United States Patent Office 3,481,719 Patented Dec. 2, 1969



3,481,719

# GASOLINE COMPOSITION

Seymour H. Patinkin, Chicago, Ill., assignor to Sinclair Research, Inc., New York, N.Y., a corporation of Delaware

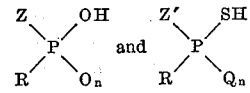
No Drawing. Continuation of application Ser. No. 723,579, Apr. 23, 1968. This application Jan. 10, 1969, Ser. No. 805,074

Int. Cl. C10l *1/26*

U.S. Cl. 44—69 24 Claims

## ABSTRACT OF THE DISCLOSURE

A gasoline composition comprising gasoline hydrocarbons having added thereto an anti-knock quantity of tetra-lower-alkyl lead compounds and a gasoline-soluble salt of certain phosphorus compounds to improve rumble which compounds have the formulae:



where Z is a radical selected from the group consisting of —R, and —OH, Z′ is a radical selected from the group consisting of —R and —SH, R is a hydrocarbon radical of up to about 30 carbon atoms, Q is oxygen or sulfur and, *n* is an integer of 0 or 1. The metal of the salt is selected from the group consisting of Groups I*a*, II*a*, III*a*, V*a*, I*b*, II*b*, III*b*, IV*b*, V*b*, VI*b*, VII*b*, VIII of the Periodic Table and tin and the metal salt is added in an amount sufficient to provide about 0.002 to 0.4 milligram atoms of the selected metal per gallon of gasoline. A gasoline-soluble nonmetallic auxiliary phosphorus compound can also be added to the composition to provide additional beneficial effects.

Continuation of application Ser. No. 723,579, filed Apr. 23, 1968, which is a continuation-in-part of applications Ser. No. 410,740 filed Nov. 12, 1964; Ser. No. 410,750 filed Nov. 12, 1964; Ser. No. 410,787 filed Nov. 12, 1964; and Ser. No. 431,171 filed Feb. 8, 1965, all now abandoned.

The present invention relates to distillate hydrocarbon gasoline compositions which when employed in spark ignition engines lead to improved engine performance.

One of the chief disadvantages attending the use of known additives to lessen abnormal combustion of gasoline in, for instance, automobile engines is that they adversely affect the nature and increase the amount of deposits in the combustion space. These effects manifest themselves in a variety of ways particularly in the case of the higher compression engines. For instance, a fuel having an octane number appropriate to the designed engine compression ratio is unable to give the same anti-knock performance after the formation of extensive deposits. To obtain the intended anti-knock performance requires a fuel of higher octane number, and this effect has become known as the "octane requirement increase" or "ORI" of the engine. Modern engines also evidence a tendency to "rumble," an objectionable shuddering noise, apparently caused by flexing of the crankshaft due to deposit-induced abnormal combustion. Surface ignition induced by deposits also often creates abnormalities such as pre-ignition, auto-ignition and wild ping. Combustion chamber deposits are known to cause piston ring wear and to reduce exhaust valve life. All of these facets of combustion abnormalities can lead to engine damage and/or loss in power and efficiency.

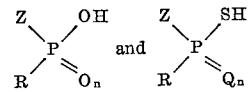
Various commonly employed gasoline additives as, for example, phosphate compounds such as tricresyl phosphate, cresyl diphenyl phosphate, etc., are known to improve engine operation with respect to certain of the problems presented by deposit-induced ignition. Relatively large amounts of these compounds are needed, however, to effectively combat the combustion abnormalities, particularly rumble.



It has now been found that leaded gasolines having added thereto about 0.002 to 0.4 millimole or milligram atoms of metal per gallon as a gasoline-soluble metal salt of certain phosphorus compounds, exhibit improved engine performance with respect to one or more of lower octane number requirement increase, improved rumble, surface ignition characteristics, reduced piston ring wear and extended exhaust valve life. The metals of the phosphorus salts can be metals of Groups I*a*, II*a*, III*a*, V*a*, I*b*, II*b*, III*b*, IV*b*, V*b*, VI*b*, VII*b*, VIII, and tin, or a mixture of two or more of these metals. Among these metals it is preferred to use sodium, potassium, lithium, calcium, barium, aluminum, antimony, bismuth, copper, zinc, cadmium, mercury, scandium, titanium, zirconium, vanadium, niobium, chromium, molybdenum, tungsten, manganese, the iron group metals (iron, cobalt and nickel) and tin. Nickel and cobalt are especially preferred. The Groups of the Periodic Chart mentioned above are as designated on the inside front cover of the Merck Index, 7th edition, Merck & Co., Rahway, N.J., 1960.

While the present invention is directed to the use of the phosphorus compounds in gasoline compositions which contain a lead anti-knock compound to reduce rumble and/or other adverse effects created by the addition of the lead compound, the additives can also be advantageously employed in metal octane-improving additive-free, e.g. non-leaded gasolines where they decrease rumble to, for example, aid in rust preventing, reducing pre-ignition and anti-stalling or carburetor de-icing.

The phosphorus compounds, the metal salts of which constitute the additive of the invention, have the following formulae:

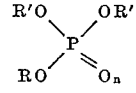


wherein Z is an —R or —OH, Z′ is an R or SH radical, R is a hydrocarbon radical of up to about 30 or more carbon atoms on the average, often at least about 5 and preferably about 8 to 18 carbon atoms, Q is a chalcogen having an atomic number of from 8 to 16, i.e. oxygen or sulfur and *n* is an integer of 0 or 1. R can be an aliphatic, aromatic or mixed alphatic-aromatic radical and is preferably non-olefinic and non-acetylenic, i.e. having adjacent carbon atoms no closer than 1.40 A. R can also be substituted with non-interfering groups if desired. The total number of carbon atoms in a molecule of the phosphorus compounds of the invention is preferably up to about 40 or even only up to about 30 and the metal salt of the acid is soluble in the gasoline at least to the extent employed in the invention. Also, the metal salts can contain more or less than the stoichiometric equivalent of the metal, thus the product can contain free phosphorus compounds or, when the selected metal is polyvalent, it can be attached to another group, for instance, the inorganic anion of the metal used to form the phosphorus salt.

R in the —R radicals of the formulae of the phosphorus compounds of the invention is preferably an alkyl group which can be straight or branch chained or an alkyl-substituted phenyl whose alkyl substituents contain a total of up to 18 carbon atoms, and preferably are lower alkyl, especially methyl. Illustrative of suitable R's in the —R radicals are pentyl, butyl, octyl, isooctyl, 2-ethylheptyl, dodecyl, oleyl, octadecyl, tetradecyl, phenyl and alkylated phenyls such as toluyl, xylenyl, propyl phenyl, butyl phenyl, dibutyl phenyl, monoamyphenyl,

diamyl phenyl, decyl phenyl, dodecyl phenyl, tetradecyl phenyl, hexadecyl phenyl and octadecyl phenyl. Non-limiting examples of specific phosphorus compounds, the salts of which can be used in the present invention are: octyl phosphonous acid, dodecyl phosphonous acid, octadecyl phosphonous acid, octadecenyl phosphonous acid, benzene phosphonous acid, butylbenzene phosphonous acid, nonylbenzene phosphonous acid, diethyl phosphinus acid, dioctyl phosphinous acid, octycyclohexyl phosphinous acid, octadecylbutyl phosphinous acid, heptylphenyl phosphinous acid, eicosylnonyl phosphinous acid, ditoluyl phosphinous acid, diethyl phosphite, dioctyl phosphite, diheptenyl phosphite, dodecylbutyl phosphite, hexyloctadecyl phosphite, propylcyclohexyl phosphite, butylphenyl phosphite, diphenyl phosphite, octyl dithiophosphonous acid, dodecyl dithiophisphonous acid, octadecyl dithiophosphonous acid, octadecenyl dithiophosphonous acid, benzene dithiophosphonous acid, butylbenzene dithiophosphonous acid, nonylbenzene dithiophosphonous acid, diethyl thiophosphinous acid, dioctyl thiophosphinous acid, octylcyclohexyl thiophosphinous acid, octadecylbutyl thiophosphinous acid, heptylphenyl thiophosphinous acid, eicosylnonyl thiophosphinous acid, ditoluyl thiophosphinous acid, diethyl thiophosphite, dioctyl thiophosphite, diheptenyl thiophosphite, dodecylbutyl thiophosphite, hexyloctadecyl thiophosphite, propylcyclohexyl thiophosphite, butylphenyl thiophosphite, diphenyl thiophosphite and the like. The basis for the above nomenclature may be found in the ACS Official Reports published in Chemical and Engineering News, vol. 30, No. 43, Oct. 27, 1952, pp. 4515–22.

In order to provide leaded gasolines of further enhanced characteristics, for instance, as to pre-ignition, spark plug fouling and even, in at least some cases, rumble, there can be included in the gasoline composition of the invention a gasoline soluble phosphorus compound having the formula:



wherein R has the value described above with respect to the phosphorus compounds from which the metal salts of the invention are made; R′ is hydrogen or R and *n* is an integer of 0 to 1. R is preferably an aromatic, e.g. phenyl hydrocarbon radical of 6 to 12 carbon atoms and can be substituted as, for instance, with lower alkyl groups say of 1 to 4 carbon atoms. Thus, the phosphorus compound can be a mono-, di-, or tri-ester. We also prefer to employ a phenyl, alkylphenyl or a mixed phenyl-alkyl phenyl ester of phosphorus. Thus, one or more of the ester groups is preferably an alkyl phenyl radical, often of about 7 to 15 carbon atoms. See U.S. Patent No. 2,889,212 for a further list of the useful phosphatse and phosphites.

These auxiliary phosphate and phosphite additives can be prepared by reacting the appropriate alcohol or aromatic hydroxy compound with phosphoric acid make the phosphate or with phosphorus trichloride to form the phosphite.

The preferred alcohols are alkanols which can be straight or branch chained and alkyl-substituted phenols whole alkyl substituents contain a total of up to 18 carbon atoms, and preferably are lower alkyl, especially methyl. The aromatic hydroxy compounds and aliphatic alcohols may be substituted with non-deleterious groups. Illustrative of suitable alcohols are pentanol, butanol, octanol, isooctanol, 2-ethyl-heptanol, dodecanol, oleyl alcohol, octadecyl alcohol, tetradecyl alcohol, alcohols prepared by the "Oxo" process, phenol and alkylated phenols such as cresol, xylenol, propyl phenol, butyl phenol, dibutyl phenol, monoamylphenol, diamyl phenol, decyl phenol, dodecyl phenol, tetradecyl phenol, hexadecyl phenol and octadecyl phenol. Particularly preferred alkyl phenols are ortho, meta and para cresol; 2,4- and 2,5-xylenol; 2,4-dimethyl-6-tertiary butylphenol; octyl and nonylphenols.

By the term "leaded gasoline" to which the additives of the present invention are incorporated is meant hydrocarbon fractions boiling primarily in the gasoline range, usually about 100 to 425° F., having added thereto a small amount, generally between about 1 to 6 cc. per gallon, preferably about 2 to 4 cc. per gallon, of a tetra-lower-alkyl lead compound as an anti-knock agent. The gasolines are usually composed of a major amount of a blend of hydrocarbon mineral oil fractions boiling primarily in the aforementioned range and will contain varying proportions of paraffins, olefins, naphthenes and aromatics derived by distillation, cracking and other refining and chemical conversion processes practiced upon crude oil fractions. Straight run gasolines, gasolines derived from reforming straight run naphtha over a platinum-alumina catalyst in the presence of hydrogen, etc. are components frequently used in making up a gasoline composition. A typical premium gasoline, besides containing a small amount of a tetra-lower-alkyl lead compound as an anti-knock agent may also contain small amounts of other non-hydrocarbon constituents used to impart various properties to the gasoline in its use in internal combustion engines, e.g., halohydrocarbon scavengers, oxidation inhibitors, etc. Such gasolines frequently have a Research Method octane number of about 90 to 105, and a Motor Method octane number of about 80 to 98.

The metal salt of the phosphorus compounds of the invention is incorporated in the leaded gasolines in small amounts sufficient to provide a composition exhibiting an advantage in spark-ignition engines, for instance, with respect to one or more of improved rumble, surface ignition characteristics, lower octane number requirement increase, reduced piston ring wear and longer exhaust valve life. The actual amount of the metal salt additive employed may vary depending upon the particular gasoline used, its lead content, etc. In any event, sufficient of the metal salt is employed to supply about 0.002 to 0.4, preferably about 0.025 to 0.3, millimole or milligram atoms of the metal per gallon of gasoline. The additive will usually provide the gasoline with about 0.00004 to 0.008 gram of one or a combination of metals of the metal salts per gram of lead, preferably about 0.0005 to 0.006 gram of the metal per gram of lead. This often means that about 0.05 to 15 or 30 or more pounds of the metal salt is added, preferably about 2 to 20 pounds, per 1000 barrels of gasoline. The alkali metal salts of the phosphorus compounds, when employed are ordinarily added in an amount of about 0.002 to 0.4 millimole or milligram atoms per gallon of gasoline and the combination of the alkali metal and selected metal salt is preferably in the range of about 0.002 to 0.4 millimole or milligram atoms per gallon of gasoline.

When used, about 0.05 to 0.6 theory, preferably about 0.15 to 0.5 theory, of the auxiliary phosphate or phosphite additive, based on the lead content of the gasoline, is generally employed. The term "theory" as applied to the amount of the phosphorus additive means the amount required to react stoichiometrically with the lead so that all of the lead atoms and all of the phosphorus atoms form $Pb_3(PO_4)_2$.

The following examples are given to illustrate the advantages provided leaded gasolines by the additives of the present invention.

## EXAMPLE I

A nickel salt of diphenyl phosphite, calculated as 11.2% by weight nickel is added in an amount of 5 lbs. of the salt per 1000 barrels to a gasoline composed of 37 volume percent light straight run gasoline, 23 volume percent light catalytically cracked gasoline, 13 volume percent heavy catalytically reformed gasoline and 27 volume percent heavy catalytically cracked gasoline containing 3 cc. per gallon of TEL as Motor Mix (TEL

Motor Mix contains 59.2% tetraethyl lead, 13.0% ethylene dibromide 23.9% ethylene dichloride and 3.9% hydrocarbon diluent, dyes, etc.) and 0.2 theory cresyl diphenyl phosphate (CDP).

Evaluation of the resulting composition in a spark ignition engine shows operation of engine to be improved with respect to rumble, surface ignition characteristics, octane number requirement increase, ring wear and exhaust valve life.

Similar benefits can be obtained by adding to the same gasoline containing TEL Motor Mix and CDP one of the following additives in the designated amounts:

| Example | Additive | Calc. percent metal | Amount of additive #/1,000 bbls. gasoline |
|---|---|---|---|
| II | Al salt of dioctylphenyl phosphite | 1.9 | 10 |
| III | Sb salt of didodecyl phosphite | 8.8 | 7 |
| IV | Cu salt of octadecylbutyl phosphite | 14.1 | 3 |
| V | V salt of dodecyl phosphonous acid | 12.8 | 4 |
| VI | Cr salt of butylbenzene phosphonous acid | 15.0 | 3 |
| VII | Sn salt of dioctyl phosphinous acid | 10.0 | 7 |
| VIII | Co salt of eicosylnonyl phosphinous acid | 6.1 | 5 |
| IX | Ni salt of diphenyl phosphite | 11.2 | 3 |
| X | Na salt of diphenyl phosphite | 9.0 | 2 |
| XI | do | 9.0 | 8 |
| XII | Potassium butylbenzene phosphonite | 16.5 | 5 |
| XIII | Calcium eicosylnonyl phosphinite | 7.4 | 7 |
| XIV | Na salt of diphenyl thiophosphite | 8.4 | 5 |
| XV | Potassium salt of octadecylbutyl thiophosphite | 6.8 | 10 |
| XVI | Sodium salt of dodecyldithiophosphonous acid | 7.9 | 6 |
| XVII | Calcium salt of eicosylnonylthiophosphinous acid | 4.1 | 15 |
| XVIII | Al salt of dioctylphenyl thiophosphite | 1.9 | 20 |
| XIX | Sb salt of didodecyl thiophosphite | 8.6 | 10 |
| XX | Cu salt of octadecylbutyl thiophosphite | 7.3 | 7 |
| XXI | V salt of dodecyl dithiophosphonous acid | 11.4 | 5 |
| XXII | Cr salt of butylbenzene dithiophosphonous acid | 13.2 | 4 |
| XXIII | Sn salt of dioctyl thiophosphinous acid | 9.3 | 8 |
| XXIV | Co salt of eicosylnonyl thiophosphinous acid | 5.9 | 10 |
| XXV | Ni salt of diphenyl thiophosphite | 10.5 | 5 |
| XXVI | Co salt of diphenyl thiophosphite | 10.6 | 5 |

The ORI of an engine is obtained by the following procedure:

After determining the clean or initial octane requirement of a 327 cubic inch 10.0:1 compression ratio engine, the gasoline without the additive of the invention is run for 216 hours and the octane requirement increase noted. The engine is then thoroughly cleaned of all deposits so that it again exhibits the same clean octane requirement and run on an identical cycle, with the same gasoline but containing the additive of the invention. After 216 hours' use, the octane requirement increase is noted and compared with the octane requirement increase found with the gasoline without the additive to determine the extent of improvement.

The rumble tendency of an engine after a given time of use is measured by a LIB number. The number represents the percent isooctane (containing 3 cc. TEL/gallon) required in a blend with benzene (containing 3 cc. TEL/gallon) after a given period of engine operation using the fuel under test, to avoid rumble at a given r.p.m., e.g. 2,000 r.p.m. The test procedure comprises stopping the gasoline to the engine at any given period of engine operation and employing as a fuel to the engine a fuel containing a certain percent of isooctane in an isooctane-benzene blend (containing 3 cc. TEL/gallon), manually opening the throttle at a given rate and recording the r.p.m. at which rumble occurs, if any in fact occurs. The faster one is able to run the engine with the lowest percent of isooctane in the blend the better the rumble resistance of the engine. Thus, the lower the LIB number the better the rumble characteristics of the engine. The gasoline with and without the additive of the invention is tested in this manner and the LIB number obtained with each are compared.

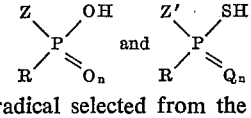
The piston ring wear is determined by equipping a single cylinder COT engine with radioactive rings installed in the grooves of the pistons. The lubricating oil system of the engine is provided with a sealed monitoring well which contains a scintillation counter. The ring wear rate is determined by passing the lubricating oil through the monitoring well and therein detecting the concentration in mg./hour of radioactive iron transported to the oil due to wear of the piston rings.

The test to determine the effect of the fuel composition on exhaust valve life involves reunning an automobile engine at a fixed number of hours at constant or varied speeds and loads depending on the engine used and then noting the number of valves that failed during this period of time.

The test used to determine the deposit-induced ignition characteristics of the fuel composition comprises equipping an engine with an L-head cylinder and an electronic wild ping counter which records the total number of wild pings which have occurred during the test periods. Since deposit-induced ignition is the tendency to ignite the fuel-air mixture erratically and to produce uncontrolled combustion noticeable as, for instance, wild ping, the electronic counter which is used in conjunction with an ionization gap, automtaically detects and records uncontrolled combustion.

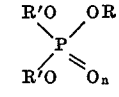
It is claimed:

1. A gasoline composition consisting essentially of hydrocarbon gasoline, an anti-knock quantity of tetra-lower-alkyl lead compound, and a gasoline-soluble metal salt of a phosphorus compound selected from the group consisting of phosphorus compounds having the formulae:



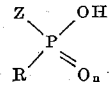

where Z is a radical selected from the group consisting of —R, and —OH, Z' is a radical selected from the group consisting of —R and —SH, R in said radicals being a hydrocarbon of up to 30 carbon atoms, Q is a chalcogen having an atomic number of from 8 to 16, and *n* is an integer of 0 to 1, the metal of said salt being selected from the group consisting of Groups I*a*, II*a*, III*a*, V*a*, I*b*, II*b*, III*b*, IV*b*, VI*b*, VII*b*, and VIII and tin, said metal salt being sufficient to provide 0.002 to 0.4 milligram atoms of selected metal per gallon of gasoline.

2. The composition of claim 1 in which there is also included about 0.05 to 0.6 theory of a gasoline-soluble phosphorus compound having the formula:

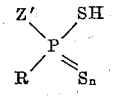



wherein R is a hydrocarbon radical of up to about 30 carbon atoms on the average, R' is selected from the group consisting of hydrogen and R, and *n* is an integer having a value of 0 or 1.

3. The composition of clam 1 wherein the phosphorus compound has the formula:



4. The composition of claim 1 wherein the phosphorus compound has the formula:



5. The composition of claim 1 wherein the metal is an iron group metal.

6. The composition of claim 5 wherein the metal is nickel.

7. The composition of cliam 1 wherein the metal is an alkali metal.

8. The composition of claim 1 wherein the metal is an alkaline earth metal.

9. The composition of claim 2 wherein at least one R in the structures of claim 2 is an alkyl phenyl radical of 7 to 15 carbon atoms.

10. The composition of claim 9 wherein the amount of phosphorus compound is about 0.15 to 0.5 theory.

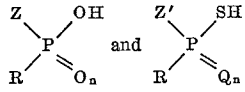
11. The composition of claim 9 wherein the metal is an iron group metal.

12. The composition of claim 11 wherein the metal is nickel.

13. The composition of claim 9 wherein the metal is an alkali metal.

14. The composition of claim 13 wherein the metal is sodium.

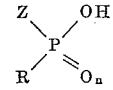
15. A gasoline composition consisting essentially of hydrocarbon gasoline, an anti-knock quantity of a tetra-lower-alkyl lead compound, and a gasoline-soluble metal salt of a phosphorus compound selected from the group consisting of compounds having the formulae:



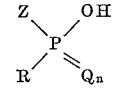
wherein Z is a radical selected from the group consisting of —R, and —OH, Z′ is a radical selected from the group consisting of —R and —SH, R in said radicals being a hydrocarbon of about 8 to 18 carbon atoms, Q is a chalcogen having an atomic number of from 8 to 16 and *n* is an integer of 0 to 1, the metal of said salt being selected from the group consisting of Groups I*a*, II*a*, III*a*, V*a*, I*b*, II*b*, III*b*, IV*b*, V*b*, VI*b*, VII*b*, VIII and tin, said metal salt being sufficient to provide about 0.025 to 0.3 milligram atoms of selected metal per gallon of said gasoline.



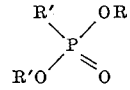
16. The composition of claim 15 wherein the phosphorus compound has the formula:



17. The composition of claim 15 wherein the phosphorus compound has the formula:



18. The composition of claim 15 in which there is also included about 0.05 to 0.6 theory of a gasoline-soluble phosphorus compound having the formula:



wherein R is a lower alkyl phenyl radical of 7 to 15 carbon atoms and R′ is selected from the group consisting of phenyl and R.

19. The composition of claim 18 wherein the metal is an iron group metal.

20. The composition of claim 19 wherein the metal is nickel.

21. The composition of claim 20 wherein the non-metallic phosphorus compound is cresyl diphenyl phosphate.

22. The composition of claim 18 wherein the metal is an alkali metal.

23. The composition of claim 22 wherein the metal is sodium.

24. The composition of claim 23 wherein the non-metallic phosphorus compound is cresyl diphenyl phosphate.


**References Cited**

UNITED STATES PATENTS

| | | |
|---|---|---|
| 2,560,542 | 7/1951 | Bartleson et al. |
| 2,889,212 | 6/1959 | Yust et al. |
| 3,055,925 | 9/1962 | Hartle. |



DANIEL E. WYMAN, Primary Examiner

W. J. SHINE, Assistant Examiner

U.S. Cl. X.R.

44—68, 76