United States Patent Office

3,034,877
Patented May 15, 1962

3,034,877

LEADED GASOLINES

Alexander H. Popkin, Maplewood, N.J., assignor to Esso Research and Engineering Company, a corporation of Delaware

No Drawing. Filed Aug. 5, 1957, Ser. No. 676,373
9 Claims. (Cl. 44—69)

The present invention relates to fuels for use in spark-ignition internal combustion engines and more particularly relates to improved additive agents for use with tetraalkyl lead compounds which are adapted to reduce octane requirement increase, surface ignition and spark plug fouling in modern high compression gasoline engines and to leaded gasolines containing such improved additive agents.

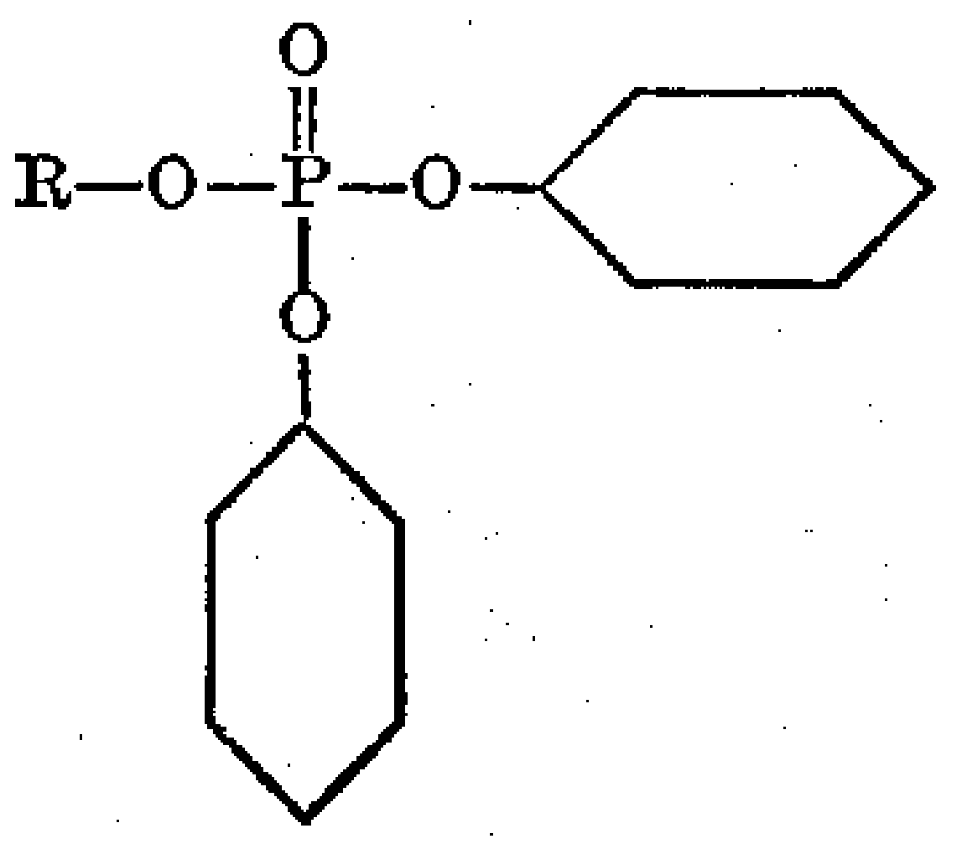
The problems associated with the use of volatile organic lead compounds such as tetramethyl lead and tetraethyl lead as anti-knock agents in gasolines are generally well recognized in the art. It is known that such lead compounds, although they reduce engine knock attributable to compression-ignition of the fuel-air mixture and hence are valuable gasoline constituents, are detrimental in that they give rise to the formation of engine deposits which result in an increase in the fuel octane level required for satisfactory engine operation, commonly called O.R.I. or octane requirement increase; become incandescent and ignite the fuel-air mixture prematurely by a phenomenon commonly called surface-ignition; and foul the points and insulators of spark plugs, thus causing misfire of the spark. In order to minimize the formation of such deposits and avoid these difficulties, it has always been customary to employ a scavenger agent, usually an alkyl halide such as ethylene dichloride or ethylene dibromide, in approximately equimolar proportion with the lead compounds in leaded gasolines. Such scavenger agents are intended to provide halogen acids to combine with the lead after combustion has begun and to sweep it as a relatively volatile lead halide from the combustion chamber, but in practice it is found that the scavenger agents are only partially effective. Deposit formation and the attendant difficulties occur despite their use, particularly in modern engines with very high compression ratios, i.e. above 9:1.

A number of different additive agents have been proposed heretofore for inclusion in leaded gasolines in order to overcome these difficulties. Several of these have proved reasonably effective in some respects, but it has been found that their use is generally accompanied by disadvantages in other respects, such as a depression of the octane quality of the gasoline in which they are incorporated. Due to the high "octane requirement" of modern automotive engines, i.e. the high octane number that the gasoline must have to give knock-free operation of the engines, and the practical limitations imposed upon the levels of octane number attainable in gasoline by available petroleum refining processes, the octane depressing or pro-knock properties of gasoline additives are becoming increasingly important. The cost of raising gasoline octane number to overcome the depressing effect of such scavenging additives as are used in the gasoline may

amount to as much as one cent per gallon at high octane levels and will increase to an even higher figure as the octane requirements of engines continue to rise. There is therefore a tremendous incentive to develop improved gasoline scavenger additives free from octane depressing properties.

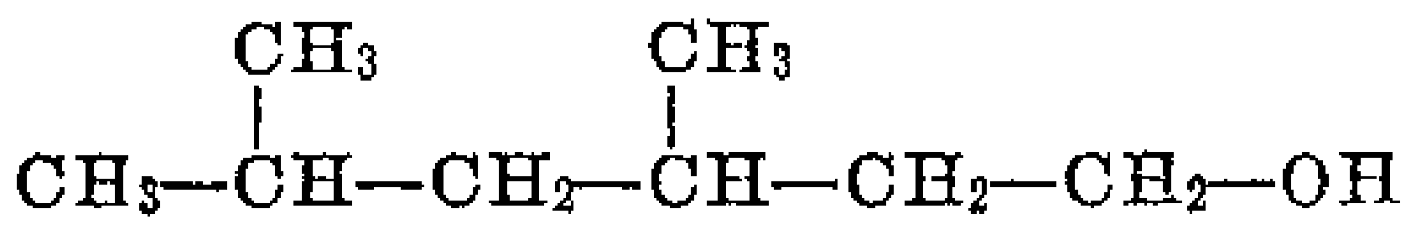
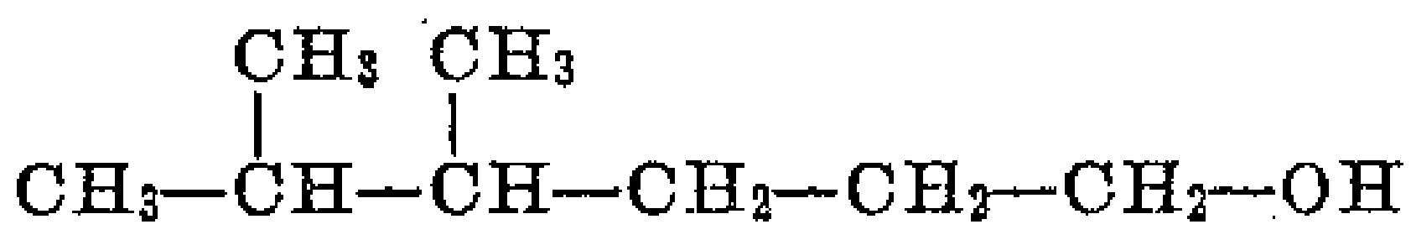
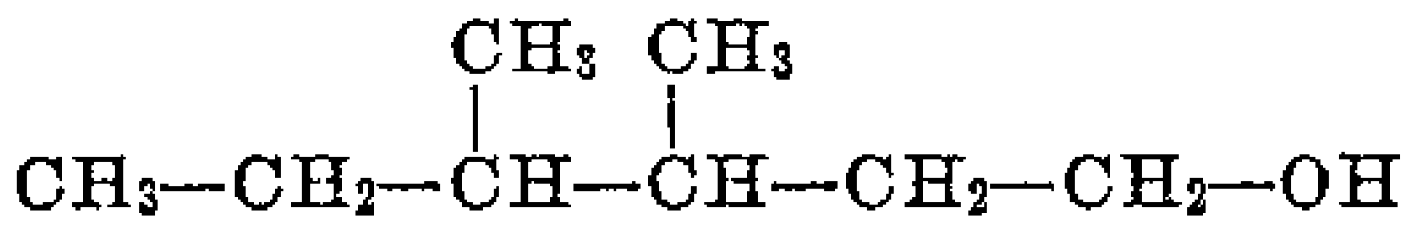
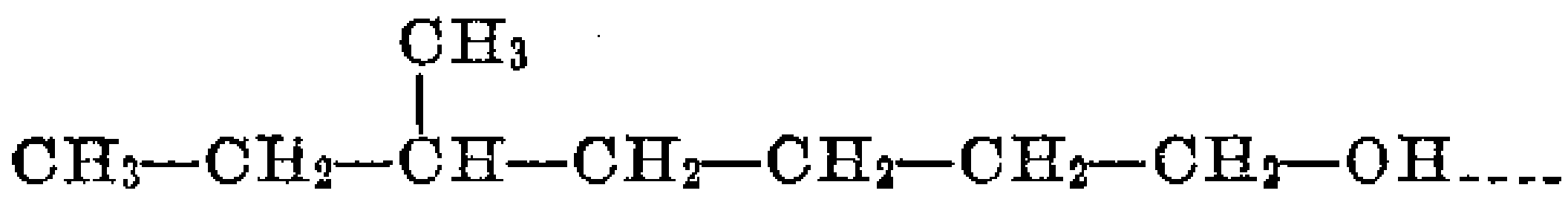
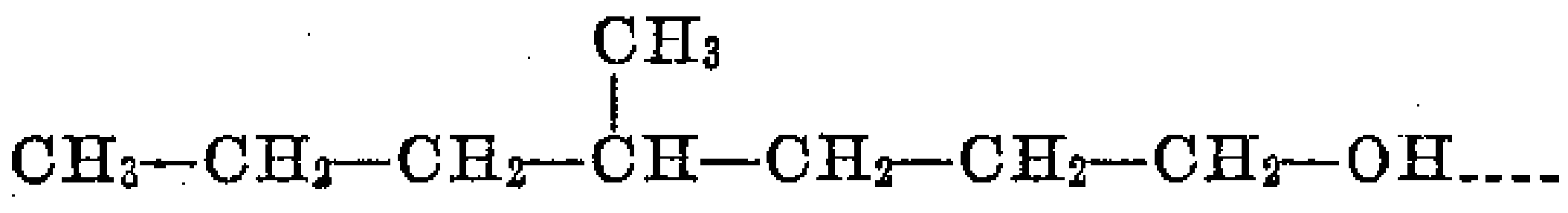
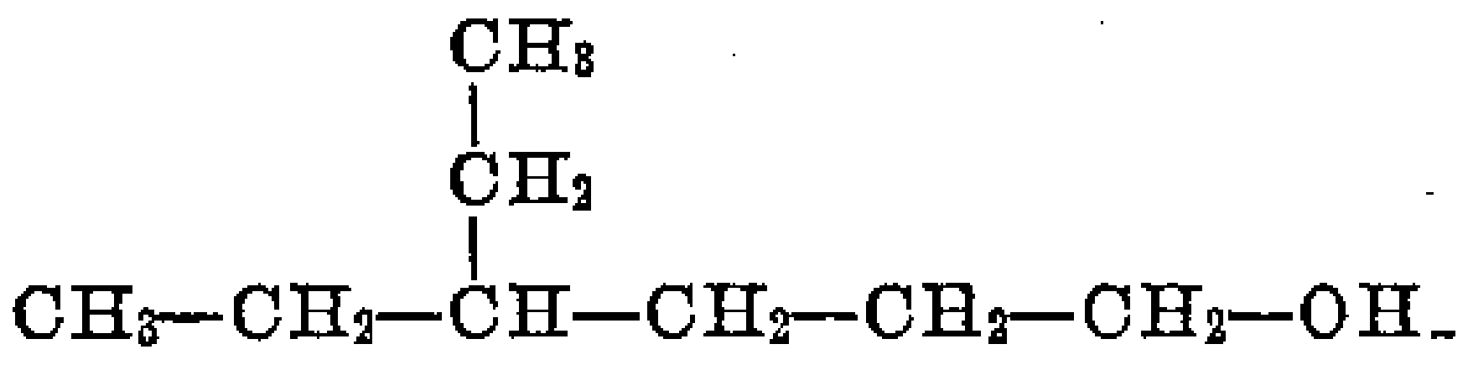
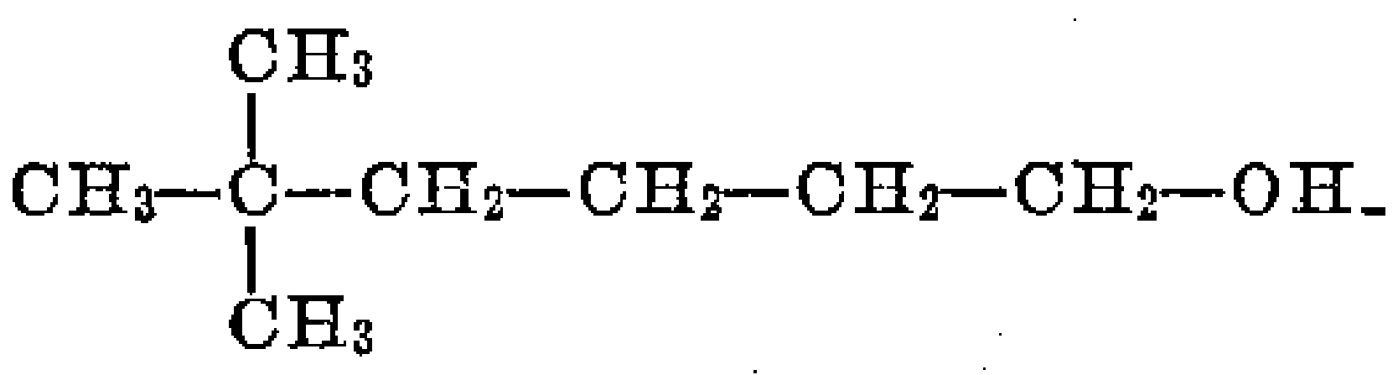
The additive agents of the present invention are effective for reducing octane requirement increase, surface ignition and spark plug fouling and not only do not depress the octane quality of the gasolines in which they are incorporated but in addition have numerous other advantages over additive compositions which have been proposed heretofore. These novel additive agents, which are particular mixtures of a monoalkyl diphenyl phosphote and a stoichiometric excess of a liquid halohydrocarbon scavenger having a boiling point between 50° C. and 250° C., preferably between 80° C. and 150° C., possess outstanding high temperature stability properties, do not separate from the fuel at extremely low temperatures, decrease the tendency of gasoline to form gum upon oxidation, have very low water solubility and reactivity, and are compatible with a wide variety of other additives commonly used in gasolines for various purposes.

The monoalkyl diphenyl phosphates used in the fuels of the invention have the general formula



where R is an alkyl group containing from 6 to about 10 carbon atoms. This chemical structure is critical for the purpose of the present invention because it insures the proper degree of chemical stability and physical solubility in gasoline without any lowering of octane number. Representative examples of such phosphates include 2-ethylbutyl diphenyl phosphate, n-hexyl diphenyl phosphate, 2-ethylhexyl diphenyl phosphate, isooctyl diphenyl phosphate, n-octyl diphenyl phosphate and decyl diphenyl phosphate. The branched-chain monoalkyl diphenyl phosphates containing about 8 carbon atoms in the alkyl group are preferred for the reasons described above; and the monoalkyl diphenyl phosphate having an alkyl group containing 8 carbon atoms and derived from a C_8-oxo alcohol, referred to as C_8-oxo diphenyl phosphate, is particularly preferred for use in the fuels of the invention.

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 C_8-oxo diphenyl phosphate prepared from such alcohol consist of series of isomeric compounds. C_8-oxo alcohol normally has the following general analysis:

Alcohol Constituent	Percent
 $CH_3-\overset{CH_3}{\overset{\vert}{C}H}-CH_2-\overset{CH_3}{\overset{\vert}{C}H}-CH_2-CH_2-OH$	29
 $CH_3-\overset{CH_3}{\overset{\vert}{C}H}-\overset{CH_3}{\overset{\vert}{C}H}-CH_2-CH_2-CH_2-OH$	25
 $CH_3-CH_2-\overset{CH_3}{\overset{\vert}{C}H}-\overset{CH_3}{\overset{\vert}{C}H}-CH_2-CH_2-OH$	17
 $CH_3-CH_2-\overset{CH_3}{\overset{\vert}{C}H}-CH_2-CH_2-CH_2-CH_2-OH$	16
 $CH_3-CH_2-CH_2-\overset{CH_3}{\overset{\vert}{C}H}-CH_2-CH_2-CH_2-OH$	
 $CH_3-CH_2-\overset{\overset{\overset{CH_3}{\vert}}{CH_2}}{\overset{\vert}{C}H}-CH_2-CH_2-CH_2-OH$	2.3
 $CH_3-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-CH_2-CH_2-CH_2-CH_2-OH$	1.4
2 alkyl alkanols unidentified for structure	4.3
Others	5.0
Total	100.0

The C_8-oxo diphenyl phosphate prepared from C_8-oxo alcohol has alkyl chains which correspond to those of the alcohol as set forth above and is thus a mixture of isomeric octyl diphenyl phosphates. Similar mixtures may be derived from mixtures of primary alcohols containing from about 6 to about 10 carbon atoms per molecule and are suitable for use in accordance with the invention. Other mixtures of monoalkyl diphenyl phosphates, having alkyl groups of from 6 to 10 carbon atoms, such as a mixture of 2 ethylhexyl diphenyl phosphate and decyl diphenyl phosphate for example, may also be used.

The monoalkyl diphenyl phosphate esters may be readily synthesized by reacting $POCl_3$ with an equivalent molar quantity of a suitable alcohol having 6 to 10 carbon atoms to form the corresponding monoalkyl phosphoryl dichloride and then further reacting this product with an aqueous sodium phenate solution. The alcohol is preferably slowly added to the $POCl_3$ with suitable agitation and at a rate to maintain the reaction temperature at from about 10 to 20° C. Agitation is continued for a period of from about 1 to 2 hours and the temperature is then allowed to rise to about 20 to 30° C., after which the reaction mixture is again agitated for a period of from about 1 to 2 hours. Hydrogen chloride gas is evolved as a result of the reaction of the $POCl_3$ and the alcohol may be continuously removed. The resulting monoalkyl phosphoryl dichloride is then added to an aqueous sodium phenate solution at a temperature of about 0 to 5° C. at a rate to maintain that temperature. The concentration of the sodium phenate solution may range from about 25 to about 40% or higher. After the alkyl phosphoryl dichloride has been added, the mixture may be agitated for about an hour and then allowed to reach room temperature while being stirred. Upon standing an ester layer and an aqueous layer will be formed. The crude ester may be recovered and washed with dilute sodium hydroxide and water to removed unreacted materials and partial esters. Further phosphate ester purification procedures well known to those skilled in the art may then be employed to obtain the finished monoalkyl diphenyl phosphate. The preparation of such esters is described in greater detail in U.S. Patent No. 2,596,141 and elsewhere in the art. Typical inspection characteristics of a C_8-oxo diphenyl phosphate prepared as described above are as follows:

Property:	Typical value
Acidity percent	0.003
Color (APHA [1])	50
Moisture percent (Karl Fischer method)	0.10
Refractive index at 25° C	1.509
Specific gravity 25/25° C	1.091

[1] American Public Health Association.

The halohydrocarbon employed in the fuels 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. The foregoing halohydrocarbons are not all equally effective for the present purpose. 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 compounds into the reactions which occur during combustion in an engine.

The amounts of the monoalkyl diphenyl phosphate and the halohydrocarbon employed in accordance with the invention are dependent upon the quantity of tetraethyl lead or 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 at least 1.75 when the gasoline contains more than 2.5 cc. of tetra ethyl lead per gallon and should not exceed 4.00. The monoalkyl diphenyl phosphate 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 mono alkyl diphenyl phosphate 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 solvent oils consisting of hydrocarbon mixtures having a Saybolt viscosity at 100° F. not above 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 phorphous-containing dimer of linoleic acid, amines and amine phosphates and nitrates; gum inhibitors such as N,N'di-secondary butyl p-phenylenediamine, 2,4-dimethyl-6-tertiary butylphenol and 2,6-ditertiary butyl-4-methylphenol; anti-icing agents such as isopropanol, hexylene glycol. Carbitol and dimethyl formamide; dyes such as 1,4-diisopropyl amino anthraquinone and p-dimethyl aminazobenzene; 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. 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 D 86. 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 member 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 2.0 theories of the monoalkyl diphenyl phosphate 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	53.5%.
C_8-oxo diphenyl phosphate	6.4% or 0.2 theory.
Ethylene dibromide	15.5% or 0.5 theory.
Ethylene dichloride	19.6% or 1.2 theories.
Gum inhibitor, rust inhibitor, dyes, dye stabilizers, etc	5.0%.

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 0.5 theory of ethylene dibromide and 1.0 theory of ethylene dichloride. 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 C_8-oxo diphenyl phosphate and 0.2 theory of ethylene dichloride, giving a total halohydrocarbon content of 1.7 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 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 3000 miles. The results of these tests are shown in the following table.

Table I

	Car I—9.5:1C.R.		Car II—10:1C.R.		Car III—9.5:1C.R.		Car IV—9.7:1.C.R.		Car V—9.25:1C.R.	
	Fuel A [1]	Fuel B [2]	Fuel A [1]	Fuel B [2]	Fuel A [1]	Fuel B [2]	Fuel A [1]	Fuel B [2]	Fuel A [1]	Fuel B [2]
Spark knock equilibrium octane requirements	94	95½	94	92	95	93½	94	93	93½	90½
Surface ignition [4] equilibrium octane requirement	96	[5] None	97½	92½	97½	93	94½	[5] None	90	89
Rumble	[3] 105	[5] None	[3] 105	[5] None	[3] 105	[5] None	[5] None	[5] None	[5] None	[5] None
Spark plug fouling, percent misfires	40	0	10	0	33	14	0	0	19	3
No-noise octane advantage for fuel B		½		5		4		1½		3

[1] Fuel A contained 3 cc. tetraethyl lead per gallon and 1.5 theories of halohydrocarbon scavenger for lead, including 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 C_8-oxo diphenyl phosphate and 0.2 theory of additional ethylene dichloride.

[3] Rumble is not strictly proportional to fuel octane quality but it can be eliminated by increasing octane number. Numbers give maximum octane fuel with which rumble is heard. It is a vibration which occurs in cars with high compression ratios.

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

[5] This notation means that the indicated phenomenon of surface ignition or rumble was wholly absent and that therefore no measurement of octane number was needed. When either of these phenomena was present after a car had been run to equilibrium with the test fuel, then an octane requirement was determined in terms of the minimum octane number of reference fuel required by the car on the road to give no noise of spark knock or surface ignition

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 C_8-oxo diphenyl phosphate, ethylene dichloride and ethylene dibromide in accordance with the present invention gave an advantage of from 1 to 5 octane numbers in the no-noise equilibrium level. In fact, in every test except that for equilibrium requirement to overcome spark-knock in car I, the requirement was consistently lower after running on fuel B than after running on fuel A.

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 theory 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 of from 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 + 0.4 theories tricresyl phosphate.	100½	99
II	Base fuel [1]	99	99½
	Base fuel + 0.4 theories tricresyl phosphate.	99½	100½
III	Base fuel [1]	96	100
	Base fuel + 0.4 theories tricresyl phosphate.	99½	98
IV	Base fuel [1]	96½	99½
	Base fuel + 0.4 theories tricresyl phosphate.	99½	97
V	Base fuel [1]	97	99½
	Base fuel + 0.4 theories tricresyl phosphate.	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 monoalkyl diphenyl phosphates 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, without and with the addition of 0.2 theory of C_8-oxo diphenyl phosphate and 0.2 theory of additional ethylene dichloride. The data obtained in these tests are shown in Table III.

Table III

Research octane number			Motor octane number		
Base fuel	Base fuel + additive [1]	Change in octane number due to additive	Base fuel	Base fuel + additive [4]	Change in octane number due to additive
101.4	101.4	0	89.2	89.2	0
102.2	102.0	−0.2	89.2	89.2	0
101.7	101.7	0	89.0	89.0	0
101.4	101.4	0	88.6	88.6	0
101.4	101.4	0	88.7	88.7	0
101.7	101.7	0	88.6	88.6	0
101.4	101.4	0	88.6	88.6	0
101.1	101.1	0	89.0	89.0	0
100.9	100.9	0	88.6	88.6	0

[1] The additive consisted of 0.2 theory of C_8-oxo dephenyl phosphate and 0.2 theory of ethylene dichloride.

From the above it can be seen that the incorporation of the monoalkyl diphenyl phosphate and halohydrocarbon in gasolines in proportions in accordance with the present invention does not significantly affect the octane quality of the fuel itself.

EXAMPLE IV

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

Table IV

Additive	Concentration, Theories	Research Octane Number			Motor Octane Number		
		Base Fuel	Base Fuel + Additive	Change in Octane Number due to Additive	Base Fuel	Base Fuel + 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
	1.0	100.5	99.5	−1.0	89.8	86.4	−3.4
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
	1.0	100.7	99.8	−0.9	89.5	87.4	−2.1
Triisopropyl Phosphite	0.2	----------	----------	----------	88.8	88.2	−0.6
	0.4	----------	----------	----------	88.8	87.5	−1.3
	1.0	----------	----------	----------	88.8	85.5	−3.3
Trichloropropyl Phosphite	0.2	----------	----------	----------	88.7	88.3	−0.4
	0.4	----------	----------	----------	88.7	87.6	−1.1
	1.0	----------	----------	----------	88.7	85.8	−2.9
Triphenyl Phosphite	0.2	101.4	101.3	−0.1	89.9	89.7	−0.2
	0.4	101.3	100.8	−0.5	90.0	90.0	0
	1.0	101.3	100.7	−0.6	90.1	89.0	−1.1
Triphenyl Phosphate	0.2	101.3	101.3	0	90.1	89.7	−0.4
	0.4	101.3	101.3	0	89.9	89.9	0
	1.0	101.1	100.5	−0.6	89.2	89.7	−0.5
Tricresyl Phosphite	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
	1.0	101.3	101.1	−0.2	88.8	88.1	−0.7
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
	1.0	100.9	100.3	−0.6	88.9	87.8	−1.1
Tributyl Phosphate	1.0	87.1	85.9	−1.2	84.1	81.4	−2.7
Tributyl Phosphite	1.0	86.7	85.1	−1.6	84.7	81.1	−3.6
Trichloroisopropyl Thionophosphate	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
	1.0	100.7	99.3	−1.4	90.3	86.9	−3.4
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
	1.0	100.9	100.5	−0.4	89.7	88.6	−1.1
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
	1.0	99.7	98.8	−0.9	89.2	85.5	−3.7
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
	1.0	100.4	99.7	−0.7	89.2	86.8	−2.4
Diethyl Ethyl Phosphonate + Equal Ethylene Dichloride	0.2	101.6	101.1	−0.5	88.9	88.6	−0.3
	1.0	101.7	100.8	−0.9	90.1	86.7	−3.4
Isooctyl Diphenyl Phosphate + Equal Ethylene Dichloride	0.2	101.5	101.5	0	89.4	89.4	0
	0.4	101.5	101.5	0	89.4	89.4	0
	1.0	101.8	101.5	−0.3	89.4	89.4	0

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 last one in Table IV, namely the additive of the present invention, did not suppress octane quality. Several of the compounds, including compounds now used commercially as gasoline additives and including butyl diphenyl phosphate, which is a monoalkyl diphenyl phosphate outside the scope of the present invention, caused a loss in motor octane number up to as high as 3.7 octane numbers when added to the gasoline in 1 theory amounts.

EXAMPLE V

Tests were also conducted to determine the suitability of the fuels of the present invention for uses where they are subjected to extremely low temperatures. Various additive agents were incorporated in samples of a commercial leaded gasoline at a concentration of 0.2 theory and the gasoline was then refrigerated to determine the temperature at which the agents were precipitated from the fuel. It was found that the leaded gasoline containing 0.2 theory of C_8-oxo diphenyl phosphate, 1.2 theories of ethylene dichloride and 0.5 theory of ethylene dibromide was stable at temperatures down to −45° C., well below the temperatures normally encountered, while the additive agents separated out of samples containing tricresyl phosphate, tolyl dimethyl phosphate, and tri-(chloroisopropyl)-thiono-phosphate, commercial additives, at temperatures considerably warmer than −45° C. In addition, the solid material which separated out of the sample containing tricresyl phosphate did not readily redissolve when the sample was warmed to room temperature.

EXAMPLE VI

Samples of C_8-oxo diphenyl phosphate, tolyl dimethyl phosphate and tri-(chloroisopropyl)-thiono-phosphate were contacted with distilled water in order to determine the solubility of the compounds. Twenty cc. samples of each compound were shaken with 80 cc. of water and allowed to stand for 36 hours, at the end of which 50 cc. of the aqueous layer in each sample bottle was dried and the residual weight determined. It was found that the C_8-oxo diphenyl phosphate was less than half as soluble as the tri-(chloroisopropyl)-thiono-phosphate and about one-one-hundredth as soluble as the tolyl dimethyl phosphate. The C_8-oxo diphenyl phosphate used in the fuels of the invention is thus less susceptible to being washed out of the fuel by water present in storage tanks and the like than are the other two compounds, both used commercially as gasoline additives.

EXAMPLE VII

In order to test the stability and compatibility of the additives used in the fuels of the invention with other additives, an additive concentrate consisting of 37.9 parts of solvent oil, 1.5 parts of C_8-oxo diphenyl phosphate, 0.6 part of ethylene dichloride and 1.14 parts of 2-methyl-2,4-pentanediol was prepared. This mixture was added to a leaded gasoline in proportion to give a fuel containing 0.5% solvent oil, 0.2 theory of C_8-oxo diphenyl phosphate, 0.2 theory of extra ethylene dichloride and 0.15% of 2-methyl-2,4-pentanediol. With this additive, the fuel had a reduced tendency to cause intake valve deposits, spark plug fouling, octane requirement increase and carburetor icing. The concentrate prepared remained homogeneous when stored for one month at −25° C. and when stored in sunlight at room temperature for one month.

EXAMPLE VIII

Two samples, No. 1 and No. 2, of commercial premium motor gasolines of spring grade volatility were tested for potential gum by ASTM method D–873, without and with the addition of phosphate additives. These gasolines contained 3 cc. of tetra ethyl lead per gallon. They also contained, as is customary in commercial motor gasoline, the usual halide scavenger consisting of 1.0 theory of ethylene dichloride and 0.5 theory of ethylene dibromide.

To each gasoline, the following agents were added:

(A) 0.2 theory of C_8-oxo diphenyl phosphate and 0.2 theory of ethylene dichloride.
(B) 0.2 theory of tricresyl phosphate.

The samples containing (A) were compositions in accordance with the present invention, containing in total a mixture of 0.2 theory of C_8-oxo diphenyl phosphate, 1.2 theory of ethylene dichloride and 0.5 theory of ethylene dibromide. The results of the tests were as follows:

Gasoline	Additive	Potential Gum, mgs. per 100 cc.
No. 1	none	104
No. 1	(A)	18
No. 1	(B)	72
No. 2	none	202
No. 2	(A)	54
No. 2	(B)	289

These results clearly show the superiority of the composition of the present invention in the lower value of potential gum, thus confirming its high degree of stability.

The additive compositions employed in the fuels of the present invention have also shown some effect like that of solvent oil in gasolines. Two 1957 high compression automobiles operated upon the fuels of the invention were found to have a lower level of intake valve underside deposits and intake system deposits than did the same cars when operated on a similar fuel not containing the mixture of C_8-oxo diphenyl phosphate, ethylene dichloride and ethylene dibromide of the present invention.

As can be seen from the preceding examples, the additive agents of this invention meet all of the criteria for an additive intended to overcome the detrimental effects of tetraethyl lead and similar anti-knock agents in gasolines and are surprisingly superior to phosphorus-containing materials which have been employed heretofore. The additives of the invention—

(1) Decrease surface ignition due to lead deposits
(2) Decrease "rumble"
(3) Decrease spark plug fouling
(4) Do not raise spark knock equilibrium requirement
(5) Do not depress fuel octane quality
(6) Are not extracted by water, and
(7) Possess excellent storage stability properties over a wide temperature range.

This surprising overall superiority makes the additives of this invention considerably more attractive for use in lead-containing gasolines than other materials proposed heretofore, all of which fail to meet one or more of the above-listed criteria.

It is apparent that, while the present invention is of application to any leaded gasoline including automotive type gasolines, marine type gasolines and aviation gasolines, it is of particular application to motor gasolines intended for use in modern high-compression engines which are especially susceptible to the adverse effects arising from the formation of lead deposits therein.

What is claimed is:

1. An improved gasoline additive composition the major proportion of which comprises a volatile tetraalkyl lead compound as an anti-knock agent and a mixture of 1 part of a C_8 monoalkyl diphenyl phosphate and from 3 to 32 parts of a halogenated hydrocarbon boiling below 250° C., as a scavenger agent, said mixture being present in a concentration between 1.75 and 4.00 theories based on the lead and said halogenated hydrocarbon scavenger agent containing from 0.1 to 1.5 theories of a stoichiometric excess of a chlorinated hydrocarbon scavenger.

2. An improved gasoline additive composition the major proportion of which comprises tetraethyl lead, from about 1.7 to about 2.1 theories of a halogenated hydrocarbon boiling between 50° C. and 250° C. containing from 0.1 to 1.5 theories of a stoichiometric excess of ethylene dichloride, and from about 0.15 to about 0.4 theory of a C_8 monoalkyl diphenyl phosphate, said halogenated hydrocarbon being present in a ratio between 3 and 32 to 1 to said monoalkyl diphenyl phosphate.

3. An additive composition as defined by claim 2 wherein said monoalkyl diphenyl phosphate is C_8-oxo diphenyl phosphate.

4. An additive composition as defined by claim 2 wherein said halogenated hydrocarbon is a mixture of ethylene dichloride and ethylene dibromide.

5. An improved gasoline anti-knock additive the major proportion of which comprises tetraethyl lead, from about 1.7 to 2.1 theories of a mixture of ethylene dichloride and ethylene dibromide in theory ratio between 2.4 and 4.2 of said dichloride to 1 of said dibromide and containing about 0.2 theory of a stoichiometric excess of ethylene dichloride and from 0.15 to 0.4 theory of C_8-oxo diphenyl phosphate.

6. A gasoline containing from about 2.0 to about 4.6 cc. of tetra-alkyl lead compound per gallon, about 1.7 to 2.1 theories of a halogenated hydrocarbon boiling below 250° C. containing from 0.1 to 1.5 theories of a stoichiometric excess of ethylene dichloride; and about 0.15 to 0.4 theory of a C_8 monoalkyl diphenyl phosphate.

7. A gasoline as defined by claim 6 wherein said monoalkyl diphenyl phosphate is isooctyl diphenyl phosphate.

8. A gasoline as defined by claim 6 wherein said monoalkyl diphenyl phosphate is C_8-oxo diphenyl phosphate.

9. An improved gasoline composition comprising at least 95% of hydrocarbons boiling between 80° F. and 450° F., from 2.0 to 4.6 cc. of tetraethyl lead per gallon, from about 1.7 to about 2.1 theories of a mixture of ethylene dichloride and ethylene dibromide and containing about 0.2 theory of a stoichiometric excess of ethylene dichloride, and from about 0.15 to about 0.4 theory of C_8-oxo diphenyl phosphate.

(References on following page)

References Cited in the file of this patent

UNITED STATES PATENTS

2,340,331	Knutson et al.	Feb. 1, 1944
2,375,218	Fry et al.	May 8, 1945
2,405,560	Campbell	Aug. 13, 1946
2,765,220	Yust et al.	Oct. 2, 1956
2,765,221	Lusebrink et al.	Oct. 2, 1956
2,857,255	Andress	Oct. 21, 1958
2,889,212	Yust et al.	June 2, 1959
2,897,068	Pellegrini et al.	July 28, 1959
2,911,431	Orloff et al.	Nov. 3, 1959
2,999,739	Heron	Sept. 12, 1961

FOREIGN PATENTS

421,568	Canada	July 18, 1944
683,405	Great Britain	Nov. 26, 1952
1,043,087	France	Nov. 5, 1953
1,134,156	France	Nov. 26, 1954

OTHER REFERENCES

Ind. and Eng. Chem., vol. 43, No. 3, March 1951, "Antiknock Antagonists," by Livingston, pp. 663–670.