United States Patent Office 3,440,028 Patented Apr. 22, 1969

3,440,028

ORGANO METAL HALIDE ORTHOPHOSPHATE GASOLINE ADDITIVE

Anthony J. Revukas, Cranford, N.J., assignor to Cities Service Oil Company, a corporation of Delaware

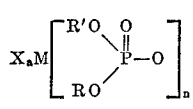
No Drawing. Continuation-in-part of application Ser. No. 127,858, July 31, 1961. This application Nov. 24, 1964, Ser. No. 413,631

Int. Cl. C10l 1/26

U.S. Cl. 44—69 8 Claims

ABSTRACT OF THE DISCLOSURE

A metal halide hydrocarbyl orthophosphate additive for leaded gasoline compositions is disclosed wherein the additive is in the amount of between 0.001 and about 5.0 times the theoretical amount (theories) to react stoichiometrically with the lead in the gasoline combustion products. A preferred metal halide hydrocarbyl orthophosphate additive is represented by the general formula



wherein M represents manganese or metals of Group I–B, II–A, II–B, IV–A, VI–B, or VIII of the Periodic Table, n and a are numbers selected so that n plus a equals the valence of the metal M, and R and R′ each represent hydrocarbyl radicals having from 2 to 30 carbon atoms and soluble to the required extent in gasoline. Preferably at least one of the R and R′ radicals represents a branched chain hydrocarbyl radical.

This invention is a continuation-in-part of my copending application, Ser. No. 127,858, filed July 31, 1961 now abandoned for Organometallic Orthophosphates.

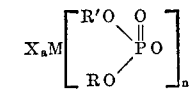
This invention relates to novel metallic hydrocarbyl orthophosphate compounds and to gasoline compositions including such compounds.

The use of lead compounds to increase the octane rating of gasoline is extremely common. Unfortunately, the addition of lead, while substantially increasing the octane ratings of gasolines to which it is added, at the same time has several drawbacks. Of these drawbacks the most serious is probably the tendency of the lead to increase undesirable surface ignition in the combustion chambers of the internal combustion engines in which the leaded gasoline is used. It has been the practice previously to utilize various phosphorus compounds in an attempt to reduce or prevent such surface ignition, but the use of such compounds has generally led to additional difficulties such as lead deposits on cylinder heads and valves.

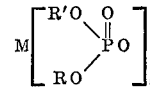
It is an object of the present invention to provide novel metallic hydrocarbyl orthophosphate compounds adapted for use in improved gasoline compositions.

It is another object of the invention to provide an improved gasoline composition especially adapted to resist surface ignition.

The novel compounds of the present invention are metallic hydrocarbyl orthophosphates represented by the general formula



wherein M represents a metal selected from the group consisting of manganese, and the metals of Groups I–B, II–A, II–B, IV–A, VI–B and VIII of the Periodic Table, X is a halogen, n and a are numbers so selected that n=the valence of metal M and a=0 except that when the valence of metal M is 5, then a=2 and n=3, and R and R′ each represent a hydrocarbyl radical having from 2 to about 30 carbon atoms. Preferred orthophosphates of these metals may be represented by the general formula



wherein M represents manganese, or a metal of Groups I–B, II–A, II–B, IV–A, VI–B or VIII of the Periodic Table, n is a number equal to the valence of the metal M and R and R′ each represent a hydrocarbyl radical having from 2 to 30 carbon atoms. In such compounds the valence of the metal M usually depends upon the starting material used. Preparation of these compounds is discussed in greater detail below. R and R′ may represent identical or different hydrocarbyl radicals. While any hydrocarbyl radicals having between 2 and about 30 carbon atoms and soluble to the required extent in gasoline may be used, at least one of R and R′ preferably represents a branched chain hydrocarbyl radical. Branched chain alkyl radicals are especially suitable. Such radicals are generally more soluble in gasoline than other hydrocarbyl radicals, thereby facilitating the use of the novel compounds of the present invention as gasoline additives. Since chains of more than about 30 carbon atoms are generally difficult or impossible to dissolve in gasoline compositions, it is preferred that the hydrocarbyl radicals of the orthophosphates of the present invention each have between 2 and about 30 carbon atoms. Typical R and R′ groups may include, for instance, alkyl, aryl, alkylaryl, arylalkyl or alicyclic hydrocarbyl radicals. Examples of suitable hydrocarbyl radicals are: ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, isopentyl, hexyl, isohexyl, 2,2,4-trimethylpentyl, 2-methylpentyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, heptyl, 2-methylhexyl, 3-methylhexyl, 3,3-dimethylpentyl, octyl, 2,3-dimethylhexyl, 2,4-dimethylhexyl, 2-ethylhexyl, 2-ethylbutyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonyldecyl, eiocosyl, henicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, phenyl, -naphthyl, benzyl, o-cresyl, p-cresyl, m-cresyl, dodecylphenyl, octylphenyl, ethylphenyl and diphenyl, pentadecyl, b-phenylethyl, omega phenylhexyl, cyclohexyl, cyclobutyl, cyclodecyl, cyclopentyl, etc. Corresponding unsaturated radicals may also be used.

Compounds of the present invention having branched chain alkyl hydrocarbon radicals include, for instance, the following:

nickel di (bis(2-methylpropenyl) orthophosphate)
manganese di(bis(3-butyloctosyl) orthophosphate)
copper di (bis(5-pentylhexadecyl) orthophosphate)
beryllium di(bis(2-ethyl-5-butyltridecyl) orthophosphate)
zinc di (bis(2-propyldecyl) orthophosphate)
silver bis(2,4-diethyloctyl) orthophosphate
chromium tri(bis(2-methyloctenyl) orthophosphate)
iron tri (bis(methylethyl) orthophosphate)
nickel di(bis(2-ethylhexyl)orthophosphate)
molybdenum III di(2-methylpropyl) methylethyl orthophosphate
magnesium di(2-methyloctyl, 2-propyldecyl orthophosphate)
cadmium di(bis(2-ethylhexynyl) orthophosphate)
nickel di(bis(isodecyl) orthophosphate)
stannic tetra (2-ethylhexyl, octyl orthophosphate)

ruthenium III (2-ethylhexyl), dibutynyl orthophosphate)
osmium II (2-ethylhexyl octyl), (methylethyl, butyl) orthophosphate)
nickel di(isodecyl, 2-ethylhexyl orthophosphate)
germanium IV di(2-ethylhexyl, di(methylethyl), di(2-methylpropyl), di(3-butyloctacosyl) orthophosphate

Compounds of the present invention having alkylaryl hydrocarbyl radicals include, for instance, the following:

tungsten hexa (bis(octylphenyl) orthophosphate)
nickel di(bis(methylphenyl) orthophosphate)
lead tetra (bis(tricosylphenyl) orthophosphate)
calcium di(bis(pentylphenyl) orthophosphate)
gold tri(octylphenyl, pentylphenyl orthophosphate)
strontium di(bis(methylphenyl) orthophosphate)
nickel di(bis(hexylphenyl) orthophosphate)
uranium tetra di(octylphenyl, 2-ethylhexenyl orthophosphate)
cobalt tri di(bis(methylnaphthyl) orthophosphate)
rhodium II (pentylnaphthyl, methylethyl), dimethylphenyl orthophosphate)

Compounds of the present invention having both alkyl and alkylaryl hydrocarbyl radicals include, for instance, the following:

barium di(2-ethylhexyl, methylphenyl) orthophosphate)
nickel II di(2-ethylhexyl, di(octylphenyl) orthophosphate)
iridium II (butyl, ethylhexyl), methylphenyl, methylethyl) orthophosphate

Compounds of the present invention having aryl hydrocarbyl radicals include, for instance:

radium di(bis(phenyl) orthophosphate)
palladium tri(phenyl, naphthyl) orthophosphate
nickel II (diphenyl), naphthyl, 2-ethylhexyl orthophosphate

Compounds of the present invention having arylalkyl hydrocarbyl radicals include, for instance;

nickel di(bis(phenylmethyl) orthophosphate)
platinum II (naphthylethyl, butyl), 2-ethylhexyl, phenylhexyl) orthophosphate
nickel di(2-methylpropyl, naphthylmethyl) orthophosphate

Compounds of the present invention having alicyclic hydrocarbyl radicals include, for instance:

mercury di(cyclohexyl, cyclodecyl orthophosphate)
nickel di(cyclobutyl, 2-ethylhexyl orthophosphate)
zinc II (methylethyl, cyclopentyl), di(2-ethylhexyl) orthophosphate)
cobalt tri(bis(cyclohexyl) orthophosphate)

Compounds of the present invention having straight chain hydrocarbyl radicals include, for instance, the following:

magnesium di(bis(octynyl) orthosphosphate)
nickel di(bis(ethyl) orthophosphate)
copper di(methyldecyl orthophosphate)
calcium II (dibutyl, ethylhexyl, dipentyl orthophosphate)
nickel di(2-ethylhexyl, butenyl orthophosphate)
mercury di(pentacosyl, hexadecyl orthophosphate)
nickel di(bis(ethyl) orthophosphate)
nickel di(2-ethylhexyl, butyl orthophosphate)
nickel di(butyl, isodecyl) orthophosphate
nickel II (diisodecyl, di(2-ethylhexyl) orthophosphate)

The novel compounds described above are especially useful as gasoline additives in forming novel gasoline compositions adapted to resist surface ignition. In addition to resisting surface ignition, these additives generally inhibit rust and carburetor icing. In accordance with a preferred embodiment of the present invention a gasoline composition is provided which comprises a major proportion of a leaded hydrocarbon base fuel boiling in the gasoline range and containing between about 0.001 and about 5.0 theories of a metallic hydrocarbyl orthophosphate of the type described above. The leaded hydrocarbon base fuel comprises at least 50 volume percent and preferably at least 75 volume percent of the gasoline composition.

By the term "leaded gasoline," "leaded hydrocarbon base fuel boiling in the gasoline range" and similar terms is meant a petroleum fraction boiling in the gasoline boiling range (e.g., between about 50° and about 450° F.) to which has been added a small amount, such as between about 0.1 and about 6.0 cc. per gallon, of a metallo-organic antiknock compound such as tetraethyl lead (TEL), tetramethyl lead (TML), tetraisopropyl lead, etc. Lead is frequently present in gasoline compositions of the present invention in the form of TEL, TML or mixtures of the same which may be present in suitable amounts such as between about 0.1 and about 6.0 cc. per gallon of gasoline composition, more usually between about 0.5 and about 4.0 cc. per gallon.

The novel metallic orthorphosphates described above for use in leaded gasoline compositions in accordance with the present invention are present in suitable amounts such as between about 0.001 and about 5.0 theories, preferably between about 0.02 and about 2.0 theories. The term "theory" in this context is intended to designate the amount of metal hydrocarbyl orthophosphate additive that would be needed in a gasoline in order that the metal and phosphorus atoms in the metal hydrocarbyl orthophosphate would be able to react stoichiometrically with all the lead in the lead antiknock compound present in a gasoline to form the appropriate lead compound upon combustion in an engine. The "theory" concept may be based on the metal only, on the phosphorus only, or on both elements in the metal hydrocarbyl orthophosphate. Thus, for example, the additive dichloromolybdenum tri [bis(2-ethylhexyl) orthophosphate] could react with TEL and TML to produce lead orthophosphate and lead molybdate. In this example the theories of additive employed would be based on the phosphorus required to form lead orthophosphate and on the metal molybdenum to produce lead molybdate. If the metal in the metal hydrocarbyl orthophosphate additive does not combine with the lead in the gasoline to form a compound upon combustion in an engine, then the theory concept is based on the phosphorus in the additive. To illustrate, nickel di(bis-isodecyl orthophosphate) in a gasoline with TEL forms only lead orthophosphate upon combustion, as no compounds of lead with nickel are known to exist.

In addition to the above described compounds, gasoline compositions contemplated by the present invention may include one or more other ingredients such as lead scavengers, gum inhibitors, lubricants, rust inhibitors, metal deactivators or other special purpose additives.

Lubricants suitable for use in the above described gasoline compositions may include, for instance, light hydrocarbon lubricating oils having viscosities at 100° F. of between about 50 and about 200 Saybolt Universal second (SUS) and viscosity indexes (VI) of between about 30 and about 120 with oil having a viscosity of about 100 SUS being preferred. Such oils may be present in suitable amounts such as between about 0.1 and about 1.0 volume percent of the gasoline composition.

When using lead compounds such as TEL, it is frequently found desirable to include with the lead a suitable lead scavenger for reducing the deposit of lead compounds within the combustion chamber. Such lead scavengers include, for example, halohydrocarbon compositions such as ethylene dibromide and ethylene dichloride.

Gum inhibitors suitable for use in the above described gasoline compositions include conventional gum inhibitors such as 2,6-ditertiarybutylpara cresol. Such gum inhibitors may be present in suitable amounts such as between about 0.001 and about 0.006 volume percent of the gasoline composition. Likewise, a suitable metal de-

activator is for example N,N'disalicylidene-1,2-diaminopropane.

Gasoline compositions of the present invention may be illustrated by the following examples. It should be understood that any of the other novel additive compounds contemplated by the invention, such as those described above, may be used in such gasoline compositions in place of or in addition to the additives specified below.

Example 1

A gasoline composition having excellent surface ignition characteristics may be prepared by adding the following ingredients to a suitable base gasoline:

TEL	cc. per gallon	2.2
Dichloromolybdenum tri(bis(2-ethylhexyl)orthophosphate), theory		0.05

The base gasoline used in blending this and other gasoline compositions of the invention may be a gasoline having the following characteristics:

Distillation:		
IBP	° F	101
Evaporation, percent:		
10	° F	130
20	° F	149
30	° F	168
50	° F	210
70	° F	260
90	° F	328
End point	° F	409
Recovery	percent	98.5
Residue	do	1
Gravity	° API	58.2

Example 2

Another suitable gasoline composition is prepared by adding the following ingredients to a suitable base gasoline:

TEL	cc. per gallon	2.2
Lead II diisodecyl, di(2-ethylhexyl)orthophosphate), theory		1.0

Example 3

Another suitable gasoline composition is prepared by adding the following ingredients to a suitable base gasoline:

TEL	cc. per gallon	0.5
Cobalt (methylethyl, cyclopentyl), di(2-ethylhexyl) orthophosphate, theory		0.25

Example 4

Another suitable gasoline composition is prepared by adding the following ingredients to a suitable base gasoline:

TEL	cc. per gallon	4.0
Manganese di(2-ethylhexyl, octyl orthophosphate), theory		0.5
Lubricating oil (100 SUS, 95 VI)	volume percent	1.0

Example 5

Another suitable gasoline composition is prepared by adding the following ingredients to a suitable base gasoline:

TEL	cc. per gallon	6.0
Nickel di(bis(2-ethylhexyl) orthophosphate), theory		5.0

Example 6

Another suitable gasoline composition is prepared by adding the following ingredients to a suitable base gasoline:

TEL	cc. per gallon	0.1
Magnesium di(bis(2-ethylhexyl) orthophosphate), theory		0.0005

Example 7

Another suitable gasoline composition is prepared by adding the following ingredients to a suitable base gasoline:

TEL	cc. per gallon	1.5
Zinc II (butyl, ethylhexyl), methylphenyl, methylethyl) orthophosphate, theory		0.01
Lubricating oil (100 SUS, 95 VI), volume percent		0.1

Example 8

Another suitable gasoline composition is prepared by adding the following ingredients to a suitable base gasoline:

TEL	cc. per gallon	3.0
Cadmium di(bis(isodecyl) orthophosphate), theory		2.0

Example 9

Another suitable gasoline composition is prepared by adding the following ingredients to a suitable gasoline:

TEL	cc. per gallon	2.0
Mercurous di(stearylbenzyl orthophosphate), theory		0.5

Example 10

Another suitable gasoline composition is prepared by adding the following ingredients to a suitable base gasoline:

TEL	cc. per gallon	2.2
Chromium tri(triacontylphenyl orthophosphate), theory		0.1
Lubricating oil (100 SUS, 95 VI), volume percent		0.25

Example 11

Another suitable gasoline composition is prepared by adding the following ingredients to a suitable base gasoline:

TML	cc. per gallon	2.5
Chromous di(bis(o-cresyl) orthophosphate, theory		0.15

Example 12

Another suitable gasoline composition is prepared by adding the following ingredients to a suitable base gasoline:

TEL	cc. per gallon	0.8
Tungsten tetra(bis(α-naphtyl) orthophosphate, theory		0.06

Example 13

Another suitable gasoline composition is prepared by adding the following ingredients to a suitable base gasoline:

TML	cc. per gallon	4.0
Iron tri(2-ethylhexyl-α-naphtyl orphosphate, theory		3.5

Example 14

Another suitable gasoline composition is prepared by adding the following ingredients to a suitable base gasoline:

TEL	cc. per gallon	2.3
Stannic tetra (bis(dodecylphenyl) orthophosphate, theory		0.2

Novel additive compounds of the type described above may be prepared in any suitable manner. According to one method of preparation, a suitable organic hydrogen phosphate or a mixture of such phosphates is placed in a reaction flask together with about half its volume of a suitable solvent such as dry toluene. The reaction flask is preferably equipped with a mechanical stirrer, thermometer gas inlet tube, reflux condenser and a pres-

sure equalizing funnel with its long stem dipping into the solution. The temperature in the reaction flask is raised to between about 110 and about 130° C. while stirring vigorously and a suitable salt such as a chloride, bromide or sulfate of the desired metal with an equal volume of the solvent is added in spurts by means of the pressure equalizing delivery funnel. When a chloride is used, hydrogen chloride is evolved copiously by the reaction. Stirring and heating under reflux to 130° C. is continued until evolution of hydrogen chloride stops. Removal of by product hydrogen chloride is promoted by flushing the reaction flask with dry nitrogen by means of the gas inlet tube. The solvent is removed by distillation at reduced pressure s ich as 10 to 80 millimeters, the final temperature being about 130° C. The yield of product is usually between about 85 and about 95% of theory based on hydrogen phosphate.

Example 15

Nickel di(bis(2 - ethylhexyl) orthophosphate) was prepared from the following ingredients:

	Gm.
Nickel chloride hexahydrate (0.137 mole)	32.6
di(2-ethylhexyl) hydrogen phosphate (0.25 mole)	80.6
Sodium hydroxide in 100 ml. water	10.0

The acid phosphate was weighed into a 3-neck round bottom flask equipped with mechanical stirrer, thermometer, and condenser. About 100 ml. of water was added to the flask and the mixture was stirred while the sodium hydroxide solution was added slowly. The temperature in the flask rose from 26° to 46° C. About 200 ml. of toluene was added and the temperature increased by external heating to 80° C. At this time the nickel chloride hexahydrate in 50 ml. of H_2O was added. The reaction temperature was raised to 87° C. and maintained at this level with vigorous stirring for 16 hours. After this time the contents were transferred to a separatory funnel and the aqueous phase drawn off and discarded. The organic layer was washed with water, dried over anhydrous Na_2SO_4, filtered to remove the hydrated salt and finally subjected to distillation to remove solvent.

The product was a brown, viscous material.

Example 16

In order to prepare dichloromolybdenum tri(bis(2-ethylhexyl) orthophosphate), 212 grams (0.66 mole) of commercial di(2-ethylhexyl) hydrogen phosphate in 150 ml. of toluene and 55 grams (0.2 mole) molybdenum pentachloride in 200 ml. of toluene were caused to react. When evolution of by-product hydrogen chloride stopped, toluene was stripped from the product, which was then washed with water and taken up in n-pentane. After drying over anhydrous sodium sulfate, the pentane solution was filtered and the filtrate subjected to distillation to remove pentane. The liquid residue was heated to 120° C. at 20 mm. pressure. An olive green liquid product weighing 203 grams resulted. Its density was 1.109 at 20° C. and the molybdenum content was 8.50 percent.

Additional compounds of the present invention were prepared according to the procedures described above from suitable starting materials as follows:

Starting materials	Amount (grams)	Product	Amount (grams)
Lead acetate	83.5	Lead di(bis(2-ethylhexyl) orthophosphate.	184
Di(2-ethylhexyl) hydrogen phosphate.	129		
Cobaltous acetate tetrahydrate.	62	Cobalt di(bis(2-ethylhexyl) orthophosphate).	158
Di(2-ethylhexyl) hydrogen phosphate.	161		
Manganous chloride tetrahydrate.	22	Manganous di(bis(2-ethylhexyl) orthophosphate).	60
Di(2-ethylhexyl) hydrogen phosphate.	64.5		

Other compounds of the present invention may be prepared from suitable starting materials. For instance, the following compounds may be prepared from the indicated starting materials with the use of suitable solvents such as toluene, heptane, etc.

Starting materials	Amount (grams)	Product
Magnesium chloride	56	Magnesium di(bis(2-ethylhexyl) orthophosphate).
Di(2-ethylhexyl) hydrogen phosphate.	161	
Zinc oxide	5	Zinc di(bis(2-ethylhexyl) orthophosphate).
Di(2-ethylhexyl) hydrogen phosphate.	32.2	
Cadmium chloride	20.1	Cadmium di(bis(2-ethylhexylphenyl) orthophosphate).
2-ethylhexyl-phenylhydrogen phosphate.	55.2	
Mercurous chloride	25.9	Mercurous di(stearylbenzyl orthophosphate).
Stearyl-benzyl-hydrogen phosphate.	41.1	
Chromic chloride	17.4	Chromic tri(triconylphenyl orthophosphate).
Triconyl-phenyl-hydrogen phosphate.	178.2m	
Chromous chloride	13.4	Chromous di(bis(o-cresyl) orthophosphate).
Di(o-cresyl) hydrogen phosphate.	55.6	
Tungsten tetrachloride	35.8	Tungsten tetra (α-naphthyl orthophosphate).
Di(α-naphthyl) hydrogen phosphate.	140	
Ferric chloride	17.8	Iron tri(2-ethylhexyl-α-naphthyl orthophosphate).
2-ethylhexyl-α-naphthyl-hydrogen phosphate.	108.9	
Ruthenium chloride	13.3	Ruthenium di(octylphenyl orthophosphate).
Di(octylphenyl) hydrogen phosphate.		

In order to evaluate the characteristics of gasoline compositions of the present invention, a number of gasoline compositions were prepared containing metallic orthophosphate additives of the present invention as indicated in Table I below. These gasoline compositions were subjected to single cylinder engine deposit tests as described below. The base gasolines used in formulation the gasoline compositions tested were similar to the base gasoline of Example 1. The base gasolines of runs 1 through 4 contained 2.2 cc. per gallon TEL and 0.25 vol. percent 100 neutral (95 V. I.) light lubricating oil. The base gasoline of run 5 contained 2.03 cc. per gallon TEL. The single cylinder engine deposit tests were run in CFR engines having L head assemblies and compression ratios of 7 to 1. Each test consisted of alternating periods of operation under idling conditions for 50 seconds followed by operation under full load conditions for 150 seconds. These cycles were continued for a total test time of 40 hours for each test. During these tests the engine air intake temperature was maintained at 115° F. while the oil temperature was maintained at 160° F. and the coolant temperature at 150° F. During the idling portions of the tests the engines were operated with an air to fuel ratio of 12 to 1 at 600 r.p.m. while during the full load portions of the tests the engines were operated with air to fuel ratios of 13 to 1 and at 900 r.p.m. During the test, the number of wild pings (indicating preignition) was counted by an Erwin Instrument Co. Wild Ping Counter. At the end of the test the average of the wild pings per hour was determined by plotting the total wild pings versus time and taking the slope of the curve. This measurement served as a reliable indication of the surface ignition characteristics of the fuel being tested.

The results of the single cylinder engine deposit test are given in Table I below. Each run involved a test of a base gasoline and a test of the same base gasoline containing the indicated metallic orthophosphate additive. While the base gasolines used were generally similar, they had been stored for varying lengths of time before testing, thus affecting their performance in the tests. The test results reported below thus provide valid comparisons within each run between the performance of a base gasoline and the performance of the same gasoline containing

the indicated additive but do not provide valid comparisons between the base gasolines used in the various runs.

TABLE I.—RESULTS OF SINGLE CYLINDER ENGINE DEPOSIT TESTS

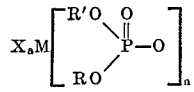
Run No.	Orthophosphate additive	Theories of additive	Average wild pings per hour of base gasoline	
			Without additive	With additive
1	Cobalt di(bis(2-ethylhexyl orthophosphate).	0.2	21	2
2	Manganous di(bis(2-ethylhexyl) orthophosphate).	0.2	31	1
3	Nickel di(bis(2-ethylhexyl) orthophosphate).	0.2	19	1
4	Zinc di(bis(2-ethylhexyl) orthophosphate.	0.2	7	1
5	Dichloromolybdenum tri(bis (2-ethylhexyl) orthophosphate.	0.05	586	15

Table I shows clearly that the addition of metallic orthophosphates of the present invention to the base gasolines resulted in gasoline compositions having very much improved surface ignition characteristics as evidenced by the extremely small number of wild pings compared with the corresponding base gasolines. As shown in Table I, the use of metallic orthophosphate additives of the present invention resulted in reductions of wild ping counts of from about 85 to about 97 percent.

While the invention has been described above with respect to certain preferred embodiments thereof, it will be understood by those skilled in the art that various changes and modifications may be made without departing from the spirit and scope of the invention and it is intended to cover all such changes and modifications in the appended claims.

I claim:

1. A gasoline composition comprising a major proportion of a hydrocarbon base fuel boiling in the gasoline range and a minor proportion of organo hydrocarbyl lead anti-knock agent, and containing between about 0.001 and about 5.0 theories of an additive having a formula



wherein M represents a metal selected from the group consisting of managanese and the metals of groups IB, IIA, IIB, IVA, VIB, and VIII of the Periodic Table, X is a halogen, *n* and *a* are numbers so selected that *n* plus *a* equals valence of metal M and R and R' each represent a hydrocarbon radical having from 2 to about 30 carbon atoms.

2. The gasoline composition of claim **1** in which at least one of R and R' is a branched chain alkyl hydrocarbon radical.

3. The gasoline composition of claim **1** in which R and R' are branched chain alkyl hydrocarbon radicals.

4. The gasoline composition of claim **3** in which the metal is nickel.

5. The gasoline composition of claim **1** in which R and R' are branched chain hydrocarbon radicals.

6. The gasoline composition of claim **1** in which R and R' are identical branched chain hydrocarbon radicals.

7. The gasoline composition of claim **1** in which the additive is dichloromolybdenum tri(bis(2-ethylhexyl) orthophosphate).

8. A gasoline composition according to claim **1** which contains at least about 75 volume percent leaded hydrocarbon base fuel having between 0.1 and 6.00 cc. per gallon of the organo hydrocarbon lead antiknock agent selected from the group consisting of tetraethyl lead and tetramethyl lead.

References Cited

UNITED STATES PATENTS

2,560,542	7/1951	Bartleson et al.	44—68
3,055,748	9/1962	Hartle	260—437
3,055,925	9/1962	Hartle	260—437
3,065,065	11/1962	Sutton et al.	44—68
2,866,732	12/1958	Hoff et al.	
3,068,259	12/1962	Hartle.	
3,193,500	7/1965	Hartle.	

DANIEL E. WYMAN, *Primary Examiner.*

Y. H. SMITH, *Assistant Examiner.*

U.S. Cl. X.R.

44—68, 76