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ANTI-KNOCK GASOLINE

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The present invention relates to fuels for use in spark-ignition internal combustion engines and more particularly relates to a new class of additive materials for incorporation into leaded gasolines in order to reduce octane requirement increase, surface ignition, spark plug fouling, and related phenomena associated with the formation of combustion chamber deposits in modern high compression gasoline engines.

Although many volatile organic metallic compounds of nickel, iron, manganese and lead, particularly tetraethyl lead and tetramethyl lead, are extremely useful as gasoline constituents for reducing knock caused in gasoline engines by auto-ignition of the fuel-air mixture as it is compressed, it is known that such compounds are not entirely beneficial. Deposits containing lead are formed upon pistons, valve surfaces, and spark plug points and insulators, for example, when tetraethyl and tetramethyl lead are used. These deposits, consisting primarily of lead oxides and salts and unburned carbon, become incandescent during operation of the engine and give rise to surface ignition, a premature igniting of the fuel-air mixture. They also cause in course of time an increase in the fuel octane quality level required for satisfactory engine operation, generally referred to as O.R.I. or octane requirement increase. In addition, by fouling the spark plugs, such deposits cause spark plug misfiring. These difficulties are particularly pronounced in modern high compression engines.

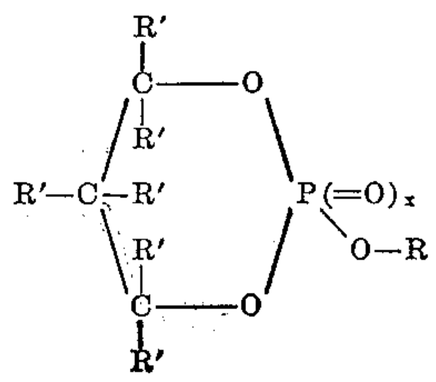
In order to minimize deposit formation in engines operated upon leaded gasolines and thus to ameliorate the difficulties set forth above, leaded gasolines always contain scavenger agents, usually alkyl halides such as ethylene dichloride, ethylene dibromide or mixtures of the two. The dihalide scavenger agents are incorporated into the gasoline in approximately the same molar concentration as are the lead compounds, conventionally designated "one theory" concentrations, and are designed to form halogen acids to react with the lead after combustion has begun and produce relatively volatile lead halides which will be swept from the combustion chamber with the exhaust gases. In practice it is found that such scavenger agents are only partially effective, however, and that deposit formation and the attendant difficulties occur despite their use, particularly in modern gasoline engines having compression ratios above about 9 to 1.

In recent years numerous additive agents have been proposed in order to overcome the problems arising from the use of lead or other organo-metallic anti-knock agents in gasolines. Although several of these have proved reasonably effective in some respects, it has been found that they all have disadvantages, particularly with respect to their tendency to depress the octane quality of the gasolines in which they are incorporated. Because of the high "octane requirement" of modern gasoline engines, that is the high octane number that gasolines must have in order to give knock-free operation of such engines, and

because of the practical limitations imposed upon octane levels by available petroleum refining processes and available gasoline blending stocks, the octane depressing or pro-knock properties of gasoline additives are becoming increasingly important. The cost of raising gasoline octane number in order to overcome the depressing effect of such additives as are presently in use frequently amounts to as much as one cent per gallon at present octane levels and will increase to an even higher figure if the compression ratios and octane requirements of automobile engines continue to rise. There is therefore tremendous incentive for the development of improved gasoline additives free from octane depressing properties.

The present invention provides a new class of gasoline additives which are effective for reducing octane requirement increase, surface ignition and spark plug fouling and which do not, to any significant extent, depress the octane quality of the gasolines to which they are added. In addition, these new additives have numerous other advantages over additive compositions which have been used or proposed for use heretofore. The additive agents of the invention, specific mixtures of certain cyclic phosphorus compounds and limited stoichiometric excesses of halohydrocarbon scavenger agents boiling between 50° C. and 250° C., preferably between 80° C. and 150° C., possess excellent stability properties, do not readily separate from gasolines to which they are added, decrease the tendency of the gasolines to oxidize and form objectionable gum, are relatively insoluble and non-reactive with water, and are compatible with a variety of other additive materials commonly used in gasolines for other purposes.

The phosphorus compounds which are incorporated in the gasolines of the present invention are heterocyclic, phosphorus-containing, organic compounds having the general formula:

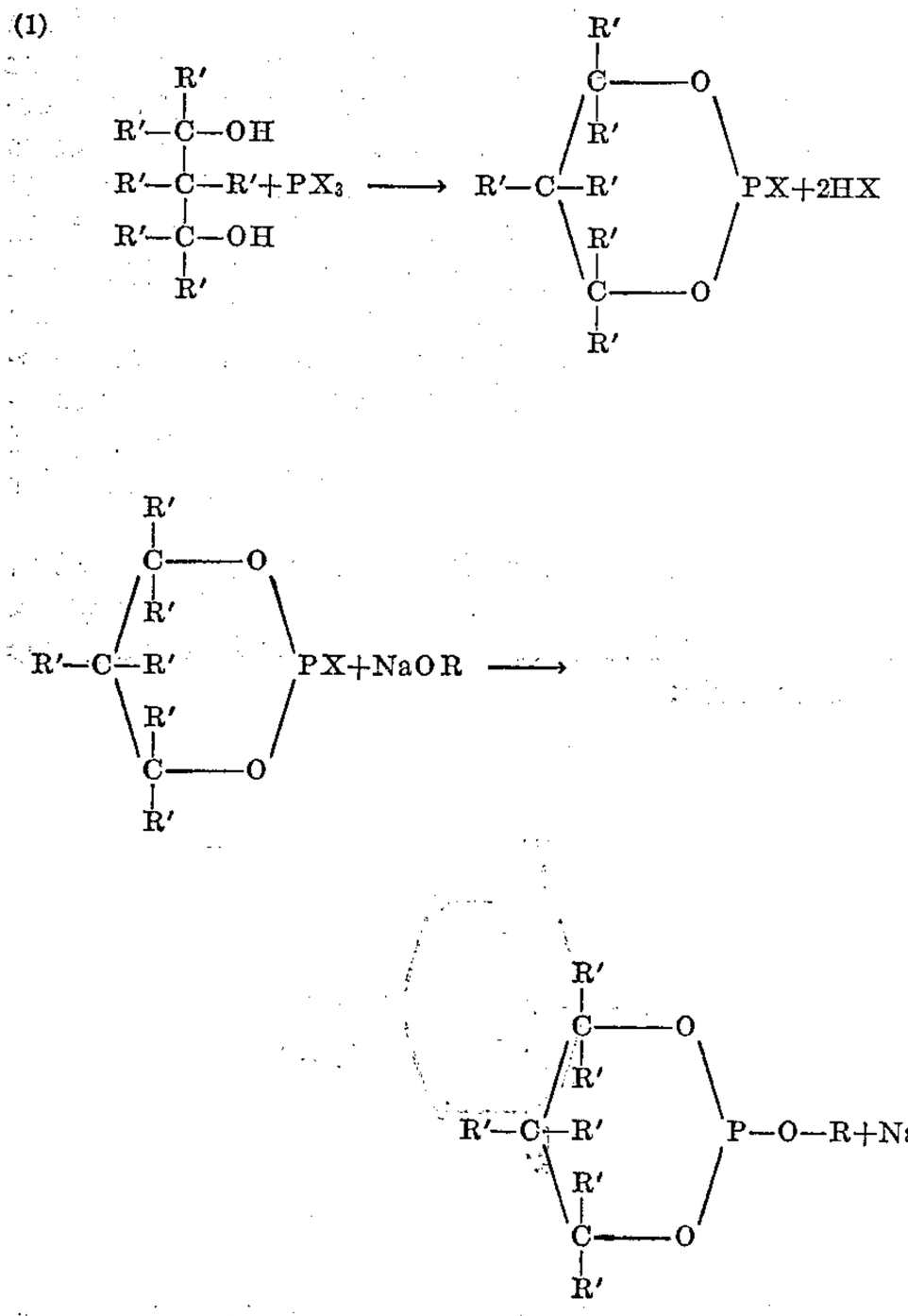


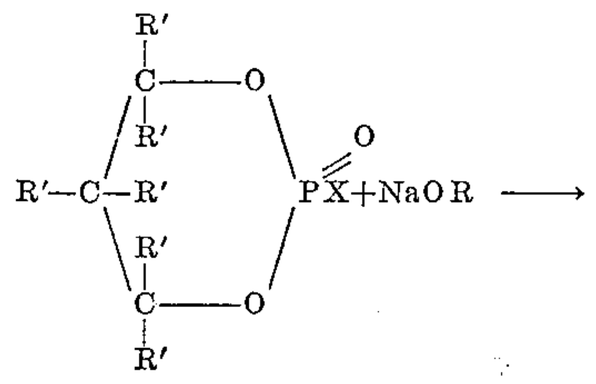
where R′ is a radical having the formula C_nH_{2n+1}, n ranging from 0 to 3 inclusive and preferably from 0 to 1 inclusive and there being at least two carbon atoms which are each attached directly to carbon atoms in the ring; where R is selected from the group consisting of the unsubstituted phenyl radical and alkyl radicals containing from 6 to 12 carbon atoms; and where x is a digit from 0 to 1 inclusive. The additive compounds thus described are heterocyclic phosphates and heterocyclic phosphites. It has been found that the 6 membered heterocyclic ring in these compounds is critical for purposes of the present

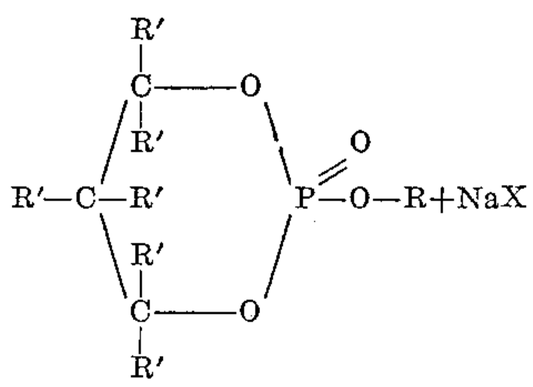
invention because it assures the proper stability and solubility of the compounds in gasoline without any appreciable lowering of gasoline octane number. Compounds having smaller heterocyclic structures, for example those having 5 membered rings, are much less stable than the compounds of the invention and are readily hydrolyzed by water, being therefore unstable in the presence of traces of water in gasoline and producing gasoline blends with lower octane numbers. Moreover, it has been found that cyclic phosphorus compounds having 5 membered rings often strongly discolor gasolines and produce oily sediments. Similarly, related compounds such as the thiophosphates produce sediment and are unsuitable for use in accordance with the invention. In general, the cyclic phosphites having the above formula are preferred to the phosphates because the latter are often solids at room temperatures and are thus more difficult to incorporate into the gasolines. The phenyl cyclic phosphites and the branched alkyl cyclic phosphites having about 8 carbon atoms in the alkyl group are particularly preferred additive materials for use in accordance with the invention.

The cyclic phosphorus compounds described above may be readily prepared by the reaction of a phosphorus halide or a phosphorus oxy-halide with a glycol having its hydroxyl groups separated by one carbon atom in accordance with the following two sets of equations:

(1)



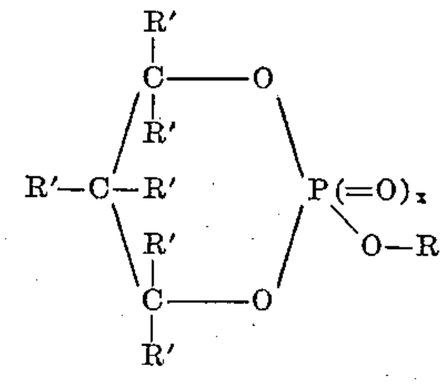




where X represents a halogen atom; R′ represents hydrogen atoms or alkyl groups containing from 1 to 3 carbon atoms, at least 2 of the R′ groups being alkyl groups; and R is a phenyl group or a branched alkyl group containing from 6 to 12 carbon atoms. The cyclic compounds may also be prepared by reacting phosphoryl dihalides with glycols in a similar manner.

The glycols which are employed in preparing the cyclic phosphorus compounds of the invention are aliphatic glycols having two hydroxyl groups attached to carbon atoms which are separated by one carbon atom. These glycols must have at least 5 carbon atoms and may concontain as many as 21 carbon atoms. Specific examples of such glycols include 1,3-pentylene glycol, 2,4-pentylene glycol, 2-methyl-2,4-pentylene glycol, 3,3-dimethyl-2,4-pentylene glycol, 1,3-hexylene glycol, 2,4-hexylene glycol, 2-propyl-3-diethyl-2,4-hexylene glycol, 2,2,-dimethyl-1,3-propane diol and 3-propyl-4,4-dipropyl-5-ethyl-3,5-octylene glycol. Glycols containing from about 5 to about 9 carbon atoms are preferred for use in preparing the additives of the invention and 2-methyl-2,4-pentylene glycol is particularly preferred.

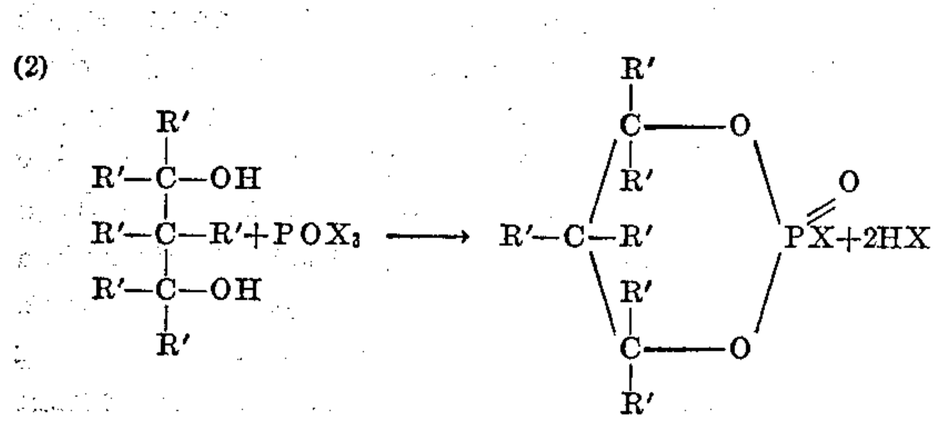
In preparing the alkyl heterocyclic phosphorus compounds having the formula:



where the symbole have the significance set forth above, the use of C_8-oxo alcohols as the source of the branched chain alkyl group has been found to be particularly advantageous.

The C_8-oxo alcohols are prepared by the oxonation and subsequent hydrogenation of a C_7 copolymer of propylene and butene. The copolymer consists of a mixture of isomers, usually being derived from a refinery gas stream containing propylene and mixed normal and isobutylenes, and therefore the C_8-oxo alcohol and the alkyl cyclic phosphorus compounds prepared from such alcohol consist of

(2)



series of isomeric compounds. C_8-oxo alcohol normally has the following general analysis:

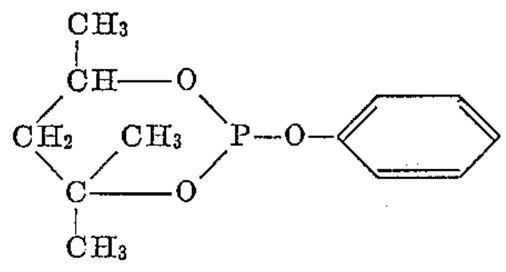
Alcohol Constituent	Percent
$CH_3-CH(CH_3)-CH_2-CH(CH_3)-CH_2-CH_2-OH$	29
$CH_3-CH(CH_3)-CH(CH_3)-CH_2-CH_2-CH_2OH$	25
$CH_3-CH_2-CH(CH_3)-CH(CH_3)-CH_2-CH_2-OH$	17
$CH_3-CH_2-CH(CH_3)-CH_2-CH_3-CH_2-CH_2-OH$	16
$CH_3-CH_2-CH_2-CH(CH_3)-CH_2-CH_2-CH_2-OH$	
$CH_3-CH_2-CH(CH_2CH_3)-CH_2-CH_2-CH_2-OH$	2.3
$CH_3-C(CH_3)_2-CH_2-CH_2-CH_2-CH_2-OH$	1.4
2 alkyl alkanols unidentified for structure	4.3
Others	5.0
Total	100.0

The C_8-oxo heterocyclic phosphorus compounds prepared from C_8-oxo alcohol have alkyl chains which correspond to those of the alcohol as set forth above and are thus mixtures of isomeric octyl heterocyclic phosphorus compounds. Similar mixtures may be derived from mixtures of primary alcohols containing from about 6 to about 12 carbon atoms per molecule and are suitable for use in accordance with the invention.

In preparing the heterocyclic phosphorus compounds of the invention by reacting a phosphorus halide or a phosphorus oxy-halide with a glycol as shown in Equations 1 and 2 above, the reactants are mixed at a temperature in the range of from about 30° C. to about 150° C., preferably about 40° C. to about 90° C. The reaction may be carried out in the presence of an inert solvent such as benzene, toluene, naphtha or the like. The reaction materials should be intimately mixed in order to assure complete reaction. The reaction period will normally be from about 0.5 to about 4 hours. Upon completion of the reaction, the product may be filtered to remove any solids present and the intermediate cyclic esters may be recovered by methods well known to those skilled in the art. These intermediate cyclic esters are then reacted with a sodium phenate solution or a sodium salt of a primary alcohol such as C_8-oxo alcohol in order to obtain the cyclic esters used as additive materials in accordance with the invention. The sodium phenate or sodium salt of the alcohol is preferably employed in aqueous solution in a concentration of from about 20 to about 40% or higher. The intermediate ester and the sodium salts may be mixed at a temperature in the range of from about 0 to about 5° C. at a rate to maintain that temperature. After the reactants have been mixed they should be allowed to reach room temperature while being stirred. Upon standing an ester layer and an aqueous layer will be formed. The produced ester may be recovered and water washed to remove unreacted materials and partial esters. Further ester purification procedures familiar to those skilled in the art may then be employed to obtain the finished cyclic phosphorus compounds.

The preparation of the cyclic compounds utilizing phosphoryl dihalides is similar to that described above. The phosphoryl dihalides are available commercially or may be prepared by reacting a phosphorus halide or phosphorus oxy-halide with sodium phenate or a sodium salt of a primary alcohol. Reaction conditions similar to those previously described are employed.

Typical inspections of a cyclic phosphorus compound prepared in the manner described above and having the formula



are as follows:

Property:	Typical value
Composition	$C_{12}H_{17}O_3P$.
Formula weight	240.24.
Density, $D_4^{25°}$	1.0934.
Boiling point	95–97°C. at 0.2 mm. Hg
Melting point	<0° C.
Refractive index, $N_D^{25°}$	1.5102.
Solubility:	
Water	Insoluble.
Hexane	Soluble.
Benzene	Do.
Acetone	Do.

This compound will be referred to hereinafter as phenyl hexylene phosphite.

The halohydrocarbon employed in the compositions of the invention may be an alkyl halide such as chlorobromomethane, tetrabromoacetylene, trichloroethylene, ethylene dichloride or ethylene dibromide; an alicyclic halogenated compound such as chlorocyclopentane or trichlorocyclopentane, an aromatic halogen compound such as chlorobenzene, dibromobenzene, trichlorobenzene, dibromotoluene or bromoxylene; or a mixture of such halohydrocarbons. Ethylene dichloride, ethylene dibromide and certain mixtures thereof are particularly preferred because of their effectiveness, which may be partly due to their volatility and chemical stability being appropriate for them to accompany the lead or other metallic compounds into the reactions which occur during combustion in an engine.

The amounts of the cyclic phosphorus compound and the halohydrocarbon employed in accordance with the invention are dependent upon the quantity of the organometallic antiknock compound, e.g. tetraethyl lead or an equivalent lead compound, employed in the gasoline. For this reason, these amounts can be best expressed in terms of "theories," one theory being the amount of a constituent stoichiometrically equivalent to the lead in the gasoline. For example it is the ratio Cl_2/Pb for chlorine or P_2/Pb_3 for phosphorus. This method of expressing additive concentrations is a conventional one and will be familiar to those skilled in the fuels art. The total theories of phosphorus, chlorine and bromine may be as low as 1.65 but are preferably between 1.75 and 2.10 when the gasoline contains more than 2.5 cc. of tetraethyl lead per gallon and should not exceed 4.00. The cyclic phosphorus compounds may be added to the fuels of the invention in amounts ranging from about 0.05 theory to about 1.0 theory, concentrations of about 0.1 to 0.8 theory being preferred and concentrations of about 0.15 to 0.4 theory being particularly advantageous.

The halohydrocarbon scavenger may be present in the fuels of the invention in amounts ranging from 1.6 theories to about 3.0 theories, concentrations of from 1.7 theories to 2.1 theories being preferred. Conventional lead fluids

contain some halohydrocarbon scavenger in addition to the alkyl lead compound. Therefore, if a conventional lead fluid is used, the amount of halohydrocarbon must be adjusted by further addition of ethylene dichloride or dibromide in order to bring the total halohydrocarbon content up to from 1.6 to 3.0 theories. Usually such fluids contain 1.0 theory of ethylene dichloride and 0.5 theory of ethylene dibromide and it is therefore necessary to add from 0.1 to 1.5 theories of additional halohydrocarbon for the purpose of the present invention. Furthermore, the theories of halohydrocarbon in total must be such as to give a ratio of at least 3 to 1 to the phosphorus compound but not more than 32 to 1. In a particularly preferred embodiment of the present invention, the theory ratio of ethylene dichloride to ethylene dibromide is between 2.4 and 4.2 to 1.

The tetraethyl lead content of the gasolines in which the additive agents of the invention are incorporated may range from about 2.0 to 4.6 cc. per gallon. In addition, the gasolines may contain a solvent oil, for example one consisting of hydrocarbon mixtures having a Saybolt viscosity at 100° F. not exceeding about 450 seconds, a 50% distillation point above about 350° F. at 10 mm. Hg and an A.P.I. gravity between about 18 and 28°; corrosion inhibitors such as Santolene C, which is a phosphorus-containing dimer of linoleic acid, amines and amine phosphates and nitrites; gum inhibitors such as N,N'-di-secondary butyl p-phenylenediamine, 2,4-dimethyl-6-tertiary butylphenol and 2,6-ditertiary butyl-4-methylphenol; anticing agents such as isopropanol, hexylene glycol, carbitol and dimethyl formamide; dyes such as 1,4-diisopropyl amino anthraquinone and p-dimethyl aminoazobenzene; dye stabilizers such as ethylene diamine; and similar additive materials commonly used in gasolines.

Gasoline as used in connection with the present invention is a well-known article of commerce for use in internal combustion engines operating on the Otto cycle. It is supplied in different grades depending upon the type of service for which it is intended. The grade of gasoline to which the invention particularly applies is motor gasoline, which the American Society for Testing Materials broadly characterizes as "a complex mixture composed almost entirely of relatively volatile hydrocarbons which vary widely in their physical and chemical properties." Motor gasoline for use in accordance with the present invention meets ASTM Specification D–439–56T, in Types A, B, and C. It is composed of a mixture of various types of hydrocarbons, including aromatics, olefins, paraffins, isoparaffins, naphthenes and sometimes some diolefins. These mixtures are obtained from petroleum by refining processes including fractional distillation, catalytic cracking, hydroforming, alkylation and extraction.

Motor gasoline boils between about 80° F. initial boiling point and about 450° F. when tested by ASTM Method D86. Its vapor pressure by ASTM Method D–323 varies for use at different seasons between 7 and 15 lbs. per square inch at 100° F. An important property of motor gasoline is its octane number as measured by ASTM Method D–908. The present invention is particularly applicable to gasoline having at least 83 octane number by this method and containing at least 2 cc. of tetraethyl lead per gallon. The composition of gasoline according to the present invention comprises at least 95% by weight of hydrocarbons. The invention is particularly effective in motor gasoline containing at least 30% aromatics and up to 60% aromatics.

A particularly preferred method of incorporating the additive materials of the invention into gasolines is to include them in an additive concentrate containing tetraethyl lead or a similar alkyl lead compound. Such a concentrate may contain in critical proportions to each other, from 0.05 to 1.0 theory of the cyclic phosphorus compound and from 1.6 to 3.0 theories of the halohydrocarbon, based on the lead content, and may include other gasoline additive materials such as those set forth above.

A typical concentrate containing tetraethyl lead and the additive materials of the invention may have the following composition by weight:

Tetraethyl lead	5.5% or 0.2 theory.
Phenyl hexylene phosphite	15.5% or 0.5 theory.
Ethylene dibromide	19.6% or 1.2 theory.
Ethylene dichloride	5.9%.
Gum inhibitor, rust inhibitor, dyes, dye stabilizers, etc	53.5%.

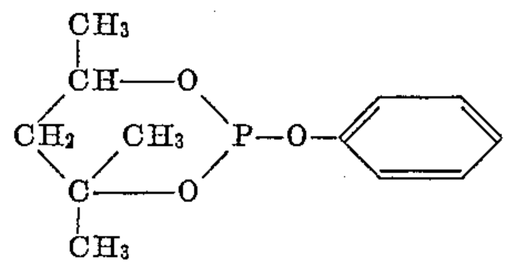
The invention may be further illustrated by referring to the following examples.

EXAMPLE I

In order to demonstrate the effectiveness of the improved fuels of the invention upon octane requirement increase, surface ignition and spark plug fouling in modern automotive engines, a series of tests was conducted in which five different makes of 1957 automobiles having compression ratios above 9.0 to 1 were operated upon a premium quality gasoline containing 3 cc. of tetraethyl lead per gallon and 1.5 theories of a scavenger agent consisting of 1.0 theory of ethylene dichloride and 0.5 theory of ethylene dibromide. Typical inspections of the gasoline used in these tests were as follows.

A.S.T.M. Distillation D–86:	
Initial boiling point, ° F	104
10% boiling point, ° F	136
50% boiling point, ° F	216
90% boiling point, ° F	291
Final boiling point, ° F	345
Residue, percent	0.8
Loss, percent	1.2
Reid vapor pressure	7.6
A.P.I. gravity	56.4
General motors gum	2.20
Research octane number	101.4
Motor octane number	89.2

The same automobiles were then operated on a similar gasoline to which had been added 0.2 theory of phenyl hexylene phosphite, the cyclic phosphorus compound having the formula



and 0.2 theory of ethylene dichloride, giving a total additive agent content of 1.9 theories. The equilibrium octane requirements of the engines were determined for both gasolines from the standpoint of spark knock and surface ignition of the "wild knock" (rolls) and "wild ping" (snap) types, using commercial reference fuels as a basis for comparison. "Rumble," a rapid surface ignition which causes vibrational noises at speeds of from 40 to 70 miles per hour and is independent of fuel octane number, was measured and spark plug fouling, as indicated by the percent of misfires at about 15 to 70 miles per hour registered by an electronic counter, was determined.

It is to be noted that the requirements in octane number, that is the levels of octane number at which both spark knock and surface ignition no longer occurred, were determined at "equilibrium." It is important that equilibrium conditions be reached in measurements of this sort because initially the addition of an intended beneficiating agent to gasoline may show some improvement in suppressing surface ignition in an engine but upon continued

use this agent may promote spark knock, with the ultimate result that a gasoline of higher octane number is required to give "no-noise" operation of the engine than was required before the agent was added to the gasoline. The attainment of equilibrium for these tests is achieved only after the test automobiles have been run for at least 3,000 miles. The results of these tests are shown in the following table.

Table I

EFFECT OF ADDITIVES UPON EQUILIBRIUM OCTANE REQUIREMENT AND SPARK PLUG FOULING

Car	Fuel [1] [2]	Spark knock equilibrium octane requirement	Surface ignition [3] equilibrium octane requirement	Rumble[4]	Spark plug fouling, percent misfires	No-noise octane advantage
I ((.5:1 C.R.)-------	A	96	97	105	32	----------
	B	93½	91	None	4	3½
II (10.0:1 C.R.)-----	A	93½	98	105	8	----------
	B	91½	91½	None	0	6½
III (9.5:1 C.R.)-----	A	96	97	105	42	----------
	B	94½	91½	None	6	2½
IV (9.7:1 C.R.)-----	A	95½	91½	None	0	----------
	B	93½	91½	None	0	2
V----------	A	93½	90	None	8	----------
	B	90½	89	None	3	3

[1] Fuel A was a high octane commercial gasoline containing 3 cc. of tetraethyl lead per gallon and 1.5 theories of halohydrocarbon scavenger in the form of 1 theory of ethylene dichloride and 0.5 theory of ethylene dibromide.

[2] Fuel B was identical to Fuel A except that it also contained 0.2 theory of phenyl hexylene phosphite and 0.2 theory of additional ethylene dichloride.

[3] "Wild knock (rolls)" and "Wild ping (snap)" types of surface ignition.

[4] Rumble is a vibration which occurs in cars with high compression ratios. It is not strictly proportional to fuel octane quality but it can be eliminated by increasing fuel octane number. The numbers in the table give the maximum octane fuel with which rumble is heard. When rumble was detected after a car had been run to equilibrium with the test fuel, the octane requirement necessary to eliminate it was determined by operating the car on commercial reference fuels. The word "none" indicates that rumble was wholly absent.

The data in the foregoing table show that the octane requirement at equilibrium for eliminating the noise of spark knock, surface ignition and rumble and the incidence of spark plug misfiring were both markedly lower when the fuels of the invention were used and that the presence of the special combination of the cyclic phosphorus compound, ethylene dichloride and ethylene dibromide in accordance with the present invention gave an advantage of from 2 to 6½ octane numbers in the no-noise equilibrium level. In fact, in every test the requirement was consistently lower after running on Fuel B than after running on Fuel A. This means that all these cars throughout their useful life would give knock-free performance on a fuel of the type of Fuel B having only 94.5 octane number; whereas if a fuel like Fuel A were used in the same cars, its octane number would have to be at least 98 and perhaps 105, to give completely noise-free performance.

EXAMPLE II

A second series of tests similar to those described in the preceding example was carried out comparing a gasoline similar to that of the preceding example but containing 2.9 cc. of tetraethyl lead per gallon and 1.5 theories of a scavenger consisting of a mixture of ethylene dibromide and ethylene dichloride with another batch of the same gasoline to which had been added 0.4 theories of tricresyl phosphate, a compound used heretofore in commercial gasolines in order to prevent spark plug fouling and associated difficulties caused by lead deposit formation. The cars were driven under city-suburban driving conditions for a total of about 12,000 miles. Tests were carried out using standard commercial reference fuels and the standard Uniontown procedure to determine equilibrium octane requirements from the standpoint of spark knock and surface ignition. It was found that although the tricresyl phosphate had a beneficial effect with respect to surface ignition in all but one of the cars, the benefit was offset by an increase in the spark-knock requirement, ½ to 3½ numbers. The fuels of the present invention as shown in Table I are thus superior to fuels containing such commercial additives of the prior art as shown by the data in Table II below.

Table II

Car	Gasoline	Equilibrium octane requirement for operation free of—	
		Spark knock	Surface ignition
I-----	Base fuel [1]----------	99	100
	Base fuel plus 0.4 theories tricresylphosphate.	100½	99
II----	Base fuel [1]----------	99	99½
	Base fuel plus 0.4 theories tricresylphosphate.	99½	100½
III---	Base fuel [1]----------	96	100
	Base fuel plus 0.4 theories tricresylphosphate.	99½	98
IV----	Base fuel [1]----------	96½	99½
	Base fuel plus 0.4 theories tricresylphosphate.	99½	97
V-----	Base fuel [1]----------	97	99½
	Base fuel plus 0.4 theories tricresylphosphate.	98½	None

[1] Base fuel contained 2.9 cc. of tetraethyl lead, 1.0 theory of ethylene dichloride and 0.5 theory of ethylene dibromide and had a research octane number of about 98.2.

EXAMPLE III

In order to determine what effect the cyclic phosphorus compounds and halohydrocarbons employed in accordance with the invention would have on the octane number of a gasoline to which they were added, direct match octane number determinations were made using premium grade commercial leaded gasolines, with and without the addition of 0.2 theory of phenyl hexylene phosphite and 0.2 theory of additional ethylene dichloride. The data obtained in these tests are shown in Table III.

Table III

EFFECT OF 0.2 T. PHENYL HEXYLENE PHOSPHITE AND 0.2 T. ETHYLENE DICHLORIDE ON RES. AND MOTOR O.N.
[Direct Match O.N. determinations]

Research Antiknock rating (iso+cc. TEL) [1]			Motor octane number		
Additive [2] blend in super premium fuel	Super premium fuel	Decrement due to additive	Additive [2] blend in super premium fuel	Super premium fuel	Decrement due to additive
.06	.08	0.02	89.1	89.2	−0.1
.11	.14	0.03	89.2	89.2	0
.14	.14	0	88.9	88.9	0
.07	.08	0.01	88.6	88.6	0
.07	.08	0.01	88.7	88.7	0
.07	.08	0.01	88.6	88.6	0
.10	.13	0.03	88.6	88.6	0
.10	.11	0.01	89.0	89.0	0
.08	.10	0.02	88.6	88.6	0
.08	.10	0.02	88.6	88.8	−0.2

[1] Research antiknock ratings above 100, which is the limit of the scale of octane numbers, are conventionally reported in terms of cubic centimeters of tetraethyl lead added per gallon of iso-octane (I.E. iso+cc. TEL) to match antiknock value of the fuel being tested.
[2] The additive was a mixture of 0.2 theory of ethylene dichloride and 0.2 theory of phenyl hexylene phosphite, added to the base fuel already containing commercial lead fluid.

From the above it can be seen that the incorporation of the cyclic phosphorus compounds and halohydrocarbons in gasolines in proportions in accordance with the present invention does not have any significant effect on the octane number of the fuel, as tested conventionally before use in an automobile.

EXAMPLE IV

For comparative purposes, additional direct match octane determinations were carried out using commercial leaded gasoline similar to that employed in the preceding example without and with the addition of various other phosphorus compounds. The results of these tests are summarized in the following table.

The above data show the effect of a large number of representative phosphorus compounds upon the octane quality of leaded gasolines to which they were added. It will be noted that of the compounds listed, only the phenyl hexylene phosphite and the isodecyl ester in Table IV, the additives of the present invention, did not suppress appreciably octane quality at 0.2 T. concentration. Several of the compounds, including the compounds now used commercially as gasoline additives, caused a loss in Motor Octane Number of as much as 1.0 octane numbers when added to the gasoline in only 0.2 T. theory amounts.

EXAMPLE V

In order to determine the suitability of the fuels of the present invention for use as additives in gasolines subjected to extreme temperature fluctuations, samples of a commercial leaded gasoline and samples of the same gasoline to which had been added 0.2 theory of phenyl hexylene phosphite were refrigerated to determine the temperature at which solid materials were precipitated. It was found that the addition of the additive material did not appreciably raise the temperature at which the separation of solids occurred and that gasolines containing the additive could be used at temperatures as low as −35° C. without loss of the additive.

EXAMPLE VI

Samples of a premium grade and a super premium grade gasoline were tested for potential gum in accordance with ASTM Method D–873, both with and without the addition of phosphorus additives. These gasolines contained 3 cc. of tetraethyl lead per gallon and, as customary in commercial motor gasoline, the usual halide scavenger consisting of 1.0 theory of ethylene dichloride and 0.5 theory of ethylene dibromide.

In each gasoline the following additives were added:

(A) 0.2 theory of phenyl hexylene phosphite and 0.2 theory of ethylene dichloride.
(B) 0.2 theory of tricresyl phosphate and 0.2 theory of ethylene dichloride.

Table IV

Additive	Concentration, theories	Research octane number [1]			Motor octane number		
		Base fuel	Base fuel plus additive	Change in octane number due to additive	Base fuel	Base fuel plus additive	Change in octane number due to additive
Triethyl phosphate	0.2	100.5	100.5	0	89.8	89.2	−0.6
	0.4	100.5	100.4	−0.1	89.8	87.8	−2.0
Triisooctyl phosphate	0.2	100.7	100.7	0	89.5	88.5	−1.0
	0.4	100.7	100.1	−0.6	89.5	88.2	−1.3
Triisopropyl phosphite	0.2				88.8	88.2	−0.6
	0.4				88.8	87.5	−1.3
Tricresyl phosphate	0.2	101.3	100.8	−0.5	88.7	88.3	−0.4
	0.4	101.6	101.3	−0.3	88.6	88.6	0
Butyl diphenyl phosphate	0.2	101.1	100.9	−0.2	89.2	88.7	−0.5
	0.4	101.1	100.8	−0.3	89.2	88.6	−0.6
Isodecyl ester of cyclic phosphite of neo pentyl glycol	0.2	100.4	100.2	−0.2	89.8	89.8	0
Ethyl hexylene phosphite plus Et. Cl_2	0.2	99.8	99.6	−0.2	89.4	88.8	−0.6
	0.2	99.6	99.2	−0.4	89.5	88.9	−0.6
Butyl hexylene phosphite	0.2	99.6	99.4	−0.2	89.7	89.2	−0.5
	0.2	99.6	99.4	−0.2	89.8	89.2	−0.6
Butyl hexylene phosphite plus Et. Cl_2	0.2	99.8	99.6	−0.2	89.7	88.8	−0.9
	0.2	99.9	99.4	−0.5	89.7	88.9	−0.8
Trichloro-isopropyl thiono-phosphate	0.2	100.7	100.5	−0.2	90.3	89.3	−1.0
	0.4	100.7	100.0	−0.7	90.3	88.6	−1.7
Dimethyl xylyl phosphate	0.2	100.9	100.9	0	89.7	89.7	0
	0.4	100.9	100.7	−0.2	89.8	89.1	−0.7
Hexamethyl phosphoramide	0.2	99.4	99.4	0	89.0	87.8	−1.2
	0.4	99.7	99.4	−0.3	89.0	87.3	−1.7
Diethyl ethyl phosphonate	0.2	100.4	100.3	−0.1	89.2	88.6	−0.6
	0.4	100.4	100.1	−0.2	89.2	87.8	−1.4
Diethyl ethyl phosphonate plus equal ethylene dichloride	0.2	101.6	100.9	−0.7	88.9	88.6	−0.3
Phenyl hexylene phosphite plus extra ethylene dichloride	0.2	[2] 100.6	[2] 100.6	0	[2] 88.6	[2] 88.5	+0.1
	0.2	[2] 100.0	[2] 99.9	−0.1	[2] 89.5	[2] 89.8	+0.3

[1] Using an empirical extrapolation above 100 Octane Number.
[2] Average of two determinations.

The samples containing additive (A) were compositions in accordance with the present invention, containing in total a mixture of 0.2 theory of phenyl hexylene phosphite, 1.2 theories of ethylene dichloride and 0.5 theory of ethylene dibromide. Tests in accordance with ASTM Method D-873 gave the following results:

Additive blend in super premium motor gasoline: [1]	Time in minutes before breakdown
None	397
Phenyl hexylene phosphite+Et. Cl_2, 0.2 T	397
TCP plus Et. Cl_2, 0.2 T	302
Additive blend in premium motor gasoline: [2]	
None	897
Phenyl hexylene phosphite+Et. Cl_2, 0.2 T	>937
TCP plus Et. Cl_2, 0.2 T	840

[1] 100 Research Octane Number and 90 Motor Octane Number.

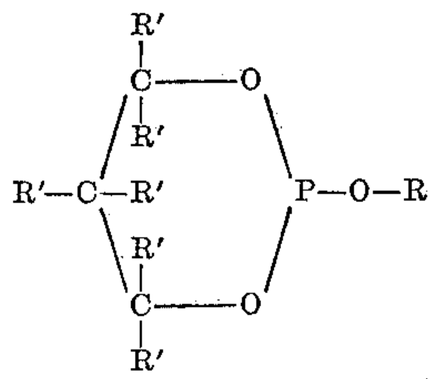
[2] 97 Research Octane Number and 87 Motor Octane Number.

As shown by the foregoing examples, the additive materials of the present invention materially reduce octane requirement increase, surface ignition, and spark-knock in engines operated upon high octane leaded gasolines containing such additive materials. Moreover, these additives possess excellent stability and compatibility properties and may be incorporated into gasolines without appreciable lowering of the gasoline octane level. These properties make the additive disclosed considerably more effective for use in overcoming the difficulties occasioned by the presence of tetraethyl lead than other phosphorus compounds which have been proposed and used heretofore.

It will be apparent that the additive materials of the invention are of application to any leaded gasoline including automotive type gasolines, marine type gasolines and aviation gasolines and are of particular application to motor gasolines intended for use in modern high compression engines which are susceptible to the adverse effects arising from the use of fuels containing tetraethyl lead.

What is claimed is:

1. An improved gasoline additive composition consisting essentially of a volatile organic lead compound; from about 1.6 to about 3.0 theories, based upon the lead, of a halogenated hydrocarbon scavenger agent boiling between about 50° and about 250° C. said halogenated hydrocarbon scavenger agent containing from 0.1 to 1.5 theories of a stoichiometric excess of a chlorinated hydrocarbon scavenger; and from about 0.05 to about 1.0 theory, based upon the lead, of a cyclic phosphorus compound having the formula

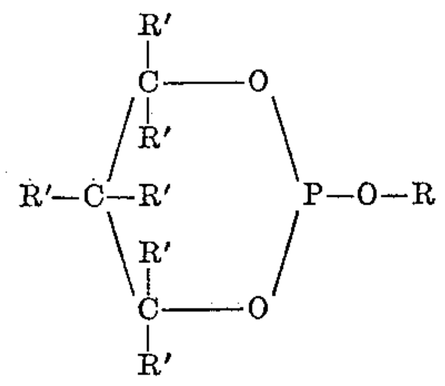


where R′ is a radical having the formula C_nH_{2n+1}, *n* ranging from 0 to 3 inclusive and there being at least 2 carbon atoms which are each attached directly to carbon atoms in the ring; and where R is selected from the group consisting of the phenyl radical and branched alkyl radicals containing from 6 to 12 carbon atoms.

2. A composition as defined by claim 1 wherein said lead compound is tetraethyl lead.

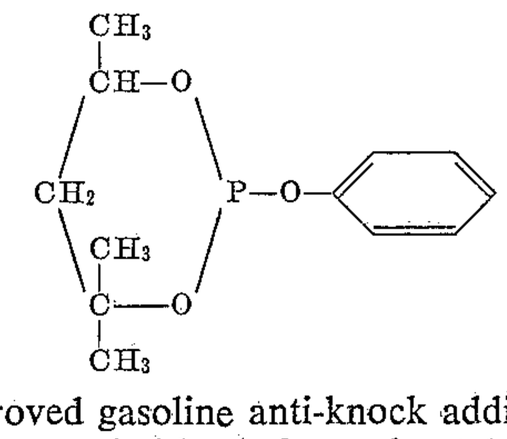
3. A composition as defined by claim 1 wherein said halogenated hydrocarbon is a mixture of ethylene dichloride and ethylene dibromide.

4. An improved gasoline anti-knock additive consisting essentially of tetraethyl lead; from about 1.6 to about 3.0 theories of a mixture of ethylene dichloride and ethylene dibromide and containing from 0.1 to 1.5 theories of a stoichiometric excess based on the lead of ethylene dichloride; and from about 0.05 to about 1.0 theory of a compound of the formula

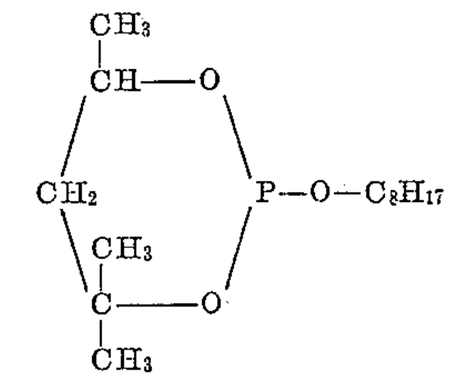


where R′ is a radical having the formula C_nH_{2n+1}, *n* ranging from 0 to 1 inclusive and there being at least 2 carbon atoms which are each attached directly to carbon atoms in the ring; and where R is selected from the group consisting of the phenyl radical and alkyl radicals containing from 6 to 12 carbon atoms.

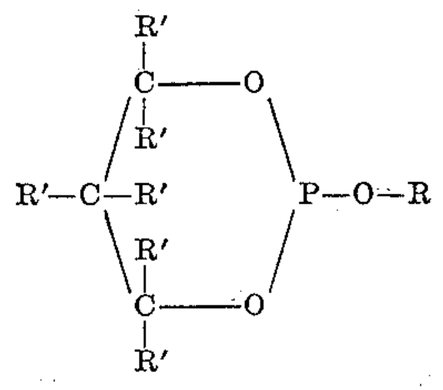
5. An improved gasoline anti-knock additive consisting essentially of tetraethyl lead; from about 1.7 to about 2.1 theories of a mixture of ethylene dichloride and ethylene dibromide and containing from 0.1 to 1.5 theories of a stoichiometric excess based on the lead of ethylene dichloride, the ratio of said dichloride to said dibromide being between 2.4 and 4.2 to 1 on a theory basis; and from 0.1 to about 0.8 theory of a compound of the formula



6. An improved gasoline anti-knock additive consisting essentially of tetraethyl lead; from about 1.7 to about 2.1 theories of a mixture of ethylene dichloride and ethylene dibromide and containing from 0.1 to 1.5 theories of a stoichiometric excess based on the lead of ethylene dichloride, the ratio of said dichloride to said dibromide being between 2.4 and 4.2 to 1 on a theory basis; and from 0.1 to about 0.8 theory of a compound of the formula



7. An improved gasoline containing a volatile organic lead compound as an anti-knock agent; from about 1.6 to 3.0 theories, based upon the lead, of a halogenated hydrocarbon scavenger agent boiling between about 50° and 250° C. said halogenated hydrocarbon scavenger agent containing from 0.1 to 1.5 theories of a stoichiometric excess of a chlorinated hydrocarbon scavenger; and from about 0.05 to about 1.0 theory, based upon the lead, of a phosphorus compound having the formula



where R′ is a radical having the formula C_nH_{2n+1}, *n* ranging from 0 to 3 inclusive and there being at least 2 carbon atoms which are each attached directly to carbon

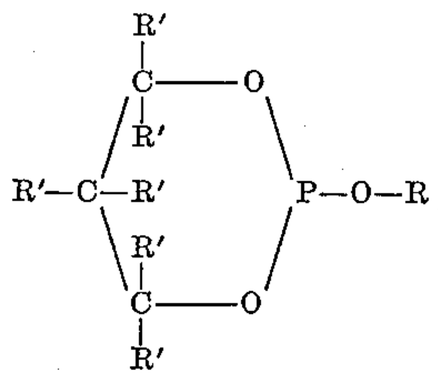
atoms in the ring; and where R is selected from the group consisting of the phenyl radical and alkyl radicals containing from 6 to 12 carbon atoms.

8. A gasoline as defined by claim 7 wherein said lead compound is tetraethyl lead.

9. A gasoline as defined by claim 7 wherein said halogenated hydrocarbon is a mixture of ethylene dichloride and ethylene dibromide.

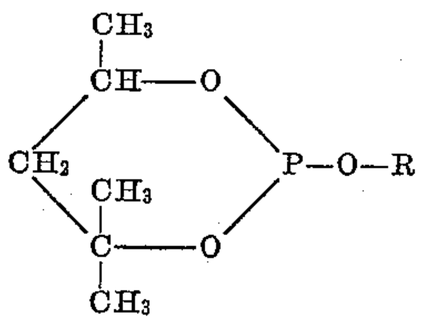
10. A gasoline as defined by claim 7 wherein said halogenated hydrocarbon is present in a concentration of from 1.7 to 2.1 theories, based upon the lead, and said phosphorus compound is present in a concentration of from 0.1 to 0.8 theory, based upon the lead.

11. An improved gasoline having incorporated therein from about 2.0 to about 4.6 cc. of tetraethyl lead per gallon; from about 1.6 to about 3.0 theories, based upon the lead, of a halogenated hydrocarbon boiling between about 50° C. and about 250° C. and containing from 0.1 to 1.5 theories of a stoichiometric excess based on the lead of ethylene dichloride; and about 0.05 to 1.0 theory, based upon the lead, of a phosphorus compound having the formula



where R′ is a radical having the formula C_nH_{2n+1}, n ranging from 0 to 1 inclusive and there being at least 2 carbon atoms which are each attached directly to carbon atoms in the ring; and where R is selected from the group consisting of the phenyl radical and alkyl radicals containing from 6 to 12 carbon atoms.

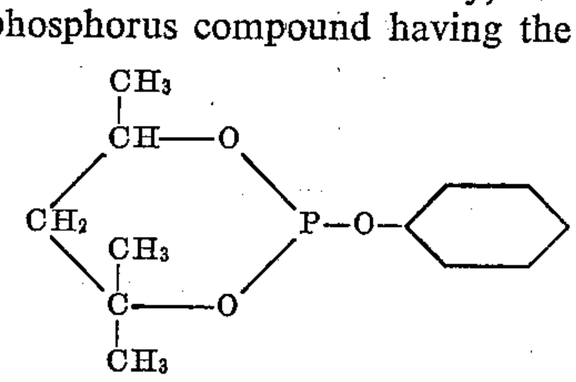
12. An improved gasoline having incorporated therein from about 2.0 to about 4.6 cc. of tetraethyl lead per gallon; about 1.6 to about 3.0 theories, based upon the lead, of a mixture of ethylene dichloride and ethylene dibromide and containing from 0.1 to 1.5 theories of a stoichiometric excess based on the lead of ethylene dichloride; and about 0.05 to 1.0 theory, based upon the lead, of a phosphorus compound having the formula



where R is an alkyl group containing from 6 to 12 carbon atoms.

13. A gasoline as defined by claim 12 wherein the alkyl ester group of said phosphorus compound is a C_8H_{17} group.

14. An improved gasoline having incorporated therein from about 2.0 to about 4.6 cc. of tetraethyl lead per gallon; about 1.6 to about 3.0 theories, based upon the lead, of a mixture of ethylene dichloride and ethylene dibromide and containing from 0.1 to 1.5 theories of a stoichiometric excess based on the lead of ethylene dichloride; and about 0.05 to 1.0 theory, based upon the lead, of a phosphorus compound having the formula



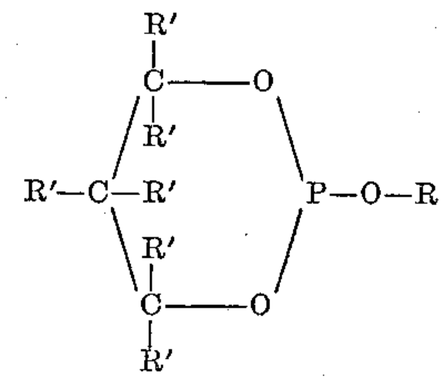
15. A gasoline as defined by claim 14 wherein said mixture of ethylene dichloride and ethylene dibromide is present in a concentration of from 1.7 to 2.0 theories, based upon the lead, and said phosphorus compound is present in a concentration of from 0.1 to 0.8 theory, based upon the lead.

16. A gasoline as defined by claim 15 wherein said ethylene dichloride and ethylene dibromide are present in a ratio between 2.4 and 4.2 to 1 on a theory basis.

17. A gasoline as defined by claim 7 wherein said lead compound is tetramethyl lead.

18. A gasoline as defined by claim 7 wherein said gasoline has an ASTM octane number of at least 83 and contains from 30 to 60% by weight of aromatic hydrocarbons.

19. An improved gasoline having an ASTM octane number of at least 83 and containing from 30 to 60% by weight of aromatic hydrocarbons and having incorporated therein from about 2.0 to about 4.6 cc. of tetramethyl lead per gallon; from about 1.6 to about 3.0 theories, based upon the lead, of a halogenated hydrocarbon boiling between about 50° C. and about 250° C. and containing from 0.1 to 1.5 theories of a stoichiometric excess based on the lead of ethylene dichloride; and about 0.05 to 1.0 theory, based upon the lead, of a phosphorus compound having the formula



where R′ is a radical having the formula C_nH_{2n+1}, n ranging from 0 to 1 inclusive and there being at least 2 carbon atoms which are each attached directly to carbon atoms in the ring; and where R is selected from the group consisting of the phenyl radical and alkyl radicals containing from 6 to 12 carbon atoms.

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