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LEAD SCAVENGER COMPOSITIONS

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This invention relates to compositions which are useful as scavengers with lead anti-knock compounds.

The use of lead compounds in gasolines to increase the octane ratings thereof is extremely widespread. There are, however, several rather serious adverse effects which accompany the use of leaded gasolines. One of these effects, the deposition of various lead compounds within the combustion chambers of the engines has been at least partially remedied by the use of halo-hydrocarbon scavengers such as ethylene dibromide. Another adverse effect, which has been attributed to the lead anti-knock compounds, is mis-firing of the engine due to spark plug fouling. This spark plug fouling is quite prevalent under conditions of high temperature engine operation and, particularly in the case of aircraft engines, is a very serious type of trouble.

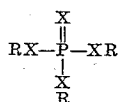
It is, therefore, an object of the present invention to overcome the previous shortcomings arising from the use of leaded gasolines. It is a further object to provide novel scavenger compositions for use with lead anti-knock compounds and in gasoline fuels. Another object is to provide novel fuel compositions containing said scavenger compositions. Other objects will be apparent hereinafter.

It has now been found that the use, as a lead scavenger in leaded gasoline fuel compositions, of a mixture of a halo-hydrocarbon scavenger and of a smaller amount of certain phosphorus compounds will result in greatly improved operation of spark ignition internal combustion engines. More particularly, the use of such scavenger compositions substantially eliminates spark plug fouling, or at least minimizes such fouling to a point where it is no longer a material consideration in engine operation. This outstanding advantage is obtained without having the anti-knock characteristics of the fuel deleteriously affected by the presence of the scavenger compositions.

The phosphorus compounds in the present scavenger compositions will be referred to hereinafter as "anti-fouling compounds."

The halo-hydrocarbon scavenger which makes up the major proportion of the scavenger compositions of the present invention may be, for example, any of the numerous halogen scavenger compounds already known, such as ethylene dibromide and ethylene dichloride (U. S. 2,398,281), acetylene tetrabromide (U. S. 2,490,606), hexachloropropylene, mono- and polyhalo propanes, butanes and pentanes (U. S. 2,479,900 and U. S. 2,479,902), polyhalo alkyl benzenes (U. S. 2,479,901 and U. S. 2,479,903), and the like, having a volatility between about 100 and about 0.1 mm. Hg at 50° C.

The phosphorus anti-fouling compounds of the present invention are compounds having the following formula:



wherein X is O, S, or NR, and R is a hydrogen atom or an organic radical, at least one R being an alicyclic radical.

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A preferred group of the foregoing class of compounds, obtained when X is an oxygen atom, is made up of the alicyclic phosphate esters.

It will be noted that at least one of the R's in the above formula must be an alicyclic radical. So long as this requirement is satisfied, the remaining R's may be either hydrogen atoms or other organic radicals such as alkyl, alkenyl, aryl, heterocyclic, alkaryl, aralkyl, etc. It is preferred, however, that all of the R's be organic radicals, and it is further preferred that they all be alicyclic radicals. Best results are obtained when the alicyclic ring is attached directly to the oxygen or sulfur atom or NR group of the above formula rather than being attached through some other radical, such as through an aliphatic chain.

The present phosphate esters and analogues thereof, may be partial esters or acid esters, but neutral esters are preferred. Likewise mixed esters can be utilized, but it is preferred that all of the R groups be the same.

The alicyclic group required in the present anti-fouling agents is a carbocyclic group, and preferably a monocyclic group, of non-aromatic character; it can be either saturated or unsaturated, but must not contain that peculiar type of resonating unsaturation typical of aromatic compounds. Alkyl (and other aliphatic hydrocarbon) groups containing up to about 12 or 15 carbon atoms, substituted upon the alicyclic groups markedly increase the anti-fouling effectiveness of the present phosphorus compounds. A multiplicity of such substitutions, e. g., two or three methyl, ethyl or propyl groups, is very advantageous. While substituents other than hydrocarbon radicals do not, in general, adversely affect the efficiency of the phosphorus compounds as anti-fouling agents, it is preferred that the R groups be unsubstituted hydrocarbyl radicals.

When using the scavenger compositions of the present invention, the total amount of halogen scavenger plus anti-fouling agent present will generally fall between about 0.6 and about 1.5 theories, based upon the lead content of the gasoline, but may advantageously be as low as 0.4 or as high as 2.0 in some cases. The preferred range is from about 0.9 to about 1.2 theories.

The ratio of the two components of the scavenger composition is rather important. For example, if the proportion of halogen scavenger present is too large, excessive wear and corrosion of certain operating parts, such as exhaust valves and valve guides, is noted. If too small a quantity of halogen scavenger is used, the lead deposits are not effectively scavenged. If too small a quantity of the anti-fouling compound is used, the spark plug fouling will not be materially reduced; and if too much of that compound is present, the amounts of deposits and the plug fouling are both increased. In general, the theory ratio of the halogen scavenger or scavengers to the anti-fouling agents should be between about 3:2 and about 100:1. For best results this ratio should be between about 2:1 and about 15:1. As an additional limitation, the total scavenger mixture and the ratio of components therein should be adjusted so that the anti-fouling compound is present in an amount of between about 0.01 and about 0.6 theories, and preferably between about 0.05 and about 0.4 theories. A particularly desirable composition comprises 1 theory of the halogen scavenger and 0.1 theory of the anti-fouling compound. It is preferred that the weight concentration of the anti-fouling additive in the fuel be kept below 0.1%. It is to be understood that more than one of the compounds from each class (i. e., halogen scavenger or anti-fouling agent), may be used in any single composition, just so the total quantity of each type falls within the limits set forth above.

The term "theory," when used in conjunction with a halogen scavenger compound, designates the amount of scavenger required to react stoichiometrically with a given

amount of lead anti-detonant so that all of the lead atoms and all of the halogen atoms form $PbBr_2$ or $PbCl_2$. In other words, a theory of scavenger is an amount which contains two atomic proportions of halogen for each atomic proportion of lead in the anti-detonant or, a theory of the halohydrocarbon scavenger is one mol of the halohydrocarbon scavenger divided by one-half the number of halogen atoms per molecule, for each gram atom of lead in the lead anti-detonant present, and therefore, the number of theories of halohydrocarbon scavenger present in a given composition is equal to the number of mols of halohydrocarbon scavenger present multiplied by one-half the number of halogen atoms per molecule, for each gram atom of lead in the lead anti-detonant present. As applied to the anti-fouling compounds, the term "theory" designates the amount required to react stoichiometrically with the lead so that all of the lead atoms and all of the phosphorus atoms form $Pb_3(PO_4)_2$. Therefore a theory of the anti-fouling compound is one mol thereof multiplied by two-thirds (that is, two thirds of a mol of the anti-fouling compound), for each gram atom of lead in the lead anti-detonant present, and therefore the number of theories of anti-fouling compound present in a given composition is equal to the number of mols of the anti-fouling compound present multiplied by three-halves, for each gram atom of lead in the lead anti-detonant present.

While it is to be understood that the present compositions may be utilized in any leaded gasoline fuel, the compositions are of particular importance with respect to use in reciprocating internal combustion engine gasoline fuels, and especially such aviation fuels. This is true because of the relatively more frequent occurrence of spark plug fouling in aviation engines, with the greater inherent danger to human life in the case of failures of such engines. In addition to the lead anti-detonant and the scavenger composition, the gasoline fuels, or the concentrates for addition thereto may also contain corrosion inhibitors and stabilizers, such as 2,4-dimethyl-6-tertiary-butylphenol and other alkyl phenols, N,N'-dibutyl p-phenylene diamine, hydroquinone, phenyl-alpha-naphthylamine, N-butyl-p-aminophenol, alpha-naphthol, etc., dyes and the like.

By the term "leaded gasoline," and the terms of similar import, is meant a petroleum fraction boiling in the gasoline hydrocarbon range (between about 50° F. and about 450° F.) to which has been added a small amount, usually between about 1 and about 6 cc. per gallon, of a metallo-organic, usually an organo-lead, anti-knock compound, such as a tetra-alkyl lead, e. g., tetra-ethyl lead, tetra-i-propyl lead, etc.

The fuels to which the present scavenger compositions are added are preferably those which are relatively stable with respect to oxidation or gum formation. The stability may result from the use of stable base stocks such as aviation alkylate, straight run gasoline fractions, or other fractions which have been highly refined to remove olefins, or the stability may result from the use of oxidation stabilizers, such as those mentioned above. A few phosphorus compounds are known to have slight oxidation inhibiting properties, but these properties are very weak. It is much preferred that an additional oxidation inhibitor, i. e., a non-phosphorus stabilizer, be used in the present gasoline compositions. Thus, the gasoline fuels to which the present anti-fouling agents are added should preferably be sufficiently stable that the addition of the normal amount of anti-fouling agent will have no substantial effect upon the oxidation stability of the fuel—e. g., the anti-fouling agents will not decrease gum formation in such fuels by more than about 5 or 10 percent.

As indicated above, the scavenger compositions of this invention are particularly useful in aviation gasoline. By the term "aviation gasoline" is meant a relatively high grade of gasoline fuel used in aviation engines, as distinguished from the lower quality gasolines, or "motor fuels" used in automotive engines. Aviation fuels have

a more closely specified boiling range, generally running from a minimum of about 100° F. to a maximum of about 350° F. The anti-knock quality of aviation fuel is considerably higher than that of motor fuel. Some grades have anti-knock ratings appreciably higher than that of 100 octane number gasoline. Because of the demand for high quality, thermally cracked fractions are never used in aviation gasolines. Catalytically cracked fractions may sometimes be used, but only after treatment to remove olefins. One of the reasons for the restrictions upon incorporation of cracked gasolines in aviation fuels is that the oxidation stability of aviation fuels must be much greater than that required for motor fuels. For example, when tested according to a method such as described in the patent issued to Thomas W. Bartram, U. S. 2,256,187, an aviation fuel base stock will go well beyond 4 or 5 hours before the oxygen pressure will have decreased by 5 pounds per square inch.

The following are examples of compositions suitable for use according to the present invention:

Example I

Tetra-ethyl lead
1.0 theory ethylene dibromide
0.2 theory tricyclohexyl phosphate

Example II

Tetra-ethyl lead
1.0 theory ethylene dibromide
0.1 theory tri-(2,4-dimethylcyclohexyl) phosphate

Example III

Tetra-ethyl lead
1.0 theory ethylene dibromide
0.1 theory tri-(4-ethylcyclohexyl)thionophosphate

Example IV

Tetra-ethyl lead
1.0 theory acetylene tetrabromide
0.4 theory 2,6-dimethylcyclohexyl di-(n-butyl) phosphate

Example V

80 octane aviation gasoline containing, per gallon:
0.5 cc. tetra-ethyl lead
1.0 theory ethylene dibromide
0.2 theory tri-(4-allylcyclohexyl) phosphate
0.02 gr. 2,4-dimethyl-6-tert.-butylphenol

Example VI

Aviation alkylate containing, per gallon:
4.6 cc. tetra-ethyl lead
1.0 theory ethylene dibromide
0.04 gr. 2,4-dimethyl-6-tert.-butylphenol
0.1 theory tri-(3,3,5-trimethylcyclohexyl) phosphate

Example VII

Tetra-ethyl lead
1.2 theories hexachloropropylene
0.2 theory S,S-di-(2-methyl-4-ethylcyclohexyl) acid dithiolphosphate

Example VIII

Tetra-ethyl lead
0.8 theory ethylene dibromide
0.2 theory 3,3,5-trimethylcyclohexyl diacid phosphate

Example IX

Tetra-ethyl lead
1.5 theories hexachlorobutadiene-1,3
0.1 theory tri-(2,6-dimethyl-4-bromocyclohexyl) phosphate

Example X

76 octane motor fuel containing, per gallon:
2.1 cc. tetra-ethyl lead
1.0 theory ethylene bromide

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0.5 theory ethylene dichloride
 0.2 theory tri-(4-(1,1,3,3-tetramethylbutyl) cyclohexyl) phosphate
 0.06 gr. N, N'-dibutyl p-phenylene diamine

Example XI

115/130 grade aviation gasoline containing, per gallon:
 4.6 cc. tetra-ethyl lead
 1.0 theory ethylene dibromide
 0.2 theory tribornyl phosphate
 0.04 gr. 2,4-dimethyl-6-tert.-butylphenol

Example XII

Tetra-ethyl lead
 0.5 theory ethylene dibromide
 0.1 theory tri-(2,6-dimethyl-4-t-butylcyclohexyl) phosphate

Example XIII

Tetra-ethyl lead
 1.0 theory ethylene dibromide
 0.1 theory tri-(cyclohexenyl-2-) phosphate

Example XIV

Motor gasoline containing, per gallon:
 1.6 cc. tetra-ethyl lead
 1.0 theory hexachloroethane
 0.2 theory N,N',N''-tricyclohexyl phosphoric amide
 0.06 gr. N-butyl-p-aminophenol

Example XV

Tetra-ethyl lead
 1.0 theory ethylene dibromide
 0.05 theory tri-(3-methylcyclohexyl) thiophosphate

Example XVI

Tetra-ethyl lead
 1.0 theory ethylene dibromide
 0.5 theory ethyl di-(4-methylcyclohexyl) phosphate

Example XVII

Tetra-ethyl lead
 1.0 theory ethylene dichloride
 0.1 theory tricyclopentyl phosphate

Example XVIII

Tetra-ethyl lead
 1.0 ethylene dibromide
 0.5 theory ethylene dichloride
 0.5 theory tri(2-i-propyl-5-methylcyclohexyl) phosphate

It is to be understood that the order of mixing the various constituents of the present compositions is immaterial. For example, the anti-fouling compound may be added to a gasoline which already contains the anti-knock compound and halogen scavenger. Likewise, the metallo-organic anti-knock agent, the halogen scavenger and the anti-fouling compound may be first mixed, stored and handled as a concentrate, and added to the gasoline at a later time. A typical concentrate of this latter type has approximately the following composition:

	Weight, percent
Tetra-ethyl lead	50-65
Ethylene dibromide	25-40
Tri-(3,3,5-trimethylcyclohexyl) phosphate	3-15
Kerosene, inhibitor, dye stabilizer, etc.	3-6

Under other circumstances it may be desirable to mix the halogen scavenger and the anti-fouling agent, or the anti-knock agent and the anti-fouling agent, in the desired relative proportions and handle or store this mixture, with or without stabilizers, inhibitors, etc., as a concentrate for later incorporation with the other components of the ultimate fuel composition. Thus, a typical suitable scavenger concentrate consists essentially of ethylene dibromide and tris-(3,3,5-trimethylcyclohexyl) phosphate

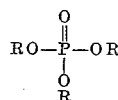
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in the relative proportions of 25-40 and 3-15 parts by weight, respectively.

The present application is a continuation-in-part of our copending application, Serial No. 242,309, filed August 17, 1951, which is in turn a continuation of our application, Serial No. 167,376, filed June 10, 1950, now abandoned.

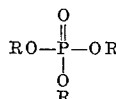
We claim as our invention:

1. A fuel composition for internal combustion spark ignition engines consisting essentially of a stable gasoline, a minor effective anti-detonant amount of a tetra lower alkyl lead anti-detonant, and a mixture consisting essentially of a halohydrocarbon scavenger for said anti-detonant and of a spark plug anti-fouling phosphorus compound having the formula:



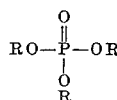
wherein each R is a hydrocarbon cyclohexyl radical containing no more than 15 substituent alkyl carbon atoms; said halohydrocarbon scavenger and said phosphorus compound being present in amounts such that where *a* is the number of mols of said halohydrocarbon scavenger present multiplied by one-half the number of halogen atoms per molecule, for each gram atom of lead in the lead anti-detonant present, and *b* is the number of mols of said phosphorus compound present multiplied by three-halves, for each gram atom of lead anti-detonant present, the total of *a* plus *b* is from about 0.4 to about 2.0, *b* is from about 0.01 to about 0.6, and the ratio of *a* to *b* is from about 3:2 to about 100:1.

2. A gasoline additive composition for use with a gasoline fuel for internal combustion spark ignition engines consisting essentially of a tetra lower alkyl lead anti-detonant and a mixture consisting essentially of a halohydrocarbon scavenger for said antidetonant and of a spark plug anti-fouling phosphorus compound having the formula:



wherein each R is a hydrocarbon cyclohexyl radical containing no more than 15 substituent alkyl carbon atoms; said halohydrocarbon scavenger and said phosphorus compound being present in amounts such that where *a* is the number of mols of said halohydrocarbon scavenger present multiplied by one-half the number of halogen atoms per molecule, for each gram atom of lead in the lead anti-detonant present, and *b* is the number of mols of said phosphorus compound present multiplied by three-halves, for each gram atom of lead anti-detonant present, the total of *a* plus *b* is from about 0.4 to about 2.0, *b* is from about 0.01 to about 0.6, and the ratio of *a* to *b* is from about 3:2 to about 100:1.

3. A lead scavenging composition for use with a leaded anti-detonant gasoline fuel for internal combustion spark ignition engines consisting essentially of a halohydrocarbon scavenger and of a spark plug anti-fouling phosphorus compound having the formula



wherein each R is a hydrocarbon cyclohexyl radical containing no more than 15 substituent alkyl carbon atoms; said halohydrocarbon scavenger and said phosphorus compound being present in amounts such that where *a* is the number of mols of said halohydrocarbon scavenger present multiplied by one-half the number of halogen atoms per molecule, and *b* is the number of mols

of said phosphorus compound present multiplied by three-halves, the ratio of *a* to *b* is from about 3:2 to about 100:1.

4. A composition in accordance with claim 1 wherein *b* is from about 0.05 to about 0.4.

5. A composition in accordance with claim 1 wherein each R is an alkyl-substituted cyclohexyl radical.

6. A composition in accordance with claim 1 wherein each R is a polyalkyl-substituted cyclohexyl radical.

7. A composition in accordance with claim 1 wherein the tetra lower alkyl lead anti-detonant is tetraethyl lead and the phosphorus compound is tri-(3,3,5-trimethylcyclohexyl) phosphate and the gasoline is an aviation gasoline boiling within the range 100° F. and 350° F., containing no thermally cracked gasoline fractions and no olefinic catalytically cracked gasoline fractions.

8. A composition in accordance with claim 1 wherein the stable gasoline is a stabilized automotive gasoline, the tetra lower alkyl lead anti-detonant is tetraethyl lead, the halohydrocarbon scavenger is a mixture of ethylene dibromide and ethylene dichloride, and the phosphorus compound is tri-(3,3,5-trimethylcyclohexyl) phosphate.

9. A composition in accordance with claim 1 wherein the stable gasoline is a stable aviation gasoline, the tetra lower alkyl lead anti-detonant is tetraethyl lead, the halohydrocarbon scavenger is ethylene dibromide, and *b* is from about 0.05 to about 0.4.

10. A composition in accordance with claim 1 wherein the stable gasoline is a stable aviation gasoline boiling within the range 100° F. and 350° F., containing no

thermally cracked gasoline fractions and no olefinic catalytically cracked gasoline fractions, the tetra lower alkyl lead anti-detonant is tetraethyl lead, the halohydrocarbon scavenger is ethylene dibromide, the phosphorus compound is tri-(3,3,5-trimethylcyclohexyl) phosphate, *a* is about 1.0 and *b* is about 0.1.

11. A composition in accordance with claim 1 wherein the stable gasoline is a stabilized automotive gasoline, the tetra lower alkyl lead anti-detonant is tetraethyl lead, the halohydrocarbon scavenger is a mixture of ethylene dibromide and ethylene dichloride, the phosphorus compound is tri-(3,3,5-trimethylcyclohexyl) phosphate, *a* is about 1.5 and *b* is about 0.2.

12. A composition in accordance with claim 1 wherein the tetra lower alkyl lead anti-detonant is tetraethyl lead and the phosphorus compound is tricyclohexyl phosphate.

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