United States Patent Office

3,502,452

Patented Mar. 24, 1970

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3,502,452

GASOLINE COMPOSITION

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

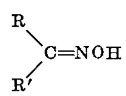
No Drawing. Continuation of application Ser. No. 675,019, Oct. 13, 1967. This application Mar. 4, 1969, Ser. No. 809,458

Int. Cl. C10l *1/26, 1/22, 1/30*

U.S. Cl. 44—69 **23 Claims**

ABSTRACT OF THE DISCLOSURE

A gasoline composition consisting essentially of hydrocarbon gasoline, an anti-knock quantity of tetra-lower-alkyl lead compound and a gasoline-soluble metal oximate of an oxime having the formula



wherein R is a hydrocarbon radical of up to 30 carbon atoms and R′ is R or hydrogen. The metal of the salt is selected from the group consisting of Groups I*a*–III*a*, V*a*, I*b*–VII*b*, VIII and tin and the salt is added in an amount sufficient to provide 0.002 to 0.8 milligram atoms of metal per gallon of gasoline.

This application is a continuation-in-part of applications Ser. No. 410,741, filed Nov. 12, 1964, and Ser. No. 410,786, filed Nov. 12, 1964, and a continuation of Ser. No. 675,019, filed March 4, 1969, 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, autoignition and wild ping. Combustion chamber deposits are known to cause piston ring wear and to reduce exhause valve life. All of these facets of combustion abnormalities can lead to engine damage and/or loss in power and efficiency.

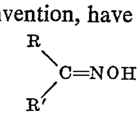
Various commonly employed gasoline additives as, for example, phosphate compounds such as tricresyl phosphate, cresyl diphenyl phosphate, etc., are known to improve engine operation with respect to certain of the problems presented by deposit-induced ignition. Relatively large amounts of these compounds 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 or even 0.8 millimole or milligram atom of metal per gallon as certain gasoline-soluble metal oximates, 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 oximates can be metals of Groups III*a*, V*a*, I*b*, II*b*, III*b*, IV*b*, V*b*, VI*b*, VII*b*, VIII, tin or a mixture of two or more of these metals. Among these metals it is preferred to use 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. Nicket 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, seventh edition, Merck & Co., Inc., Rahway, N.Y., 1960.

It has also been found in accordance with a second embodiment that leaded gasolines having added thereto about 0.002 to 0.4 or even 0.8 millimole or milligram atom of metal per gallon as a gasoline-soluble alkali or alkaline earth metal oximate 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 preferred alkali metal oximates are those of sodium, potassium and lithium and the preferred alkaline earth metal oximates are those of calcium, barium and strontium.

Also as another embodiment, the invention contemplates adding in combination with the aforementioned metal oximates, small amounts of alkali metal oximates. The preferred alkali metal oximates are those of sodium, potassium and lithium.

The oximes, the metal oximates of which constitute the additive of the invention, have the following formula:

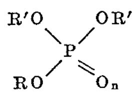


wherein R is a hydrocarbon radical of up to about 30 or more carbon atoms on the average, often at least about 4 and preferably about 8 to 18 carbon atoms, and R′ is hydrogen or R. R can be an aliphatic, aromatic or mixed aliphatic-aromatic radical and is preferably non-olefinic and non-acetylenic, i.e. having adjacent carbon atoms no closer than 1.40 A. R can also be substituted with non-interfering groups. The total number of carbon atoms in a molecule of the oximate is preferably up to about 40 or even up to about 30 and the metal oxime is soluble in the gasoline at least to the extent employed in the invention. Also the metal oximate can contain more or less than the stoichiometric equivalent of the metal, thus the product can contain free oxime or if the metal is polyvalent, it can be attached to another group, for instance, the inorganic anion of the metal compound used to form the metal oximate. The metal oximates can be prepared by any of the methods of the art.

The preferred R groups include the straight or branched chain alkyl groups, phenyl and alkyl-substituted phenyl groups whose alkyl substituents contain a total of up to 18 carbon atoms, and preferably are lower alkyl, especially methyl. Illustrative of suitable R groups are pentyl, butyl, octyl, isoctyl, 2-ethyl-heptyl, dodecyl, oleyl, octadecyl, tetradecyl, phenyl and alkylated phenyls such as cresyl, xylenyl, propyl phenyl, butyl phenyl, dibutyl phenyl, monoamyl phenyl, diamyl phenyl, decyl phenyl, dodecyl phenyl, tetradecyl phenyl, hexadecyl phenyl and octadecyl phenyl.

Non-limiting examples of suitable oximes are dibutyl oxime, dipentyl oxime, dihexyl oxime, dioctyl oxime, decyl oxime, didecyl oxime, dodecyl oxime, didodecyl oxime, ditetradecyl oxime, hexadecyl oxime, dihexadecyl oxime, octadecyl oxime, dioctadecyl oxime, eicosyl oxime, dieicosyl oxime, octyl benzene oxime, dodecyl benzene oxime, octadecyl benzene oxime and the like.

In order to provide leaded gasolines of further enhanced characteristics, for instance, as to preignition, 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 phosphorous compound having the formula:



wherein R has the value described above with respect to the oximes 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 phosphorous compound can be a mono-, di-, or tri- ester. We also prefer to employ a phenyl, alkyl-phenyl or a mixed phenyl-alkyl phenyl ester of phosphorous. 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 phosphates and phosphites.

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

The preferred alcohols are alkanols which can be straight or branched chain and alkyl-substituted phenols whose 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, iso-octanol, 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, monoamyl phenol, 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 butyl phenol; octyl and nonyl phenols.

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 ccs. per gallon, preferably about 2 to 4 ccs. 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 cracking gas oil, gasolines or reformate 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 oximate of the invention is incorporated in the leaded gasoline 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 value 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 oximate is employed to supply 0.002 to 0.4 or even 0.8 preferably 0.025 to 0.3, millimole or milligram atoms of the metal per gallon of gasoline. The additive will usually provide the gasoline with 0.00004 to 0.008 grams of one or a combination of the metal of the oximates per gram of lead, preferably 0.0005 to 0.006 gram of the metal per gram of lead. This often means that about 0.5 to 15 or 30 or more pounds of the metal oxime is added, preferably about 4 to 10 pounds, per 1000 barrels of gasoline. The alkali metal oximate, when employed, is ordinarily added in an amount of about 0.002 to 0.8 millimole or milligram atom of metal per gallon of gasoline and when a combination of the selected metal oximate and alkali metal oximate is preferably 0.002 to 0.8 milligram atom of metal per gallon of gasoline.

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

Nickel dihexadecyl oximate, calculated as 5.5% by weight nickel, is added in an amount of 5.8 pounds 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 ccs. 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 results can be obtained by adding to the same gasoline containing TEL Motor Mix and CDP the following additives in the designated amounts:

Examples	Additive	Calc. percent metal	Amount of additive, #/1,000. bbls gasoline
II	Na ditetradecyl oximate	5.0	2
III	Ca didodecyl oximate	5.75	3.6
IV	Al didecyl oximate	2.60	5.2
V	Sb didecyl oximate	6.90	8.0
VI	Cu dihexadecyl oximate	5.9	5.2
VII	Zn dioctadecyl oximate	5.6	6.0
VIII	Sc ditetradecyl oximate	5.4	4.8
IX	Ti didecyl oximate	3.55	7.0
X	Zr didecyl oximate	6.5	7.1
XI	V didodecyl oximate	4.2	6.2
XII	Cr didodecyl oximate	4.3	6.3
XIII	Co ditetradecyl oximate	6.3	4.9
XIV	Ni dihexadecyl oximate	5.5	5.8
XV	Sn octyl benzene oximate	11.4	5.2
XVI	Mn dodecyl benzene oximate	9.1	3.3
XVII	Na ditetradecyl oximate	5.0	1

EXAMPLE XVIII

Sodium dieteradecyl oximate, calculated as 5.0% by weight sodium, is added in an amount of 2 pounds 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 ccs. 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.

EXAMPLE XIX

Similar results can be obtained by adding to the same gasoline containing TEL Motor Mix and CDP of Example XVIII, 3.6 pounds per 1000 barrels of gasoline of calcium didodecyl oximate, calculated at 5.75% by weight calcium.

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 numbers 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 running 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, automatically 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 oximate of an oxime having the formula:

$$\begin{matrix} R \\ & \diagdown \\ & & C{=}NOH \\ & \diagup \\ R' \end{matrix}$$

wherein R is a hydrocarbon radical of up to 30 carbon atoms and R′ is selected from the group consisting of hydrogen and R, said metal 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, the amount of said metal oximate being sufficient to provide 0.002 to 0.8 milligram atoms of metal of said oximate per gallon of gasoline.

2. A gasoline composition consisting essentially of hydrocarbon gasoline, an anti-knock quantity of tetra-lower-alkyl lead compound, and a gasoline soluble metal oximate of an oxime having the formula:

$$\begin{matrix} R \\ & \diagdown \\ & & C{=}NOH \\ & \diagup \\ R' \end{matrix}$$

wherein R is a hydrocarbon radical of up to 30 carbon atoms and R′ is selected from the group consisting of hydrogen and R, said metal being selected from the group consisting of Groups III*a*, V*a*, I*b*, II*b*, III*b*, IV*b*, V*b*, VI*b*, VII*b*, VIII and tin, the amount of said metal oximate being sufficient to provide 0.002 to 0.8 milligram atoms of metal of said oximate per gallon of gasoline.

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

$$\begin{matrix} R'O & & OR \\ & \diagdown \;\; \diagup & \\ & P & \\ & \diagup \;\; \searrow & \\ R'O & & O_n \end{matrix}$$

wherein R is a hydrocarbon radical of up to about 20 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 to 1.

4. The composition of claim **2** wherein the selected metal is an iron group metal.

5. The composition of claim **4** wherein the metal is nickel.

6. The composition of claim **3** wherein at least one R in the structure of claim **3** is an alkyl phenyl radical of 7 to 15 carbon atoms.

7. The composition of claim **6** wherein the amount of phosphorous compound is about 0.15 to 0.5 theory.

8. The composition of claim **6** wherein the selected metal is an iron group metal.

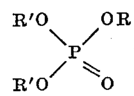
9. The composition of claim **8** wherein the metal is nickel.

10. A gasoline composition consisting essentially of hydrocarbon gasoline, an anti-knock quantity of a tetra-lower-alkyl lead compound, and a gasoline soluble metal oximate of an oxime having the formula:

$$\begin{matrix} R \\ & \diagdown \\ & & C{=}NOH \\ & \diagup \\ R' \end{matrix}$$

wherein R is a hydrocarbon radical of up to 30 carbon atoms and R' is selected from the group consisting of hydrogen and R, said metal being selected from the group consisting of Groups III*a*, V*a*, I*b*, II*b*, III*b*, IV*b*, V*b*, VI*b*, VII*b*, VIII and tin, the amount of said metal oximate being sufficient to provide about 0.025 to 0.3 millimole of selected metal per gallon of said gasoline.

11. The composition of claim **10** in which there is also included about 0.05 to 0.6 theory of a gasoline-soluble phosphorous compound having the formula:



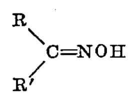
wherein R is a lower alkyl phenyl radical of 7 to 15 carbon atoms and R' is selected from the group consisting of phenyl and R.

12. The composition of claim **11** wherein the selected metal is an iron group metal.

13. The composition of claim **12** wherein the metal is nickel.

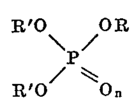
14. The composition of claim **13** wherein the phosphorous compound is cresyl diphenyl phosphate.

15. A gasoline composition consisting essentially of hydrocarbon gasoline, an anti-knock quantity of tetra-lower-alkyl lead compound, and a gasoline soluble metal oximate of an oxime having the formula:



wherein R is a hydrocarbon radical of up to 30 carbon atoms and R' is selected from the group consisting of alkali and alkaline earth metals, the amount of said metal salt being sufficient to provide 0.002 to 0.8 milligram atom of metal per gallon of gasoline.

16. The composition of claim **15** in which there is also included about 0.05 to 0.6 theory of a gasoline-soluble phosphorous 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 to 1.

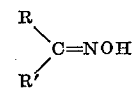
17. The composition of claim **16** wherein at least one R in the structure of claim **16** is an alkyl phenyl radical of 7 to 15 carbon atoms.

18. The composition of claim **17** wherein the amount of phosphorous compound is about 0.15 to 0.5 theory.

19. The composition of claim **15** wherein the metal is an alkaline earth metal.

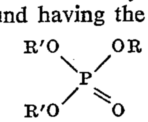
20. The composition of claim **15** wherein the metal is an alkali metal.

21. A gasoline composition consisting essentially of hydrocarbon gasoline, an anti-knock quantity of a tetra-lower-alkyl lead compound, and a gasoline soluble metal oximate of an oxime having the formula:



wherein R is a hydrocarbon radical of up to 30 carbon atoms and R' is selected from the group consisting of alkali and alkaline earth metals, the amount of said metal salt being sufficient to provide about 0.025 to 0.3 millimole of selected metal per gallon of said gasoline.

22. The composition of claim **21** in which there is also included about 0.05 to 0.6 theory of a gasoline soluble phosphorous 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.

23. The composition of claim **22** wherein the phosphorous compound is cresyl diphenyl phosphate.

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DANIEL E. WYMAN, Primary Examiner

W. J. SHINE, Assistant Examiner

U.S. Cl. X.R.

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