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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 halohydrocarbon scavengers such as ethylene dibromide. Another adverse effect, which has been attributed to the lead anti-knock compounds, is misfiring 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. Another object to to provide novel compounds for the above and other uses. Other objects will be apparent hereinafter.

It has now been found that the use, as a lead scavenger in leaded fuel compositions, of a mixture of a halohydrocarbon scavenger and of a smaller amount of a phosphite and/or phosphate containing at least one and preferably more than one heterocyclic radical, and preferably hydrocarbyl-substituted heterocycle radical linked to the phosphorus atom through a chalcogen preferably oxygen or sulfur in the molecule, will result in greater 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 other necessary characteristics (such as stability, performance rating, etc.) of the fuel deleteriously affected to any material degree by the presence of the scavenger compositions.

The heterocyclic containing phosphites and/or phosphates of the present invention will be referred to hereinafter as "anti-fouling compounds" or "anti-fouling agents."

The halohydrocarbon scavenger which makes up the major proportion of the scavenger compositions of the present invention may be, for example, any one or more 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 particular phosphites and/or phosphates of the present invention can be readily prepared by reacting phosphorus halides, e. g., PCl_3, PCl_5, PBr_3, phosphorus oxyhalides, e. g., $POCl_3$: phosphorus oxides, e. g., phosphorus pentaoxide or phosphorus sulfides (P_4S_3, P_2S_5) and mixtures thereof with hydroxy and/or mercapto containing five and six member heterocyclic ring compounds and preferably such heterocyclic compounds which contain attached to the ring a hydrocarbyl radical such as alkyl, alkary, aralkyl radicals. The higher molecular weight alkyl groups, up to about 12 or 15 are preferred.

The essential heterocyclic group required in the present anti-fouling agents can be a five or six member heterocyclic group, preferably monoheterocyclic group. Alkyl (and other aliphatic hydrocarbon) groups containing a total up to about 12 or 15 carbon atoms, substituted upon the heterocyclic groups markedly increase the anti-fouling effectiveness of the present anti-fouling 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 compounds of this invention as anti-fouling agents, it is preferred that the substituent groups be unsubstituted hydrocarbyl radicals.

A preferred class of above compounds are the polyalkyl substituted heterocyclic derivatives of phosphorus, namely, polyalkyl six member oxygen, sulfur or nitrogen-containing heterocyclic phosphates.

Representative examples of heterocyclic compounds include, furfuryl alcohol, 2-methyl furfuryl alcohol, 2,4-dimethyl furfuryl alcohol, dihydrobenzo furfuryl alcohol, tubaic acid, waxyl thiophenyl alcohol, waxyl pyridyl alcohol, 2,4-dimethyl pyranyl alcohol, maltol, tocopherol, quinolinol, hydro quinolinol, waxyl quinolinol, 2,4-dimethyl quinolinol, dihydroxy anthraquinone, 2,4 - dimethyl furfuryl mercaptan, waxyl thiophenethiol, pyridyl mercaptan.

A preferred compound, is tris(tetra-hydropyran-2-methyl) phosphate. Other specific compounds include tris(waxyl thienyl) phosphate, di(2-methyl thienyl) acid phosphate, tris(2,4-dimethyl furfuryl) phosphate, tris-(tocopheryl) phosphate, 2,4-dimethyl quinolinyl phosphate, tris(waxyl thienyl) phosphite, tri(2,4-dimethyl pyranyl) phosphite, tris(waxyl furfuryl) phosphite, S,S,S, tris(waxyl furfuryl) thiophosphate, S,S,S tris-(waxyl thienyl) thiophosphate, tritocopheryl thionophosphate, S,S,S tris(2-methyl furfuryl) thiophosphite, di-(3,5,5-trimethyl cyclohexyl) furfuryl phosphate, di(2,5-dimethyl phenyl) thienyl phosphate, di(2,4-dimethyl quinolinyl) cresyl phosphate, dicresyl(tetrahydropyran-2-methyl) phosphate.

The phosphorus compounds of this invention can be supplied to the combustion zone of the engine in various ways to accomplish reduction in fouling of spark plugs due to the combustion of leaded fuels therein. Thus, they can be injected directly into the combustion zone, separately from either or both the fuel and the anti-detonant, or injected directly and separately into the intake manifold, either intermittently or substantially continuously, as desired, or they can be incorporated with the leaded fuel. They can be added separately to the leaded fuel, or they can be blended first with either the gasoline or the anti-detonant; in the latter case, an anti-detonant, scavenger and anti-foulant concentrate is suitably prepared which can be stored and shipped as such and blended with the gasoline as desired.

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

Example I

Tetra-ethyl lead
1.0 theory ethylene dibromide
0.2 theories tris(tetrahydropyran-2-methyl) phosphate

Example II

Tetra-ethyl lead
1.0 theory ethylene dibromide
0.1 theory tris(waxyl thienyl) phosphate

Example III

Tetra-ethyl lead
1.0 theory ethylene dibromide
0.1 theory tris(2,4-dimethyl furfuryl) phosphate

Example IV

Tetra-ethyl lead
1.0 theory acetylene tetrabromide
0.4 theory tritocopheryl phosphate

Example V

80 octane aviation gasoline containing, per gallon
0.5 cc. tetra-ethyl lead
1.0 theory ethylene dibromide
0.2 theory tris(tetrahydropyran-2-methyl)phosphite
0.02 gr. 2,4-dimethyl-6-tertiary-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-tertiary-butylphenol
0.1 theory di(3,5,5-trimethylcyclohexyl) furfuryl phosphate

Example VII

Tetra-ethyl lead
1.2 theories hexachloropropylene
0.2 theory tris(waxyl thienyl) phosphite

Example VIII

Tetra-ethyl lead
0.8 theory ethylene dibromide
0.2 theory dicresyl(tetrahydropyran-2-methyl) phosphate

Example IX

Tetra-ethyl lead
1.5 theories hexachlorobutadiene-1,3
0.1 theory S,S,S tris(waxyl furfuryl) thiophosphate

Example X

76 octane motor fuel containing, per gallon
2.1 cc. tetra-ethyl lead
1.0 theory ethylene dichloride
0.5 theory ethylene dibromide
0.2 theory tritocopheryl phosphite
0.06 gr. N,N'-dibutyl p-phenylene diamine

As already indicated, 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:

	Wt. percent
Tetra-ethyl lead	55–60
Ethylene dibromide	25–30
Tris(tetra-hydropyran-2-methyl) phosphate	10–15
Kerosene, inhibitor, dye stabilizer, etc	3–6

Under other circumstances it may be desirable to mix the halogen scavenger and the anti-fouling agents, 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.

When using the scavenger compositions of the present invention, the total amount of halogen scavenger plus anti-fouling agent 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 both may be 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 theory, and preferably between about 0.1 and about 0.2 or if desired between about 0.05 and about 0.4 theory. A particularly desirable composition comprises 1 theory of the halogen scavenger and 0.1 theory of the anti-fouling compound. 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 could be in the form of $Pb_3(PO_4)_2$. 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 spark ignition 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 compositions, 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 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. The term "stable gasoline" as used herein refers to gasoline fuels having a maximum of 5 mg. existent gum per 100 ml. of fuel (ASTM D–381–50), and a maximum of 10 mg. of gum per 100 ml. of gasoline after accelerated aging for 16 hours at 100° C. and 100 p. s. i. O_2 pressure. (The foregoing gum values apply to the fuel before addition of non-volatile additives, such as the anti-fouling agents of the present invention.)

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 clearly specified boiling range, generally running from a minimum of about 100° F. to a maximum of about 350° F. The anti-knock rating of such fuels is often 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 present application is a continuation-in-part of our copending application Serial No. 242,309, filed August 17, 1951, now abandoned, 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 engines consisting essentially of a stable gasoline, a minor effective anti-detonant amount of a tetra lower alkyl lead anti-detonant, and a scavenger mixture for said anti-detonant consisting essentially of a halohydrocarbon scavenger and of a phosphorus compound selected from the group consisting of tri-heterocyclic phosphates and tri-heterocyclic phosphites, each heterocyclic ring of which contains from 5 through 6 atoms consisting of carbon and only a single atom selected from the group consisting of oxygen, sulfur and nitrogen and each heterocyclic group of which is attached to the phosphorus atom through a chalcogen atom having an atomic number of from 8 through 16, 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 in the 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 fuel additive composition consisting essentially of a tetra lower alkyl lead anti-detonant and a scavenger mixture for said anti-detonant consisting essentially of a halohydrocarbon scavenger and of a phosphorus compound selected from the group consisting of tri-heterocyclic phosphates and tri-heterocyclic phosphites each heterocyclic ring of which contains from 5 through 6 atoms consisting of carbon and only a single atom selected from the group consisting of oxygen, sulfur and nitrogen and each heterocyclic group of which is attached to the phosphorus atom through a chalcogen atom having an atomic number of from 8 through 16, 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 in the 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 gasoline fuel for internal combustion engines which gasoline fuel contains tetra-lower-alkyl-lead anti-detonant consisting essentially of a halohydrocarbon scavenger and of a phosphorus compound selected from the group consisting of tri-heterocyclic phosphates and tri-heterocyclic phosphites, each heterocyclic ring of which contains from 5 through 6 atoms consisting of carbon and only a single atom selected from the group consisting of oxygen, sulfur and nitrogen and each heterocyclic group of which is attached to the phosphorus atom through a chalcogen atom having an atomic number of from 8 through 16, 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 the heterocyclic groups of the phosphorus compounds are hydrocarbyl-substituted-heterocyclic groups.

5. A composition in accordance with claim 1, wherein the chalcogen atom is oxygen.

6. A composition in accordance with claim 1, wherein the chalcogen atom is sulfur.

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

8. A composition in accordance with claim 1, wherein the phosphorus compound is tris(tetrahydropyranyl-2-methyl) phosphate and wherein the gasoline is an aviation gasoline boiling within the range between about 100° F. and 350° F., having an octane number higher than 100 and containing no thermally cracked gasoline fractions and no olefinic catalytically cracked gasoline fractions.

9. A composition in accordance with claim 1, wherein the phosphorus compound is tris(2,4-dimethylfurfuryl) phosphite.

10. A composition in accordance with claim 4, wherein

the heterocyclic groups of the phosphorus compounds are polyalkyl-substituted heterocyclic groups.

11. A fuel composition for internal combustion engines consisting essentially of a stabilized automotive gasoline a minor effective anti-detonant amount of tetraethyl lead, and a scavenger mixture for said tetraethyl lead consisting essentially of ethylene dibromide, ethylene dichloride and tris(tetrahydropyranyl-2-methyl) phosphate, said ethylene dibromide, ethylene dichloride and said tris(tetrahydropyranyl-2-methyl) phosphate being present in amounts such that where *a* is the total number of mols of ethylene dibromide and ethylene dichloride present for each mol of tetraethyl lead present and *b* is the number of mols of tris(tetrahydropyranyl-2-methyl) phosphate present multiplied by three-halves, for each mol of tetraethyl lead 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.

12. A fuel composition for internal combustion engines consisting essentially of a stable aviation gasoline boiling within the range between about 100° F. and 350° F., having an octane number higher than 100 and containing no thermally cracked gasoline fractions and no olefinic catalytically cracked gasoline fractions, a minor effective anti-detonant amount of tetraethyl lead, and a scavenger mixture for said tetraethyl lead consisting essentially of ethylene dibromide and tris(tetrahydropyranyl-2-methyl) phosphate, said ethylene dibromide being present in an amount such that the number of mols of ethylene dibromide, for each mol of tetarethyl lead present, is about 1.0, and said tris(tetrahydropyranyl-2-methyl) phosphate being present in an amount such that the number of mols of tris(tetrahydropyranyl-2-methyl) phosphate multiplied by three-halves, for each mol of tetraethyl lead present, is about 0.1.

13. A composition in accordance with claim 10, wherein each polyalkyl-substituted heterocyclic group of the phosphorus compound contains from 2 to 3 alkyl substituent groups of 1 to 3 carbon atoms each.

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