3	98.6
A	do	1:3	98.9
B	None	P-free	98.7
B	Dixylyl phosphoramidate	0.2:3	98.7
B	do	0.4:3	98.7
B	do	0.6:3	98.7
B	do	0.8:3	98.7
B	do	1:3	98.7
B	None	P-free	98.7
B	Dicresyl phosphoramidate [1]	0.2:3	98.7
B	do	0.4:3	98.7
B	do	0.6:3	98.7
B	do	0.8:3	98.7
B	do	1:3	98.7

[1] Made from petroleum cresylic acid which contains cresols and xylenols.

It will be seen from the data in Table VI that in no case did the presence of the additives of this invention cause any reduction in the octane number of the leaded gasoline.

The 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, methylamine, dimethylamine, ethylamine, diethylamine or methylethylamine with a di-(phenyl)-phosphoryl monochloride having the general formula



in which R_3 through R_8 inclusive are as defined hereinabove. The above primary or secondary alkylamines or ammonia are added in a 100 mole percent excess of the amount required to replace the phosphorus-bonded chlorine. Such excess amount acts as an acceptor of hydrogen chloride.

In general, the above reaction is carried out at a temperature between about 0 to about 50° C. When conducting such reactions, it is advantageous to use a suitable solvent, such as diethyl ether, petroleum ether, or the like.

The di-(phenyl)phosphoryl monochlorides of the above general formula are obtainable by reacting phosphoryl trichloride and the appropriate phenol or mixture of phenols under known reaction conditions. About two moles of the phenol are reacted per mole of phosphoryl trichloride using a Lewis acid catalyst, and temperatures between about 80 and 140° C.

Typical phosphoramidates as above defined and used according to this invention include di-(phenyl)phosphoramidate, (phenyl) - (4 - methylphenyl)phosphoramidate, di-(phenyl)-N-methylphosphoramidate, di-(2 - ethylphenyl)-N-methylphosphoramidate, di-(3,5 - dimethylphenyl)-N-methylphosphoramidate, di-(3,5-diisopropylphenyl)-N-methylphosphoramidate, (4 - methylphenyl)-(4-n-propylphenyl)-N-methylphosphoramidate, di-(phenyl)-N,N-dimethylphosphoramidate, di - (4 - methylphenyl)-N,N-dimethylphosphoramidate, (3,5-diethylphenyl) - (4-isopropylphenyl)-N,N-dimethylphosphoramidate, di-(3-methylphenyl) - N - ethylphosphoramidate, di-(4 - ethylphenyl)-N,N - diethylphosphoramidate, di - (4 - methylphenyl)-N-methyl-N-ethylphosphoramidate, and the like. Preferred phosphoramidates used according to this invention are typified by and include di-(2-methylphenyl)phosphoramidate, di - (3 - methylphenyl)phosphoramidate, di-(4-methylphenyl)phosphoramidate, di-(2,4-dimethylphenyl)-phosphoramidate, di-(3,5 - dimethylphenyl)phosphoramidate, di-(4-ethylphenyl)phosphoramidate, di-(3,5-diethylphenyl)phosphoramidate, di - (3 - n - propylphenyl)phosphoramidate, di-(4-isopropylphenyl)phosphoramidate, di-(3,4,5 - triisopropylphenyl)phosphoramidate, (4 - methylphenyl)-(3,5-diethylphenyl)phosphoramidate, di-(2,3-dimethylphenyl)phosphoramidate, di-(2,5-dimethylphenyl)-phosphoramidate, di-(3,4 - dimethylphenyl)phosphoramidate, di-(2,6-dimethylphenyl)phosphoramidate, and the like. These preferred phosphoramidates exhibit a surprisingly high solubility in gasoline despite the fact that they are free from alkyl substitution on the nitrogen atom. Moreover, these preferred phosphoramidates are easily made and are relatively inexpensive.

Mixtures of the foregoing phosphoramidates can be used according to this invention. For example, mixed phosphoramidates prepared from petroleum cresylic acids or coal tar-derived cresylic acids (both of which are composed principally of various cresols and xylenols) are well suited for the preparation of the improved antiknock compositions of this invention.

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, such as triethyllead bromide may also be used in the compositions of this invention.

The scavengers which are preferably, but not necessarily present in the compositions of this invention are organic halide compounds which react with the lead during combustion in the engine to form volatile lead halide. 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; β,β'-dichlorodi-

ethyl ether; trichlorobenzene; dibromotoluene; 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 employed 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, chlorohydrocarbons, 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 used 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 phosphoramidate additives of this invention having one or two lower alkyl substituents on the nitrogen atom are soluble in alkyllead antiknock compounds, alkyllead antiknock fluids and in gasoline-type fuel in excess of the amounts used to impart thereto the improvements of this invention. The same high solubility in these media exists in the case of my preferred phosphoramidates, i.e., those in which the nitrogen atom is substituted with two hydrogen atoms and in which both phenyl groups are substituted with at least one alkyl group containing from one to three carbon atoms. Thus, additional solvents for these additives are unnecessary. The other phosphoramidates of this invention are also sufficiently soluble in the above media under normal conditions of temperature. However, under special conditions, such as when blending is to occur at subzero temperatures or when highly concentrated stock solutions are to be employed in blending operations, a solvent may be advantageously employed. Particularly suitable solvents include benzene, toluene, xylene, acetone, methylethyl ketone, methanol, ethanol, isopropanol, methylisobutylcarbinol, and the like. In general, ketones and alcohols containing up to about 6 carbon atoms and aromatic hydrocarbons containing 6 to 18 carbon atoms are excellent solvents. Formulations of the phosphoramidates of this invention using such solvents are also very useful in refinery operations where the phosphoramidate is to be blended into the gasoline apart from the alkyllead antiknock agent or conventional antiknock fluid.

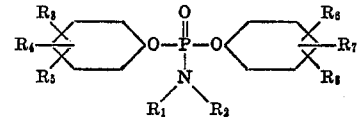
The antiknock compositions of this invention can contain other ingredients, such as dyes for identification purposes; metal deactivators, such as N,N'-disalicylidene-1,2-diaminopropane, etc.; other antiknock agents, such as the carbonyls of iron, nickel and like elements; aromatic amines such as N-methylaniline, xylindine, etc.; anti-icing and anti-rust additives; other surface ignition control additives; upper cylinder lubricants; induction system cleanliness agents; antioxidants, such as N,N'-di-sec-butyl-p-phenylene diamine, 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. A hydrocarbon fuel of the gasoline boiling range adapted for use in spark ignition internal combustion engines containing an antiknock quantity of an alkyllead antiknock compound, said quantity being from about 0.02 to about 6.5 grams of lead per gallon of said fuel and, in amount sufficient to reduce surface ignition, a phosphoramidate having the general formula



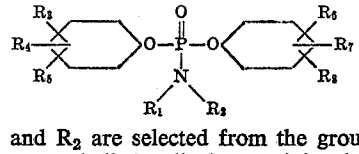
wherein R_1 and R_2 are selected from the group consisting of hydrogen and alkyl radicals containing from one to two carbon atoms, and R_3, R_4, R_5, R_6, R_7 and R_8 are selected from the group consisting of hydrogen and alkyl radicals containing from one to three carbon atoms.

2. The composition of claim 1 in which said phosphoramidate is di-(methylphenyl)-phosphoramidate.

3. The composition of claim 1 in which said phosphoramidate is dixylyl phosphoramidate.

4. A hydrocarbon fuel of the gasoline boiling range adapted for use in spark ignition internal combustion engines containing an antiknock quantity of tetraethyllead, said quantity being from about 0.02 to about 6.5 grams of lead per gallon of said fuel, a bromohydrocarbon and chlorohydrocarbon scavenger complement present in amount sufficient to control the amount of deposits formed in the engine, and di-(methylphenyl)-phosphoramidate present in amount such that the phosphorus-to-lead atom ratio is from about 0.1:3 to about 1.6:3.

5. An antiknock composition adapted for use as an additive for spark ignition internal combustion engine fuel consisting essentially of an alkyllead antiknock compound and a phosphoramidate having the general formula



wherein R_1 and R_2 are selected from the group consisting of hydrogen and alkyl radicals containing from one to two carbon atoms, and R_3, R_4, R_5, R_6, R_7 and R_8 are selected from the group consisting of hydrogen and alkyl radicals containing from one to three carbon atoms, the phosphorus-to-lead atom ratio of said composition being from about 0.1:3 to about 1.6:3.

6. The composition of claim 5 in which said phosphoramidate is di-(methylphenyl)phosphoramidate.

7. The composition of claim 5 in which said phosphoramidate is dixylyl phosphoramidate.

8. A hydrocarbon fuel of the gasoline boiling range adapted for use in spark ignition internal combustion engines containing an antiknock quantity of tetraethyllead, said quantity being from about 0.02 to about 6.5 grams of lead per gallon of said fuel, a bromohydrocarbon and chlorohydrocarbon scavenger complement present in amount sufficient to control the amount of deposits

formed in the engine, and dixylyl phosphoramidate present in amount such that the phosphorous-to-lead atom ratio is from about 0.1:3 to about 1.6:3.

9. An improved antiknock composition adapted for use as an additive for spark ignition internal combustion engine fuel consisting essentially of tetraethyllead, a scavenger amount of ethylene dibromide and ethylene dichloride capable of reacting with the lead during combustion in a spark ignition engine, and di-(methylphenyl)-phosphoramidate present in amount such that the phosphorus-to-lead atom ratio is from about 0.1:3 to about 1.6:3.

10. An improved antiknock composition adapted for use as an additive for spark ignition internal combustion engine fuel consisting essentially of tetraethyllead, a scavenging amount of ethylene dibromide and ethylene dichloride capable of reacting with the lead during combustion in a spark ignition engine, and dixylyl phosphoramidate present in amount such that the phosphorus-to-lead atom ratio is from about 0.1:3 to about 1.6:3.

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