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ANTIKNOCK FLUIDS

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The instant invention relates to improved antiknock fluids which, when blended in fuels for internal combustion engines, provide products of superior performance qualities. This application is a continuation-in-part of my co-pending application, Serial No. 313,615, filed October 7, 1952, and now abandoned.

Shortly after the pioneering discovery of the antiknock effectiveness of organolead compounds, particularly tetraethyllead, it became apparent that commercial utilization of such antiknock agents depended upon providing a method for reducing the amount of lead salts which accumulated on engine parts. Accordingly, this reduction in the deposition of lead salts has been accomplished by providing corrective agents or scavengers for use with organolead antiknock agents. Such mixtures of organolead antiknock agents and scavengers are known in the art as antiknock fluids. The use of fuels containing these antiknock fluids causes the lead to be converted to fairly volatile lead salts which are discharged from the engine in the exhaust gas stream. Many corrective agents or scavengers have been proposed of which the most successful have been organic bromine and chlorine compounds, notably ethylene dibromide and ethylene dichloride. Thus, for commercial purposes, the most successful antiknock composition for use in aviation fuels has been a mixture of tetraethyllead and ethylene dibromide, the dibromide being present in an amount of one theory, which is the quantity theoretically required to stoichiometrically react with all the tetraethyllead to form lead dibromide. Such a composition has two bromine atoms for each atom of lead. In the case of automotive fluids, the most efficacious composition comprises tetraethyllead in admixtures with one-half theory of bromine as ethylene dibromide and one theory of chlorine as ethylene dichloride. However, in spite of the high efficiency of scavenging produced by such compositions, the deposition of a certain amount of lead salts on engine parts is not entirely prevented.

One of the more serious problems directly attributed to such deposits is spark plug failure, commonly termed "spark plug fouling." This results from the formation on the spark plug insulators of deposits that are somewhat electrically conductive, thereby unduly lowering the electrical resistance between the spark plug electrodes. When this resistance becomes too low, the production of a spark at the spark gap is prevented. To inhibit such spark plug failures, it has been proposed in the prior art to utilize phosphorous-containing materials as additives to leaded fuels. In this manner the lead deposits become converted to lead phosphates, which have higher electrical resistivities and are less prone to cause spark plug fouling.

The phosphorus-containing materials have been proposed as additives to supplement or to partially or totally replace halide scavengers. Although satisfactory engine operation can be obtained with such compositions, it has been found that the alleviation of spark plug fouling is attained at the expense of exhaust valve life. As will be more apparent from the discussion hereinafter, this serious reduction in exhaust valve life is ultimately the result of exhaust valve burning and corrosion which are promoted by such phosphorus-containing materials when

employed in accordance with the teachings of the prior art. More particularly this reduction in exhaust valve life is a reduction in the length of time during which the valve operates without either excessive leakage or in extreme cases by mechanical failure because of the separation of the valve head from its stem. Such effects in turn result from corrosion and/or burning away of the valve, particularly at its head and throat area. The local removal of metal from the valve face causes valve leakage, and the removal of metal from the throat area can so weaken the resistance of the valve to tensile stresses that the valve stretches in length and may even break apart. Corrosion and burning is most readily measured by the weight loss of the valve.

Among the objects of the present invention is the provision of improved antiknock fluids and fuels which obviate spark plug fouling and also improve exhaust valve life. Other important objects of the present invention will become apparent from the following description of some of its exemplifications.

It has been discovered that excessive corrosion and burning of exhaust valves caused by the addition of the phosphorous-containing spark plug anti-fouling compound to the above composition is strikingly decreased by a critical increase in the organic bromine content of the scavenger. At the same time, this increase does not significantly impair any of the other operating or storage characteristics of the fuels or fluids.

This effect is quite unexpected since in the absence of the phosphorus-containing material, an increase in halogen content, and particularly bromine, was known to cause excessive exhaust valve corrosion and burning. For some unexplained reason, however, when the added bromine content is present along with the phosphorus compounds, neither is effective to produce the expected corrosion and burning. On the other hand, the phosphorus compounds in such a composition still produce their anti-fouling results.

The critical increase in the organic bromine content of the scavenger used in combination with the phosphorus-containing, organolead compositions according to this invention is a 15 to 20 percent increase above the bromine scavenger content used in standard commercial practice. In aviation applications, this practice has been the provision of one theory of bromine as a bromine scavenger, the bromine:lead atom ratio therefore being 2:1. In automotive applications, this practice has been the provision of 0.5 theory of bromine as a bromine scavenger and 1.0 theory of chlorine as a chlorine scavenger, in which case the bromine:lead atom ratio was 1:1.

According to this invention greatly enhanced engine performance is achieved by improving an antiknock composition consisting essentially of organolead material as the principal antiknock ingredient, organic halogen scavenger material of the class of that providing two atoms of chlorine plus one atom of bromine per atom of lead, and that providing two atoms of bromine per atom of lead, and a phosphorus-containing spark plug anti-fouling compound, the phosphorus-to-lead atom ratio of said composition being from about 0.02:3 to about 0.7:3 by increasing the bromine content of the organic halogen scavenger material by about 15 to 20 percent.

One embodiment of this invention is an antiknock composition consisting essentially of an organolead antiknock compound—preferably a lead alkyl antiknock compound—a phosphorus-containing spark plug anti-fouling

compound present in amount such that the phosphorus-to-lead atom ratio of said composition is from about 0.02:3 to about 0.7:3, and an organic halogen scavenger complement selected from the group consisting of (1) an organic bromine scavenger capable of reacting with the lead during engine combustion to form volatile lead salts containing bromine and present in amount such that the bromine-to-lead atom ratio is from about 2.3:1 to about 2.4:1; and (2) a mixture of an organic chlorine scavenger and an organic bromine scavenger capable of reacting with the lead during engine combustion to form volatile lead salts containing chlorine and bromine, said organic chlorine scavenger being present in amount such that the chlorine-to-lead atom ratio is about 2:1 and said organic bromine scavenger being present in amount such that the bromine-to-lead atom ratio is from about 1.15:1 to about 1.2:1. Another embodiment of this invention is hydrocarbons of the gasoline boiling range containing an antiknock quantity of the above antiknock compositions. Such antiknock quantity ranges from about 0.5 to about 6.3 grams of lead per gallon of gasoline.

The amount of phosphorus-containing material used is generally between the limits of 0.01 to 0.35 theory of phosphorus, one theory of phosphorus being defined in the amount of phosphorus theoretically required to react with the lead to form lead orthophosphate, which quantity is two atoms of phosphorus per three atoms of lead. On a phosphorus-to-lead atom ratio basis, the above amounts to from 0.02:3 to 0.7:3. Particularly favorable results can be obtained with amounts of phosphorus-containing materials contributing at least 0.05 theory of phosphorus. More than 0.2 theory of phosphorus is not as desirable as the lower concentration. On a phosphorus-to-lead atom ratio basis, this particularly favorable range is from 0.1:3 to 0.4:3.

The above improvements are obtained without exception from all types of phosphorus compounds that are soluble in the fuel in the above proportions. It is preferable to use organo-phosphorus materials, that is, materials in which phosphorus is linked either directly to a carbon atom in an organic radical, or is linked to an organic radical through oxygen, nitrogen or sulfur. However, inorganic compounds, such as triphosphonitrilic chloride ($[PNCl_2]_3$) and tetraphosphorus trisulfide (P_4S_3), are also effective. The organic phosphorus-containing materials include phosphines and related compounds; halophosphines; halophosphine halides and phosphonyl halides; quaternary phosphonium compounds; tertiary phosphine oxides and sulfides; phosphinous, phosphonous and phosphonic acids, the sulfur analogs and esters of the aforesaid acids, phosphites and thiophosphites; phosphates; halophosphates and thio analogs; compounds with phosphorus-to-nitrogen bonds; and derivatives of anhydro phosphorus acids.

As used in the discussion hereinafter, the term organic radicals denotes a univalent aliphatic, alicyclic or aromatic radical which can be further substituted with negative radicals, such as hydroxy, halide and the like. By the term univalent aliphatic radical is intended a univalent radical derived from an open chain saturated or unsaturated carbon compound, that is, an acyclic radical. The term univalent alicyclic radical denotes a monovalent radical derived from the corresponding aliphatic compounds by ring formation. The term univalent aromatic radical denotes a monovalent radical derived from a compound of the benzene series containing a ring with the peculiar type of unsaturation inherent in such aromatic compounds.

Thus, when the organic radical or radicals of the organo-phosphorus materials of the improved antiknock fluids of the present invention is a univalent aliphatic radical or radicals, such can be a radical or radicals selected from the group consisting of alkyl, alkenyl, aralkyl, and aralkenyl. Consequently, when the organic radical or radicals of the organophosphorus materials described hereinafter is a univalent aliphatic radical, it can be an alkyl radical, such as for example, methyl, ethyl n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, t-butyl, n-amyl, and the various positional isomers thereof as, for example, 1-methylbutyl; 2-methylbutyl; 3-methylbutyl; 1,1-dimethylpropyl; 1,2-dimethylpropyl; 2,2-dimethylpropyl and 1-ethylpropyl, and likewise the corresponding straight and branched chain isomers of hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octodecyl, nondecyl, eicosyl and the like. In addition, the univalent aliphatic radical or radicals of the organophosphorus materials of the improved antiknock fluids of this invention can be an alkenyl radical, such as for example, ethenyl; Δ^1-propenyl; Δ^2-propenyl; isopropenyl; Δ^1-butenyl; Δ^2-butenyl; Δ^3-butenyl, and the corresponding branched chain isomers thereof as, for example, Δ^1-isobutenyl; Δ^2-isobutenyl; Δ^1-sec-butenyl; Δ^2-sec-butenyl; Δ^1-pentenyl; Δ^2-pentenyl; Δ^3-pentenyl; Δ^4-pentenyl, and the corresponding branched chain isomers thereof; Δ^1-hexenyl; Δ^2-hexenyl; Δ^3-hexenyl; Δ^4-hexenyl; Δ^5-hexenyl; and the corresponding branched chain isomers thereof, including 3,3-dimethyl-Δ^1-butenyl; 2,3-dimethyl-Δ^1-butenyl; 2,3-dimethyl-Δ^2-butenyl; 2,3-dimethyl-Δ^3-butenyl; and 1-methyl-1-ethyl-Δ^2-propenyl; and similarly, the various isomers of heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, hexadecenyl, heptadecenyl, octodecenyl, nondecenyl, eicosenyl, and the like. Moreover, when the organic radical or radicals of the organophosphorus materials described hereinafter is a univalent aliphatic radical, it can be an aralkyl radical, such as for example, benzyl; α-phenyl-ethyl; β-phenyl-ethyl; α-phenyl-propyl; β-phenyl-propyl; γ-phenyl-propyl; α-phenyl-isopropyl; β-phenyl-isopropyl; α-phenyl-butyl; β-phenyl-butyl; γ-phenyl-butyl; δ-phenyl-butyl; α-phenyl-isobutyl; β-phenyl-isobutyl; γ-phenyl-isobutyl; α-phenyl-sec-butyl; β-phenyl-sec-butyl; γ-phenyl-sec-butyl; β-phenyl-t-butyl; α'-naphthyl-methyl; β'-naphthyl-methyl; α-(α'-naphthyl)-ethyl; α-(β'-naphthyl)-ethyl; β-(α'-naphthyl)-ethyl; β-(β'-naphthyl)-ethyl; α-(α'-naphthyl)-propyl; α-(β'-naphthyl)-propyl; β-(α'-naphthyl)-propyl; β-(β'-naphthyl)propyl; γ-(α'-naphthyl)-propyl; γ - (β'-naphthyl)-propyl; α - (α'-naphthyl)-isopropyl; α-(β'-naphthyl)-isopropyl; α-(α'-naphthyl)-butyl; α-(β'-naphthyl)-butyl; β-(α'-naphthyl)-butyl; β-(β'-naphthyl)butyl; γ-(α'-naphthyl)-butyl; γ-(β'-naphthyl)-butyl; δ-(α'-naphthyl)-butyl; δ-(β'-naphthyl)-butyl; α-(α'-naphthyl)-isobutyl; α-(β'-naphthyl)-isobutyl; β-(α'-naphthyl)-isobutyl; β-(β'-naphthyl)-isobutyl; γ-(α'-naphthyl)-isobutyl; γ-(β'-naphthyl)-isobutyl; α-(α'-naphthyl)-sec-butyl; α - (β'-naphthyl)-sec-butyl; β - (α'-naphthyl)-sec-butyl; β-(β'-naphthyl)-sec-butyl; γ - (α'-naphthyl)-sec-butyl; γ-(β'-naphthyl)-sec-butyl; β - (α'-naphthyl)-t-butyl; β-(β'-naphthyl)-t-butyl; the corresponding α'- and β'-naphthyl derivatives of n-amyl and the various positional isomers thereof such as, for example, said derivatives of 1-methyl-butyl; 2-methyl-butyl; 3-methyl-butyl; 1,1-dimethyl-propyl; 1,2-dimethyl-propyl; 2,2-dimethyl-propyl; 1-ethyl-propyl, and likewise said derivatives of the corresponding isomers of hexyl, heptyl, octyl, and the like including eicosyl. Other such aralkyl radicals of the organophosphorus compounds of the improved antiknock fluids of this invention include the α'-, β'-, and γ'-anthryl derivatives of alkyl radicals, such as for example, α'-anthryl-methyl; α-(β'-anthryl)-ethyl; β-(γ-anthryl)-ethyl; α - (α'-anthryl)-butyl; δ - (β'-anthryl)-2-methyl-amyl, and the like, and the corresponding alkyl derivatives of phenanthrene, fluorene, acenaphthene, chrysene, pyrene, triphenylene, naphthacene, and the like. Moreover, the univalent aliphatic radical or radicals of the organophosphorus materials of the improved antiknock fluids of the instant invention can be an aralkenyl radical such as for example α-phenyl-ethenyl; β-phenyl-ethenyl; α-phenyl-Δ^1-propenyl; β-phenyl-Δ^1-propenyl; γ-phenyl-Δ^1-propenyl; α-phenyl-Δ^2-propenyl; β-phenyl-Δ^2-

propenyl; γ-phenyl-Δ²-propenyl; α-phenyl-isopropenyl; β-phenyl-isopropenyl; γ-phenyl-isopropenyl; and similarly the phenyl derivatives of the isomers of butenyl, pentenyl, hexenyl, heptenyl, and the like, up to and including about eicosenyl. Other such arylalkenyls include α-(α'-naphthyl)-ethenyl; α-(β'-naphthyl)-ethenyl; β-(α'-naphthyl)-ethenyl; β-(β'-naphthyl)-ethenyl; α-(α'-naphthyl)-Δ¹-propenyl; α-(β'-naphthyl)-Δ¹-propenyl; β-(α'-naphthyl)-Δ¹-propenyl; β-(β'-naphthyl)-Δ¹-propenyl; α-(α'-naphthyl)-Δ²-propenyl; α-(β'-naphthyl)-Δ²-propenyl; β-(α'-naphthyl)-Δ²-propenyl; β-(β'-naphthyl)-Δ²-propenyl; α-(α'-naphthyl)-isopropenyl; α-(β'-naphthyl)-isopropenyl; β-(α'-naphthyl)-isopropenyl; β-(β'-naphthyl)-isopropenyl, and the like. In addition, such aromatic derivatives of alkenyls, that is, aralkenyl radicals include derivatives of phenanthrene, fluorene, acenaphthene, chrysene, pyrene, triphenylene, naphthacene, and the like.

When the organic radical or radicals of the organophosphorus materials utilized in the improved antiknock compositions of the present invention is a univalent alicyclic radical or radicals, these can be selected from the group consisting of cycloalkyl and cycloalkenyl radicals. Thus, the univalent alicyclic radicals can be cycloalkyl radicals, such as for example, cyclopropyl, cyclobutyl, cycloamyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cycloundecyl, cyclododecyl, cyclotridecyl, cyclotetradecyl, cyclopentadecyl, cyclohexadecyl, cycloheptadecyl, cyclooctadecyl, cyclononadecyl, cycloeicosyl, and such cycloaliphatic radicals as α-cyclopropylethyl, β-cyclopropylethyl, α-cyclobutylpropyl, β-cyclobutylpropyl, γ-cyclobutylpropyl, α-cycloamylisopropyl, β-cycloamylisopropyl, and the like. Similarly, the alicyclic radicals of the organophosphorus materials of the improved antiknock fluids of the present invention can be cycloalkenyl radicals, such as for example, α-cyclohexylethenyl; β-cyclohexylethenyl; α-cycloheptyl-Δ¹-propenyl; γ-cycloheptyl-Δ¹-propenyl; α-cyclooctyl-Δ²-propenyl; β-cyclooctyl-Δ²-propenyl; γ-cyclooctyl-Δ²-propenyl; β-cyclononylisopropyl; α-methylene-β-cyclododecylethyl, and the like.

When the organic radical or radicals of the organophosphorus materials of the improved antiknock fluids of the present invention is a univalent aromatic radical or radicals, these can be selected from the group consisting of aryl and alkaryl radicals. Thus, the univalent aromatic radical or radicals can be aryl radicals, such as for example, α-naphthyl, β-naphthyl, α-anthryl, β-anthryl, γ-anthryl, and the like, including the various monovalent radicals of such aromatic as indene, isoindene, acenaphthene, fluorene, phenanthrene, naphthacene, chrysene, pyrene, triphenylene, and the like. Moreover, the univalent aromatic radical or radicals can be alkaryl radicals, such as for example, o-tolyl, m-tolyl, p-tolyl, 2,3-xylyl, 2,4-xylyl, 2,5-xylyl, 2,6-xylyl, 3,4-xylyl, 3,5-xylyl, o-cumenyl, m-cumenyl, p-cumenyl, mesityl, o-ethylphenyl, m-ethylphenyl, p-ethylphenyl, 2-methyl-α-naphthyl, 3-methyl-α-naphthyl, 4-methyl-α-naphthyl, 5-methyl-α-naphthyl, 6-methyl-α-naphthyl, 7-methyl-α-naphthyl, 8-methyl-α-naphthyl, 1-ethyl-β-naphthyl, 3-ethyl-β-naphthyl, 4-ethyl-β-naphthyl, 5-ethyl-β-naphthyl, 6-ethyl-β-naphthyl, 7-ethyl-β-naphthyl, 8-ethyl-β-naphthyl, 2,3-dipropyl, α-naphthyl, 5,8-diisopropyl-β-naphthyl, and the like.

The term phosphines and related compounds is considered herein as being generic to such compounds as phosphines, biphosphines and phosphine methylenes.

Phosphines are derivatives of trivalent phosphorus in which one or more phosphorus-to-carbon bond exists, with the remaining phosphorus valences, if any, being bound by hydrogen. Therefore, phosphines can be represented by the general formula

$$R_1R_2R_3P$$

wherein R_1 is an organic radical and each of R_2 and R_3 can be the same or different and is selected from the group consisting of hydrogen and organic radicals. Illustrative examples of phosphine include

ethylphosphine,
propylphosphine,
isopropylphosphine,
isobutylphosphine,
isoamylphosphine,
phenylphosphine,
isopropenylphosphine,
Δ¹-pentenylphosphine,
α-phenylethylphosphine,
γ-phenylbutylphosphine,
β-phenylethenylphosphine,
cyclohexylphosphine,
o-tolylphosphine,
3-methyl-α-naphthylphosphine,
dimethylphosphine,
methylethylphosphine,
diethylphosphine,
methylisopropylphosphine,
ethylbutylphosphine,
isopropylisobutylphosphine,
diisoamylphosphine,
methylphenylphosphine,
diphenylphosphine,
phenyl-m-tolylphosphine,
sec-butylethenylphosphine,
di-Δ¹-butenylphosphine,
di-(α-phenylpropyl)-phosphine,
methyl-(α-phenylethenyl)-phosphine,
butylcycloamylphosphine,
dicyclohexylphosphine,
di-(2,3-xylyl)-phosphine,
trimethylphosphine,
tri-(chloromethyl)-phosphine,
triethylphosphine,
triisopropylphosphine,
tributylphosphine,
triphenylphosphine,
tri(2-chlorophenyl)-phosphine,
tri-(2-methylphenyl)-phosphine,
dimethyl-(ethylphenyl)-phosphine,
dimethylphenylphosphine,
diethylpropylphosphine,
diethylphenylphosphine,
dipropylphenylphosphine,
diallylphenylphosphine,
diisobutylphenylphosphine,
diphenylmethylphosphine,
diphenyl-p-tolylphosphine,
dicyclobutylphenylphosphine,
ethylisopropylisobutylphosphine,

and the like.

Biphosphines are derivatives of phosphines containing a phosphorus-to-phosphorus bond which can be represented by the general formulae

$$R_1R_2P—PR_2R_4;\ R_1P{=}PR_2$$

wherein R_1 is an organic radical and each of R_2, R_3, and R_4 can be the same or different and is selected from the group consisting of hydrogen and organic radicals. Illustrative examples of biphosphines include tetraphenyl biphosphine, diphenyl biphosphine, tetramethyl biphosphine, and the like.

Phosphinemethylenes are derivatives of phosphines wherein the three organic radicals on the phosphorus atom are supplemented by a fourth group attached to the phosphorus by a semipolar bond. Illustrative examples of phosphinemethylenes include $(C_6H_5)_3P{=}C(C_6H_5)_2$, $(C_6H_5)_3P{=}C(C_6H_4\text{-}o)_2$, and the like.

Halophosphines can be dihalophosphines or monohalophosphines represented by the general formulae

$$R_1PX_1X_2;\ R_1R_2PX_3$$

wherein R_1 is an organic radical and R_2 is hydrogen or an organic radical; wherein each of X_1, X_2, and X_3 can be the same or different, and is selected from the group consisting of bromide, chloride, and iodide radicals. Thus, halophosphines include such compounds as, for example,

ethyldichlorophosphine,
propyldichlorophosphine,
isopropyldichlorophosphine,
butyldichlorophosphine,
butyldibromophosphine,
isobutyldichlorophosphine,
isoamyldichlorophosphine,
phenyldichlorophosphine,
phenyldibromophosphine,
phenyldiiodophosphine,
4-chlorophenyldichlorophosphine,
4-bromophenyldichlorophosphine,
4-methylphenyldichlorophosphine,
4-methylphenyldibromophosphine,
4-methylphenyldiiodophosphine,
4-methylphenyldibromophosphine,
2,4-dimethylphenyldichlorophosphine,
α-naphthyldichlorophosphine,
methylethylchlorophosphine,
methylethylbromophosphine,
methylethyliodophosphine,
diethylchlorophosphine,
diethylbromophosphine,
diethyliodophosphine,
dipropylchlorophosphine,
dipropylbromophosphine,
propyliodophosphine,
methylphenylchlorophosphine,
methylphenylbromophosphine,
ethylphenylchlorophosphine,
diphenylchlorophosphine,
diphenylbromophosphine,
di-(phenyl)-phosphine,
and the like.

Halophosphine halides and phosphenyl halides are halogen derivatives of phosphorus in its higher oxidation state that contain one or more radicals bound to the central atom by carbon-to-phosphorus bonds. Such compounds can be represented by the general formulae

$$R_1PX_1X_2(X_3)_2;\ R_1R_2PX_1X_2X_3;\ R_1R_2R_3PX_1X_2;$$
$$R_1PChX_1X_2;\ R_1R_2PChX_1$$

wherein R_1 is an organic radical and each of R_2 and R_3 can be the same or different and is selected from the group consisting of hydrogen and organic radicals; each of X_1, X_2, and X_3 can be the same or different and is selected from the group consisting of bromide, chloride and iodide radicals and Ch is a divalent radical selected from the group consisting of oxygen, sulfur and selenium, that is, a chalkogen. Illustrative examples of halophosphine halides include such compounds as ethyl phosphorus tetrachloride, propyl phosphorus tetrachloride, isopropyl phosphorus tetrachloride, isobutyl phosphorus tetrachloride, phenyl phosphorus tetrachloride, phenyl phosphorus dibromidedichloride, phenyl phosphorus tetrabromide, 4-chlorophenyl phosphorus tetrachloride, 4-chlorophenyl phosphorus dichloridedibromide, 4-bromophenyl phosphorus tetrachloride, 4-methylphenyl phosphorus tetrabromide, 2-indenyl phosphorus tetrachloride, α-naphthyl phosphorus tetrachloride, diphenyl phosphorus trichloride, (4-bromophenyl)-phenyl phosphorus trichloride, m-tolyl phenyl phosphorus trichloride, (2,4,5-trimethylphenyl)-phenyl phosphorus trichloride, triethyl phosphorus dichloride, diethyl phenyl phosphorus dichloride, triphenyl phosphorus dichloride, triphenyl phosphorus dibromide, tri-(2,4,5-trimethylphenyl)-phosphorus dichloride, and the like.

Illustrative examples of phosphenyl halides include such compounds as methane phosphonyl dichloride, β-chloroethane phosphonyl dichloride, β-bromoethane phosphonyl dichloride, propane phosphonyl dichloride, isobutane phosphonyl dichloride, cyclohexane phosphonyl dichloride, dimethyl phosphonyl chloride, methylethyl phosphonyl chloride, diethyl phosphonyl chloride, benzene phosphonyl dichloride, 4-chhorobenzene phosphonyl dichloride, 2-chloro-4-methylbenzene phosphonyl dichloride, 4-methylbenzene phosphonyl bromochloride, 2,4,5-trimethylbenzene phosphonyl dichloride, methylphenyl phosphonyl chloride, di-(phenyl)-phosphonyl chloride, hexanethiono phosphonyl dibromide, isobutane thiono phosphonyl dichloride, methylcyclohexyl phosphonyl chloride, ethanethiono phosphonyl dichloride, benzene phosphonyl dibromide, and the like.

Quaternary phosphonium compounds can be represented by the general formula

$$R_1R_2R_3R_4PX$$

wherein R_1 is an organic radical and each of R_2, R_3, and R_4 can be the same or different and is selected from the group consisting of hydrogen and organic radicals and X is selected from the group consisting of chloride, bromide, iodide and hydroxyl radicals. Illustrative examples of quaternary phosphonium compounds include tetramethyl phosphonium hydroxide, tetraethyl phosphonium chloride, tetrapropyl phosphonium iodide, tetraisopropyl phosphonium bromide, tetrabutyl phosphonium iodide tetraphenyl phosphonium iodide, tetraphenyl phosphonium bromide, tetraphenyl phosphonium hydroxide, tetra-p-tolyl phosphonium chloride, trimethylethyl phosphonium chloride, trimethyl-(β-bromoethyl)-phosphonium bromide, trimethyl-(isoamyl)-phosphonium iodide, trimethyl-(iodomethylene)-phosphonium chloride, triethylpropyl phosphonium chloride, triethylphenyl phosphonium bromide, tripropylethyl phosphonium iodide, dimethylethylphenyl phosphonium iodide, diethylmethylphenyl phosphonium iodide, diethylmethyl-m-tolyl phosphonium iodide, diisobutylethylphenyl phosphonium iodide, dimethyldiethyl phosphonium chloride, phenylethyltetramethylene phosphonium iodide, phenylethylpentamethylene phosphonium iodide, and the like.

Tertiary phosphine oxides and sulfides are compounds consisting of three radicals bound by phosphorus-carbon bonds to the phosphoryl and thiophosphoryl groups respectively. Thus, the compounds can be represented by the general formula

$$R_1R_2R_3PCh$$

wherein R_1 is an organic radical and each of R_2 and R_3 can be the same or different and is selected from the group consisting of oxygen and sulfur, that is, a chalkogen. Illustrative examples of tertiary phosphone oxides include such compounds as trimethyl phosphine oxide, trichloromethyl phosphine oxide, triethyl phosphine oxide, tripropyl phosphine oxide, triphenylphosphine oxide, tri-2,3-xylyl phosphine oxide, tri-3-indelyl phosphine oxide, dimethylethyl phosphine oxide, dimethylphenyl phosphine oxide, diphenylmethyl phosphine oxide, diphenylethyl phosphine oxide, methylethylphenyl phosphine oxide, methylpropylphenyl phosphine oxide, and the like. Illustrative examples of tertiary phosphine sulfides include such compounds as trimethyl phosphine sulfide, triethyl phosphine sulfide, triisobutyl phosphine sulfide, triphenyl phosphine sulfied, tri-(4-methylphenyl)-phosphine sulfide, tri-(β-naphthyl)-phosphine sulfide, diethyl phosphine sulfide, diphenylethyl phosphine sulfide, diphenyl-(isoamyl)-phosphine sulfide, and the like.

Compounds of the generic term phosphinous, phosphonous and phosphenic acids, their sulfur analogs and esters of the aforesaid acids are compounds possessing one or two organic radicals bound directly to the central phosphorus atom, the residual valences of which constitute an acid function or ester based on such acid function. Thus, in general, such substances can be primary or secondary phosphonic acids, phosphonous acids, phos-

phinous acids, the thio analogs of the aforesaid substances in which one or more oxygen atoms are replaced with sulfur including primary and secondary thiophosphionous acids, and the esters of all of the aforesaid acids in which one or more acidic hydrogen atoms are replaced by organic radicals.

Phosphinous and thiophosphionous acids and esters thereof can be represented by the general formula

$$R_1R_2PChR_3$$

wherein each of R_1, R_2 and R_3 can be the same or different and is selected from the group consisting of hydrogen and organic radicals but wherein not all of R_1, R_2 and R_3 are hydrogen, and Ch is a divalent radical selected from the group consisting of oxygen and sulfur, that is, a chalkogen. Illustrative examples of such compounds include diethyl phosphinous acid, diphenylbutyl phosphinite, dipropyl thiophosphinous acid, phenylpropylmethyl thiophosphinite, dicresylphenyl phosphinite and the like.

Phosphonous and thiophosphonous acids and esters thereof can be represented by the general formula

$$R_1P(Ch_1R_2)(Ch_2R_3)$$

wherein each of R_1, R_2, and R_3 can be the same or different and is selected from the group consisting of hydrogen and organic radicals but are not all hydrogen, and each of Ch_1 and Ch_2 can be the same or different and is selected from the group consisting of divalent oxygen and sulfur radicals, that is, chalkogens. Illustrative examples of phosphonous and thiophosphonous acids and esters thereof include such compounds as benzene phosphonous acid, benzene thiophosphonous acid, ethyl phosphonous acid, isopropyl thiophosphonous acid, methylethylbenzene phosphonite, isopropylphenylethane phosphonous acid, methylamylbenzene phosphonite, isopropylbutylbenzene phosphonite, diphenylbenzene phosphonite, dibutylbenzene phosphonite, diethylbenzene thiophosphonite, di-sec-amylbenzene thiophosphonite, and the like.

Phosphonic and thiophosphonic acids and esters thereof can be represented by the general formulae

$$R_1P(Ch_1)(Ch_2R_2)(Ch_3R_3);\ R_4R_5P(Ch_4)(Ch_5R_6)$$

wherein R_1 is hydrogen or an organic radical and each of R_2, R_3, R_4, R_5, and R_6 can be the same or different and is selected from the group consisting of hydrogen and organic radicals and each of Ch_1, Ch_2, Ch_3, Ch_4, and Ch_5 can be the same or different and is selected from the group consisting of divalent oxygen and sulfur radicals, that is, chalkogens. Illustrative examples of phosphonic and thiophosphonic acids and esters thereof include such compounds as diethylmethane phosphonate, dibutylbenzene phosphonate, diisopropylbutane phosphonate, diethylbenzene phosphonate, di - (2 - ethylhexyl) - benzene phosphonate, diphenylpropane phosphonate, dicresylbenzene phosphonate, benzene phosphonic acid, ethylphenyl phosphonic acid, dimethylbutane thiophosphonate, methylethylbenzene thiophosphonate, diamylbenzene thiophosphonate, diphenylbenzene thiophosphonate, dicresylbenzene thiophosphonate, benzene thiophosphonic acid, ethylphenyl thiophosphonic acid, and the like.

Phosphites and thiophosphites are the esters of phosphorus acid and thiophosphorus acid. Thus, phosphites and thiophosphites can be represented by the general formulae

$$-(R_1Ch_2)P(Ch_2R_2)(Ch_3R_3);$$
$$(R_4Ch_4)(R_5Ch_5)P(Ch_6R_6)$$
$$(R_7Ch_7)(R_8Ch_8)(R_9Ch_9)P$$

wherein R_1, R_4 and R_7 are organic radicals and each of R_2, R_3, R_5, R_6, R_8 and R_9 can be the same or different and is selected from the group consisting of hydrogen and organic radicals, and each of Ch_1, Ch_2, Ch_3, Ch_4, Ch_5, Ch_6, Ch_7, Ch_8 and Ch_9 can be the same or different and is selected from the group consisting of divalent oxygen and sulfur radicals, that is, chalkogens. Illustrative examples of phosphites and thiophosphites include such substances as monomethyl phosphite, monoethyl phosphite, monoisopropyl phosphite, dimethyl phosphite, diethyl phosphite, dipropyl phosphite, diisopropyl phosphite, diisobutyl phosphite, trimethyl phosphite, triethyl phosphite, tripropyl phosphite, triisopropyl phosphite, tributyl phosphite, tri-o-cresyl phosphite, triisoamyl phosphite, tri-o-cyclohexyl phosphite, triethyl thiophosphite, tripropyl thiophosphite, tributyl thiophosphite, triphenyl thiophosphite, monoethoxydiethyl thiophosphite, diethoxymono thiophosphite, and the like.

Phosphates, halophosphates and thio analogs are the esters of phosphoric acid and the esters of halides of phosphoric acid, including analogs of such substances wherein either part or all of the oxygen atoms are replaced by sulfur. Thus, phosphates can be represented by the general formulae

$$R_1Ch_1P(Ch_2R_2)(Ch_3R_3);$$
$$(R_4Ch_1)(R_5Ch_2)P(Ch_3)(Ch_4R_6)$$
$$(R_7Ch_1)(R_8Ch_2)(R_9Ch_3)P(Ch_4)$$

wherein R_1, R_4 and R_7 are organic radicals and each of R_2, R_3, R_5, R_6, R_8 and R_9 can be the same or different and is selected from the group consisting of hydrogen and organic radicals and each of Ch_1, Ch_2, Ch_3, and Ch_4 can be the same or different and is selected from the group consisting of oxygen and sulfur, that is, chalkogens. Illustrative examples of phosphates and thiophosphates include such compounds as dimethyl phosphate, tributyl phosphate, tri-o-cresyl phosphate, tri-m-cresyl phosphate, tri-p-cresyl phosphate, phenyldicresyl phosphate, methyldibutyl phosphate, cresyldiphenyl phosphate, triphenyl phosphate, tri-(2-ethylhexyl)phosphate, triethyl phosphate, monooctyl acid phosphate, dimethyl thiophosphate, tri-sec-butyl thiophosphate, tricresyl thiophosphate, phenyldicresyl thiophosphate, dimethylbutyl thiophosphate, cresyldiphenyl thiophosphate, triphenyl thiophosphate, triethyl thiophosphate, monooctyl acid thiophosphate, and the like.

Halophosphates and halothiophosphates are halogen derivatives of phosphates and thiophosphates which can be represented by the general formulae

$$(R_1Ch_1)PX_1X_2;\ (R_2Ch_2)(R_3Ch_3)PX_3$$

wherein each of R_1 and R_2 are organic radicals and R_3 hydrogen or an organic radical; each of Ch_1, Ch_2 and Ch_3 can be the same or different and is selected from the group consisting of divalent oxygen and sulfur radicals, that is, chalkogens, and each of X_1, X_2 and X_3 can be the same or different and is selected from the group consisting of fluoride, bromide, chloride and iodide radicals. Illustrative examples of halophosphates and halothiophosphates include such compounds as ethyldifluorophosphate, methyldichlorophosphate, ethyldichlorophosphate, butyldichlorophosphate, isopropyldibromophosphate, ethyldifluorothionophosphate, ethylfluorochlorothionophosphate, methyldichlorothionophosphate, ethyldichlorothionophosphate, propyldichlorthionophosphate, butyldichlorothionophosphate, isobutyldichlorothionophosphate, ethyldibromothionophosphate, (S)-ethyldichlorothiothionophosphate, dimethylfluorothiophosphate, diethylfluorophosphate, dipropylfluorophosphate, dimethylchlorothionophosphate, diethylchlorothionophosphate, dibutylchlorothionophosphate, di-(SS)-ethylfluorodithiophosphate, di-(SS)-ethylchlorodithiophosphate, di-(SS)-ethylchlorodithiothionophosphate, phenyldichlorophosphate, 2-methylphenyldichlorophosphate, 2-isopropyl-5-methylphenyldichlorophosphate, 4-butyl-2-methylphenyldichlorophosphate, (4 - tert-butylphenyl) - dichlorophosphate, phenyldichlorothionophosphate, phenyldibromothionophosphate, (S)-phenyldichlorothiothionophosphate, diphenylfluorophosphate, diphenylchlorophosphate, ethylphenylchlorophosphate, diphenylchlorothionophosphate, diphenylbromothionophosphate, diphenylchlorothiophosphate, and the like.

Compounds with phosphorus-to-nitrogen bonds are compounds containing single, double or semi-polar bonds, and are represented by amides of phosphorus acid, phosphoric acid, the halides and esters thereof, phosphonic acids, and the thio analogs of each of the aforesaid classes of compounds. Furthermore, compounds with phosphorus-to-nitrogen bonds include a class of imido derivatives of the aforesaid classes of compounds as well as compounds known as phosphinimines which are essentially semi-polarly linked substances. Illustrative examples of compounds containing phosphorus-to-nitrogen bonds include such substances as ethyl-N,N'-dimethyldiamidophosphate; N,N'-diphenyldiamidophosphate; dichloro - N,N - di-ethylamidophosphate; N,N',N'' - triethylphosphoric triamide; N,N',N''-triethylphosphorus triamide; ethyl-N-methylimidophosphite; phenyl-N-ethylimidophosphate; N,N'-diethylbenzenephosphondiamide; N,N-dipropyldiethylphosphinamide; triphenylphosphine ethylimine; ethyl-N,N'-dipropyldiamidothiophosphate; N,N-diphenyldiamidothiophosphate; N,N',N''-tributylthiophosphoric triamide; ethyl-N-ethylamidothiophosphite; phenyl-N-ethylamidothiophosphate, and the like.

The term "derivatives of anhydrophosphorus acids" includes, in general, esters of pyrophosphoric acid, anhydro of pyrophosphoric acid, esters of thiono and dithionophosphorus acids, esters of pyrophosphonic acids, esters of m-phosphonous acid, esters of m-phosphoric acid, amides of m-phosphoric acid, and m-phosphonic acids. Illustrative examples of derivatives of anhydrophosphorus acids include such substances as tetraethylpyrophosphite, tetrapropylpyrophosphite, tetrabutylpyrophosphite, tetramethylpyrophosphate, tetraethylpyrophosphate, tetraisopropylpyrophosphate, tetrabutylpyrophosphate, tetraethylpyrophosphonate, methyl-m-phosphate, ethyl-m-phosphate, phenyl-m-phosphonite and the like.

The general methods for the preparation of the organophosphorus compounds fully enumerated hereinbefore, are known to those skilled in the art. Most of these general methods are fully described in kosolapoff, "Organo Phosphorus Compounds." Although the preceding discussion with regard to organophosphorus compounds has been concerned with pure phosphorus compounds, there are available as articles of commerce, mixtures of the various positional isomers of given phosphorus compounds. Such mixtures are also within the spirit and scope of the present invention, for I have found that I can successfully employ in my improved antiknock fluids such mixtures as the various positional isomers of tributyl phosphates, triamyl phosphates, tributyl thiophosphates, triamyl thiophosphates, tricresyl phosphates, tritolyl phosphates, tripropyl phosphites, tributyl phosphites, triamyl phosphites and the like.

The scavengers of the improved antiknock fluids of my invention can, in addition to ethylene dibromide and ethylene dichloride, be those disclosed in U.S. 1,592,954; 1,668,022; 2,364,921; 2,389,281; 2,479,900; 2,479,901; 2,479,902; 2,479,903; 2,496,983. Illustrative examples of such additional scavengers include such substances as carbon tetrachloride; hexylchloride; ethyl chloride; carbon tetrabromide; hexyl bromide; ethyl bromide; carbon tetraiodide; hexyl iodide; ethyl iodide; propylene dibromide; butylene dichloride; trichloroaniline; 1,3,4-tribromopentane; 4,5-dibromo-1,2-dimethylbenzene; 1,6-dibromohexane; 1,2,5 - tribromopentene - 1; 1,2,3-tribromopentane; 1,2,3-tribromobutane; 3,4-dibromomethylcyclohexane; 6-bromo-4'-(bromomethyl)-heptene-1; 1,2-dibromocyclohexane; 1,2,3-tribromo-2-methylpropane; (5-chloroamyl)-benzene; 1,8-dichloroctane; 1,2,4-trichlorobenzene; 2,4-dichloro-toluene; 1-chlorooctane; 4-bromo-1,2-dimethylbenzene; 3-bromo-1,2-dimethylbenzene; 1-bromo-4-ethylbenzene; 1,1-dichlorobutane; 1,4-dichlorobutane; 2,3-dichlorobutane; 1,3-dichloropentane; 2,3-dichloropentane; 3,3 - dichloropentane; 1,3-dibromo-2,2-dimethylpropane; 3,4-dichlorocumene; 2,4-dichlorotoluene; β,β'-dibromodiethyl ether; α-bromobutyl-β-bromoethyl ether; β-chloroethyl-β-chloroisopropyl ether; and the like.

Any organic halides can be used as scavengers in accordance with the present invention so long as they do not resist decomposition by the combustion in the cylinders. Some aryl chlorides, such as monochlornaphthalene, are not good scavengers. For example, alkyl halides, aryl bromides and chlorobenzenes are very effective. However, to obtain the improved exhaust valve life described above, the bromine content of the fluid or fuel should be increased 15 to 20 percent above those of the standard prior art compositions. An increase in chlorine content without an accompanying increase in bromine does not appear to give any improvement. On the other hand, a decrease in chlorine content without compensating increases in bromine significantly reduces the scavenging.

The minor proportions of the improved antiknock fluids of the present invention which are employed in fuels for internal combustion engines are the same as with conventional antiknock fluids. Thus, in providing improved fuels for automotive engines and the like, amounts of the improved antiknock fluids of the present invention equivalent to up to 2.5 or 3 milliliters of tetraethyllead per gallon are used. In providing improved fuels for use in aviation engines, amounts of the improved antiknock fluids of the invention equivalent to up to 6 milliliters of tetraethyllead per gallon can be used.

Although the antiknock agent utilized in the improved antiknock fluids of the present invention can be any of the diverse organolead compounds possessing antiknock activity, a preferred embodiment of the present invention consists of improved antiknock fluids comprising the phosphorus-containing materials and the halide corrective agents or scavengers in combination with tetraalkyllead compounds, particularly tetraethyllead. Likewise, the so-called mixed alkyllead antiknocks which have from time to time been proposed can be so employed, such as, for example, mixtures of the various methylethyllead antiknocks, such as methyltriethyl-, dimethyldiethyl- and trimethylethyllead as well as tetramethyllead itself.

In compounding the improved antiknock fluids of the instant invention, phosphorus compounds that are mutually soluble in organolead compounds and/or in organic halides are the simplest to use. Those phosphorus compounds which do not possess the requisite solubility in the aforesaid organic materials can be incorporated with the help of a common solubilizing agent, such as acetone or alcohol. In some cases, the maximum solubility of the phosphorus compound is adequate but the solution rate is low, so that it is advantageous to warm and/or agitate a mixture of the components of the improved antiknock fluids of the present invention in compounding operations.

In order to demonstrate the beneficial effects of the invention, the following specific examples are given:

EXAMPLE I

To 1000 gallons of a commercial blend of straight-run and catalytically and thermally cracked stocks was added three liters of tetraethyllead in a fluid containing 1.0 theory of chlorine as ethylene dichloride, and 0.5 theory of bromine as ethylene dibromide. The resulting blend was intimately mixed producing a homogeneous fuel composition containing 3.0 milliliters of tetraethyllead per gallon. A truck containing a standard six-cylinder I-head engine having a displacement of 235 cubic inches and a 6.7 to 1 compression ratio was operated with this fuel under heavy duty road operating conditions until two exhaust valve failures were detected. It was found that under such heavy duty road operating conditions the truck ran an average of 17,040 miles before two valve failures.

EXAMPLE II

To 1000 gallons of the commercially available fuel described in the preceding example was added 3 liters of tetraethyllead in a fluid comprising 1.0 theory of chlorine as ethylene dichloride, 0.5 theory of bromine as ethylene dibromide and 0.2 theory of phosphorus as tricresyl phosphate. A homogeneous fuel composition was produced by intimately mixing the aforementioned components which thus contained 3.0 milliliters of tetraethyllead per gallon. The same truck as described in the preceding example was then operated under identical road test conditions until two exhaust valve failures were detected. It was found that after an average of 6480 miles of operation, two such failures occurred. Therefore, the utilization of phosphorus-containing materials in an antiknock fluid in accordance with the teachings of the prior art produced a reduction in exhaust valve performance amounting to 62.0 percent.

EXAMPLE III

To 100 gallons of the commercial base stock described in Example I was added 300 milliliters of tetraethyllead in a fluid containing 1.0 theory of chlorine as ethylene dichloride and 0.5 theory of bromine as ethylene dibromide. The resulting blend was intimately mixed producing a homogeneous fuel composition containing 3.0 milliliters of tetraethyllead per gallon. A modern six-cylinder truck engine was operated on the aforementioned fuel composition for a period of 387 hours under light duty cycling service operating conditions. It was found that during this period of operation, no exhaust valve failures occurred.

EXAMPLE IV

To 100 gallons of the commercial base stock described in Example I was added 300 milliliters of tetraethyllead as a fluid comprising 1.0 theory of chlorine as ethylene dichloride, 0.5 theory of bromine as ethylene dibromide and 0.2 theory of phosphorus as tricresyl phosphate. The resulting blend was intimately mixed producing a homogeneous fuel composition containing 3.0 milliliters of tetraethyllead per gallon. The same truck engine as described in the preceding example was operated under the same light duty cycling service operating conditions until two exhaust valve failures were detected. It was found that the average time required for such failures was 140 hours. Therefore, the incorporation of phosphorus-containing materials in an anti-knock fluid in accordance with the teachings of the prior art produced a reduction in exhaust valve life amounting to 63.8 percent.

EXAMPLE V

To 100 gallons of a standard paraffinic fuel containing 0.003 percent of sulfur was added 400 milliliters of tetraethyllead as a fluid comprising 1.2 theories of bromine as ethylene dibromide ($EtBr_2$), and 0.1 theory of phosphorus as tricresyl phosphate (TCP). The resulting blend was intimately mixed producing a homogeneous fuel composition containing 4.0 milliliters of tetrethyllead per gallon, that is, one of the improved antiknock fuels of the present invention was provided. A single-cylinder laboratory test engine having a 17.6 cubic inch displacement and equipped with a hemispherical combustion chamber was operated on the aforementioned improved fuel containing one of the improved antiknock fluids of the present invention for a period of 100 hours under conditions such that the exhaust valve throat temperature was 1450° F. The same engine was then operated on three other phosphorus-containing fuels produced by adding to the

standard paraffinic fuel antiknock fluids containing phosphorus materials in accordance with the teachings of the prior art. The criteria for exhaust valve performance were the weight loss of the exhaust valve which occurred during 100 hours of engine operation and the reduction in exhaust valve throat area during the same period of time. The data are presented in Table I.

Table I

Fluid Mix	Exhaust valve weight loss per 100 hours, grams	Reduction in exhaust valve throat area per 100 hours, percent
1.2 T $EtBr_2$+0.1 T TCP	0.41	3.6
1.0 T $EtBr_2$+0.2 T TCP	1.77	14.9
1.0 T $EtBr_2$+0.1 T TCP	1.74	14.4
1.0 T $EtBr_2$+0.05 T TCP	0.60	5.6

EXAMPLE VI

To 100 gallons of a standard paraffinic fuel containing sulfur was added 400 milliliters of tetraethyllead as a fluid comprising 1.2 theories of bromine as ethylene dibromide ($EtBr_2$) and 0.1 theory of phosphorus as tricresyl phosphate (TCP). A homogeneous fuel composition containing 4.0 milliliters of tetraethyllead per gallon, one of the improved antiknock fuels of the present invention, was provided by intimately mixing the aforementioned components. A single-cylinder laboratory test engine having a 17.6 cubic inch displacement and equipped with a hemispherical combustion chamber was operated on the improved antiknock fuel containing one of the improved antiknock fluids of the present invention for a period of 100 hours under conditions such that the exhaust valve throat temperature was 1385° F. The same engine was then operated on two other phosphorus-containing fuels produced by adding to the standard paraffinic fuel antiknock fluids containing phosphorus materials in accordance with the teachings of the prior art. As in the preceding example, the criteria for exhaust valve performance were the weight loss of the exhaust valve which occurred during 100 hours of engine operation, and the reduction in exhaust valve throat area during the same period of time. The data are shown in Table II.

Table II

Fluid Mix	Exhaust valve weight loss per 100 hours, grams	Reduction in exhaust valve throat area per 100 hours, percent
1.2 T $EtBr_2$+0.1 T TCP	1.36	9.2
1.0 T $EtBr_2$+0.1 T TCP	2.60	16.0
0.8 T $EtBr_2$+0.1 T TCP	5.82	51.9

EXAMPLE VII

Road tests—multi-cylinder engines.—A fleet of standard 1953 automobiles was operated on the road under controlled driving conditions. These fleet tests were designed to study the effect of various fuel additive combinations on the engine durability of the test cars. One criterion in this series of tests was the effect of these fuel additive combinations on exhaust valve life.

The vehicles were operated on a closely controlled 60 miles per hour top-speed schedule and accumulated approximately 5000 miles per week at an average speed

of 54 miles per hour. The cars were equipped with new cylinder heads and standard exhaust valves at the beginning of the test. These cars were then operated on the road under the above conditions until an exhaust valve failure was detected. The defective valve was then removed and replaced with a new valve and the test continued until a second valve failure occurred. Thus, in each test the exhaust valve life was expressed as the average of the number of miles to the first failure and the number of miles to the second failure.

The cars were operated on the same test gasoline and crankcase lubricating oil. The inspection data of the fuel and lubricating oil used are as follows:

FUEL

Process composition, percent vol.:	
Straight run	100
TEL content, ml./gal	3.00
Dissolved gum, mg./100 ml	0.4
Oxidation stability, min	1440
Total sulfur, percent weight	0.006
Gravity, ° API	66.7
Vapor pressure, p.s.i	6.6
Distillation, ° F.:	
Initial evaporation	116
10% evaporated	150
50% evaporated	184
90% evaporated	239
Final evaporation	300
Octane number:	
F–1 (research)	91.8
F–2 (motor)	88.4
Hydrocarbon type, percent vol.:	
Paraffins	58
Olefins	
Aromatics	8
Naphthenes	34

OIL

Crude type	Paraffinic base.
Refining process	Solvent.
Type	Heavy duty.
Viscosity grade	SAE 20.
Gravity, ° API	28.0.
Viscosity, SUS:	
100° F	323.1.
210° F	57.5.
Viscosity index	119.3.
Pour point, ° F	—20.
Cloud point, ° F	+16.
Ash, percent weight	0.954.
Total sulfur, percent weight	0.32.
Metals, percent weight:	
Barium	0.40.
Calcium	0.07.
Phosphorus	
Zinc	

In all of the tests the above test gasoline contained 3 milliliters of tetraethyllead per gallon. In one series of tests this leaded fuel contained 0.5 theory of bromine as ethylene dibromide and 1.0 theory of chlorine as ethylene dichloride. In another series of tests this leaded fuel contained 0.5 theory of bromine as ethylene dibromide, 1.0 theory of chlorine as ethylene dichloride and 0.2 theory of phosphorus as tri-(β-chloropropyl)-thionophosphate, which is herein designated as phosphorus additive A. In a third series of tests the leaded fuel contained 0.6 theory of bromine as ethylene dibromide, 1.0 theory of chlorine as ethylene dichloride and 0.2 theory of phosphorus as phosphorus additive A. As used herein, the term "theory" is used in its established sense in the art. One theory of bromine or chlorine is defined as the amount thereof theoretically required to react with the lead to form lead bromide or lead chloride, respectively. Thus, one theory of these halogens is two atoms of halogen per atom of lead. The term "theory" as applied to the phosphorus fuel additive is defined as the amount of phosphorus theoretically required to react with the lead to form lead orthophosphate, that is, two atoms of phosphorus per each three atoms of lead. For example, a phosphorus concentration of 0.2 theory (T) is equivalent to a phosphorus-to-lead atom ratio of 0.4:3.

The results of these road tests are shown in Table III.

Table III

Halohydrocarbon scavenger	Phosphorus additive, conc.	Number of tests	Valve life, miles	Rel. valve life, percent
0.5 T of bromine (ethylene dibromide), 1.0 T of chlorine (ethylene dichloride)	None	14	11,484	100
Do	[1] 0.2	13	8,960	78
0.6 T of bromine (ethylene dibromide), 1.0 T of chlorine (ethylene dichloride)	[1] 0.2	8	18,497	161

[1] P:Pb=0.4:3.

EXAMPLE VIII

Dynamometer tests—multi-cylinder engines.—Another series of durability engine tests designed to demonstrate the effect of various fuel additive combinations on exhaust valve life was conducted. In these tests a standard 1953 automobile engine attached to an engine dynamometer was operated at 2500 r.p.m. constant speed with alternate three-minute periods at half throttle and at full throttle. This engine was operated under these conditions until an exhaust valve failure was encountered. The defective valve was removed and replaced with a new valve and the test recontinued until a second valve failure occurred. In this instance, the criterion of exhaust valve life in any one test was the average of hours to the first failure and hours to the second failure.

The engine was operated on a commercial gasoline containing 3.0 milliliters of tetraethyllead per gallon. The inspection data of the test gasoline are as follows:

FUEL

Process composition, percent vol.:	
Catalytically cracked	92
Thermally cracked	6
Reformed	2
TEL content, ml./gal	3.00
Dissolved gum, mg./100 ml	0.7
Oxidation stability, min	790
Total sulfur, percent weight	0.043
Gravity, ° API	59.6
Vapor pressure, p.s.i	9.8
Distillation, ° F.:	
Initial evaporation	91
10% evaporated	127
50% evaporated	231
90% evaporated	364
Final evaporation	414
Octane number:	
F–1 (research)	93.2
F–2 (motor)	83.2
Hydrocarbon type, percent vol.:	
Paraffins	[1] 53
Olefins	20
Aromatics	27

[1] Includes naphthenes.

The crankcase lubricating oil was the same as that used in the multi-cylinder engine road tests described hereinabove.

Tests were made to show the effect of three different fuel additive combinations on exhaust valve life. One such combination was 0.5 theory of bromine and 1.0 theory of chlorine as ethylene dibromide and ethylene dichloride, respectively. Another fuel additive combination tested was 0.5 theory of bromine as ethylene dibromide, 1.0 theory of chlorine as ethylene dichloride and 0.2 theory of phosphorus as phosphorus additive A. The other combination tested was 0.6 theroy of bromine as ethylene dibromide, 1.0 theory of chlorine as ethylene dichloride and 0.2 theory of phosphorus as phosphorus additive A.

The data obtained from these tests are shown in Table IV.

Table IV

Halohydrocarbon scavenger	Phosphorus additive, conc.	Number of tests	Avg. hours to 2 valve failures	Percent of baseline
0.5 T of bromine (ethylene dibromide), 1.0 T of chlorine (ethylene dichloride)	None	2	156	100
Do	[1] 0.2 T	2	101	65
0.6 T of bromine (ethylene dibromide), 1.0 T of chlorine (ethylene dichloride)	[1] 0.2 T	1	295	189

[1] P:Pb=0.4:3.

EXAMPLE IX

Dynamometer tests—single-cylinder engines.—Another series of engine tests was conducted to determine the effect of various fuel additive combinations on exhaust valve life. In these tests the test equipment comprised 17.6 single-cylinder engines attached to engine dynamometers. These engines were equipped with XCR exhaust valves and Stellite No. 3 exhaust valve seat inserts. These engines were operated at 2700 r.p.m., 100° F. intake air, 212° F. jacket temperature and a fuel-air ratio of 0.07. These conditions resulted in a valve throat operating temperature of 1540° F.±30° F.

The gasoline used was a standard reference fuel, technical isooctane, containing 3.0 milliliters of tetraethyllead per gallon. The sulfur content of this gasoline was adjusted to 0.05 percent by weight of sulfur by the addition of disulfide oil. A conventional Grade 1120 aviation oil was used as the crankcase lubricant. The characteristics of the lubricant were as follows:

OIL

Crude type	Mixed base
Refining process	Solvent
Type	Str. mineral
Viscosity grade	Grade 1120
Gravity, ° API	28.0
Viscosity, SUS:	
100° F	1695
210° F	118.4
Viscosity index	97.1
Pour point, ° F	+10
Cloud point, ° F	+14
Ash, percent wt	0.002
Total sulfur, percent wt	0.17

In this series of tests the criterion of exhaust valve life was the average hours required to produce an exhaust valve failure.

The fuel additive combinations studied in this series

of tests were (1) 0.5 theory of bromine and 1.0 theory of chlorine as ethylene dibromide and ethylene dichloride respectively, (2) 0.5 theory of bromine as ethylene dibromide, 1.0 theory of chlorine as ethylene dichloride and 0.1 theory of phosphorus as phosphorus additive A and (3) 0.6 theory of bromine as ethylene dibromide, 1.0 theory of chlorine as ethylene dichloride and 0.1 theory of phosphorus as phosphorus additive A. The phosphorus content of fuel additive combinations designated above as (2) and (3) was such that the phosphorus-to-lead atom ratio was 0.2:3 in each instance.

The results of these engine tests are shown in Table V.

Table V

Halohydrocarbon scavenger	Phosphorus additive conc.	Number of tests	Hours to failure	Relative hours to failure
0.5 T of bromine (ethylene dibromide), 1.0 T of chlorine (ethylene dichloride)	None	3	120	100
Do	[1] 0.1 T	3	108	90
0.6 T of bromine (ethylene dibromide), 1.0 T of chlorine (ethylene dichloride)	[1] 0.1 T	3	205	171

[1] P:Pb=0.2:3.

EXAMPLE X

Recognizing the fact that exhaust valve throat corrosion was a problem in some aircraft engines with some valve materials, a series of tests was initiated to determine the extent by which this objectionable corrosion was increased by the use of phosphorus additives and means by which it might be reduced. In this series of tests, 17.6 engines coupled to engines were equipped with either of two types of exhaust valves fabricated by an exhaust valve manufacturer of materials currently in use for large aircraft engine valves.

The engines were operated at 2700 r.p.m., 0.07 fuel-air ratio, 20° spark advance, 100° F. intake air temperature, 212° F. jacket temperature and at an indicated mean effective pressure (IMEP) of 114 (a measure of power output).

The gasoline used in these tests was technical isooctane and contained 4.0 milliliters of tetraethyllead per gallon and had a sulfur content of 0.003 percent by weight. A commercially available crankcase lubricating oil, Aviation Grade 1120, was used in the engines. This inspection data for this oil are set forth in the description concerning the next preceding series of tests.

In all, six engine tests were conducted, three tests using exhaust valves fabricated of one type of materials of construction and the remaining three tests using exhaust valves fabricated from other materials of construction. Each of these two types of valves was representative of exhaust valves used in aircraft engines.

Three different fuel additive combinations were tested. One such combination involved use of the above leaded fuel containing 1.0 theory of bromine as ethylene dibromide. Another combination was that the above leaded gasoline contained 1.0 theory of bromine as ethylene dibromide and 0.1 theory of phosphorus as tricresyl phosphate. The third fuel additive combination used was 1.2 theory of bromine as ethylene dibromide and 0.1 theory of phosphorus as tricresyl phosphate.

In these tests the measures of exhaust valve performance were the corrosion of the exhaust valves measured by weight loss of the valves incurred per 100 hours of engine operation and the reduction in the throat area of the exhaust valves incurred per 100 hours of engine operation.

The results of these engine tests are shown in Table VI.

Table VI

EXHAUST VALVE MATERIAL 1

Test	Halohydrocarbon scavenger	Phosphorus additive conc.	Hours	Valve weight loss, gr./100		Reduction in throat area	
				Gr.	Hrs.	Percent	Percent 100 hrs.
1	1.0 T of bromine (ethylene dibromide).	None	240	0.659	0.274	0	0
2	do	[1] 0.1 T	150	2.613	1.74	23.8	15.9
3	1.2 T of bromine (ethylene dibromide).	[1] 0.1 T	240	0.975	0.406	8.7	3.63

EXHAUST VALVE MATERIAL 2

4	1.0 T of bromine (ethylene dibromide).	None	240	3.060	1.274	9.1	3.75
5	do	[1] 0.1 T	150	3.904	2.60	24.0	16.0
6	1.2 T of bromine (ethylene dibromide).	[1] 0.1 T	240	3.273	1.36	22.0	9.17

[1] P:Pb=0.2:3.

The same degrees of improvement are obtained by employing in fuels for internal combustion engines minor proportions of such fluids as, for example, tetraethyllead in combination with 1.2 theories of bromine as the various isomers of dibromotoluene, and 0.1 theory of phosphorus as triphenylthiophosphite; tetraethyllead in combination with 1.0 theory of chlorine as ethylene dichloride, 0.6 theory of bromine as ethylene dibromide, and 0.1 theory of phosphorus as triphenylphosphite; tetraethyllead in combination with 1.1 theories of chlorine as ethylene dichloride, 0.6 theory of bromine as ethylene dibromide, and 0.15 theory of phosphorus as dibutylbenzenephosphonate; tetraethyllead in combination with 1.4 theories of chlorine as ethylene dichloride, 0.6 theory of bromine as ethylene dibromide, and 0.2 theory of phosphorus as tricresylthiophosphate; tetraethyllead in combination with 1.0 theory of chlorine as 1,2,4-trichlorobenzene, 0.6 theory of bromine as dibromotoluene, and 0.1 theory of phosphorus as diphenylbenzenethionophosphonate; tetraethyllead in combination with 1.0 theory of chlorine as 1,2-dichloroethane, 0.6 theory of bromine as 1,2-dibromoethane and 0.1 theory of phosphorus as diphenylmonocresylphosphate; tetraethyllead in combination with 1.2 theory of chlorine as hexachlorocyclohexane, 0.6 theory of bromine as hexabromocyclohexane, and 0.15 theory of phosphorus as diphenylphosphine; tetramethyllead in combination with 1.4 theories of chlorine as 1,2,4-trichlorobenzene, 0.6 theory of bromine as dibromotoluenes, 0.05 theory of phosphorus as diphenylbutylphosphinite; tetrabutyllead in combination with 1.1 theories of chlorine as 1,2-dichloroethane, 0.6 theory of bromine as 2-bromo-2-methylpropane, 0.1 theory of phosphorus as dicresylbenzenethiophosphonate, and the like.

An additional advantage produced by the improved antiknock fluids of the instant invention is the fact that some of the phosphorus-containing materials described hereinbefore, such as tricresylphosphate, triphenylphosphate, and pyrocatecholphosphite, impart to such fluids the stabilizing or antioxidant effectiveness of such materials. Furthermore, some of the phosphorus-containing materials, such as triphenylphosphite, tricresylphosphite, tricresylphosphate, trilaurylphosphite, and tri-(p-tert-butylphenyl)-phosphate, are known to alleviate corrosion problems particularly in fuel storage tanks made of aluminum, magnesium, and diverse alloys thereof. Moreover, some of the phosphorus-containing materials, such as tri-(β - chloropropyl)thionophosphate, dimethyltolylphosphate, and dimethylxylylphosphate, are particularly good preignition suppressants. Additional advantages of the improved antiknock fluids and fuels of the present invention are the reduction of the total amount of solids normally found in the crankcase and a reduction in the total amount of metallic lead present in such solids. These reductions lessen the likelihood of interferences with normal oil flow and lubrication of critical engine parts.

In compounding some of the improved antiknock fluids of the present invention, I can also employ other antioxidants and other stabilizing compositions including ortho dialkylated phenols and N,N'-di-sec-butyl-p-phenylene diamine. Furthermore, I can also employ diverse organic dyes and the like which have long been recognized in the prior art, in such improved antiknock fluids of the present invention.

The improved antiknock fluids of this invention can be effectively utilized by supplemental injection into internal combustion engines and in dual fuel systems. Likewise, concentrated fuels containing substantially greater amounts of my antiknock fluids than ordinary treated fuels for internal combustion engines can be utilized in this manner.

Having fully described my invention, the need therefor, and the best method devised for carrying it out, it is not intended that it be limited except within the spirit and scope of the appended claims.

I claim:

1. In an antiknock composition consisting essentially of organolead material as the principal antiknock ingredient, organic halogen scavenger material selected from the class consisting of that having two atoms of chlorine plus one atom of bromine per atom of said anti-knock lead, and that having two atoms of bromine per atom of said antiknock lead, and a gasoline soluble phosphorus-containing, spark plug anti-fouling compound, the phosphorus-to-lead atom ratio of said composition being from about 0.02:3 to about 0.7:3; the improvement in which the bromine content of the organic halogen scavenger material is increased by about 15 to 20 percent.

2. In an antiknock composition consisting essentially of tetraethyllead, ethylene dichloride, ethylene dibromide, and a gasoline soluble phosphorus-containing, spark plug anti-fouling compound, the phosphorus-to-lead atom ratio of said composition being from about 0.1:3 to about 0.4:3, and the ethylene dichloride content being that which furnishes about two atoms of chlorine for every atom of lead, the improvement in which the ethylene dibromide content is such that for every atom of lead there are 1.2 atoms of bromine.

3. The antiknock composition of claim 2 wherein the phosphorus-containing compound is tricresylphosphate.

4. The antiknock composition of claim 2 wherein the phosphorus-containing compound is tri-β-(chloropropyl) thionophosphate.

5. In an antiknock composition consisting essentially of tetraethyllead, ethylene dibromide and a gasoline sol-

uble phosphorus-containing, spark plug anti-fouling compound, the phosphorus-to-lead atom ratio of said composition being from about 0.1:3 to about 0.4:3, the improvement in which the ethylene dibromide content is such that for every atom of lead there are 2.4 atoms of bromine.

6. A gasoline containing the composition of claim 1 in amount sufficient to provide effectively improved antiknock, but not more than equivalent to six milliliters of tetraethyllead per gallon.

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