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GASOLINE COMPOSITIONS

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13 Claims. (Cl. 44—69)

This application is a continuation-in-part of co-pending application Serial No. 79,535, filed December 30, 1960.

This invention relates to an improved gasoline composition for spark ignition internal combustion engines, especially for such engines having high compression ratios.

Since spark ignition engines were first manufactured, their compression ratios have steadily been raised, especially in aviation and automotive engines. This has made possible greater power for the same size engine and more efficient utilization of the gasoline fuel. Increased compression ratios have of course necessitated the use of fuels of increased resistance to detonation, or spark knock, but heretofore it has been possible, by the development of new hydrocarbon conversion processes for example cracking and reforming, and by using anti-knock agents such as tetraethyl lead, to manufacture high quality fuels fully adequate to take advantage of engine design.

Of the many aspects of gasoline performance (such as ease of starting, vapor-locking tendencies, cleanliness, motor combustion noise and the like) which the manufacturer of gasoline must consider carefully, the control of combustion noise is probably the most important because it indicates a reduced efficiency in utilizing available fuel energy and a resulting loss of power and mileage. In the past the control of combustion noise has been primarily a matter of suppressing spark knock, but the compression ratios of the newer engines have reached a point where other related phenomena have become serious. "Wild ping," a sharp engine noise something like the noise of spark knock randomly occurring, is likely if the deposits in the combustion chamber glow and ignite the fuel mixture prematurely. Even less familar problems now becoming prevalent include "pounding" or "high speed rumble."

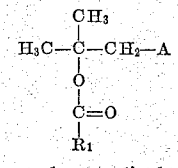
Rumble is an engine noise which has been described as sounding like "broom handle dragged along a picket fence." It is encountered especially in the case of high compression engines, usually at fairly high speeds under moderate to heavy loads and, like spark knock, is aggravated by increasing the compression ratio of the engine. Unlike spark knock however, raising the octane number of the gasoline will not prevent rumble. Precision measurements of high frequency combustion chamber pressure fluctuation have shown that pounding noise is not due to these as are the noises of spark knock and wild ping: analyses of rumble noise have shown that it involves highe intensity sound in the low frequencies, especially in the 400 to 1500 cycles per second range, as compared to spark knock which is characterized by high intensity sound in the 6000 cycles per second range as well as a somewhat lesser intensity sound at about 600 cycles per second. It is possible that rumble is a vibration of the power train components such as connecting rods, crank shafts and the like caused by excessive rise in pressure during the combustion of the fuel, i.e., too rapid a burning rate. It has been found that rumble is aggravated by increasing the concentration of aromatic hydrocarbons in the gasoline; this makes it likely that it will be a problem of increasing seriousness because the trend in refining processes has been toward gradually increasing concentrations of aromatics in gasoline.

Many gasoline quality characteristics besides the avoidance of combustion irregularities have also recently become more critical. For example the gasoline should have a minimum tendency to form deposits not only in the combustion chamber but also in the fuel system. The carburetor and intake manifold in particular are critical in this respect because there the gasoline-air mixture is subjected to relatively high temperatures after the engine has been operated for some time and gums and resins are prone to form and interfere with the free flow of the fuel mixture and with the operation of the intake valves. This problem has been aggravated of late by the low profiles of the newer automobiles and the additional accessories in the engine compartment, such as air-conditioning systems, which have considerably raised the normal engine compartment operating temperatures.

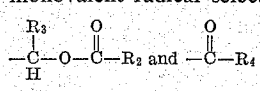
These problems of course are by no means all that the manufacturer of gasoline must overcome. However, it is evident that they are among the more important ones and a gasoline improved in a number of these respects would be highly desirable.

It has now been found that when certain phosphorus compounds and certain substituted tertiary ester compounds are used in particular proportions in leaded gasolines, the resulting gasoline compositions possess improved performance characteristics in regard to abnormal combustion noise and engine cleanliness.

The substituted tertiary ester compounds of this invention are gasoline soluble compounds composed solely of carbon, hydrogen and oxygen. They are defined by the formula:

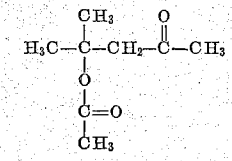


wherein A is a monovalent radical selected from

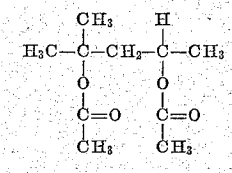


R_1, R_2 and R_3 each is hydrogen or a low molecular weight alkyl radical containing up to 4 carbon atoms and R_4 is a low molecular weight alkyl radical containing up to 4 carbon atoms. A few examples of suitable such esters are:

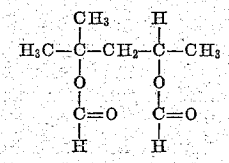
(1) 2-methyl-2-acetoxy-4-pentanone



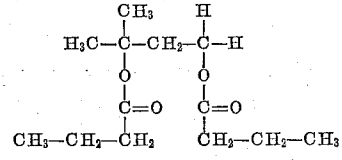
(2) 2,4-diacetoxy-2-methyl pentane



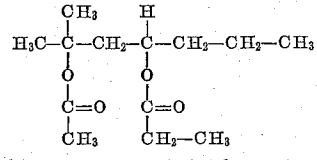
(3) 2,4-diformyloxy-2-methyl pentane



(4) 1,3-dibutyryloxy-3-methyl butane



(5) 2-methyl-2-acetoxy-4-propionyloxy heptane



The phosphorus compounds in the compositions of the invention are trihydrocarbon phosphates and trihydrocarbon phosphites. They may be conveniently represented by the formula:



where R_5, R_6, and R_7 are the same or different hydrocarbyl groups having from 1 to about 15 carbon atoms and the X's are oxygen or sulfur. The X's can also be the same or different within the same phosphorus compound. The hydrocarbyl groups can be alkyl or aryl (including alkaryl or arylalkyl) radicals or mixtures thereof. Hydrocarbyl groups having from 1 to 10 carbon atoms are particularly preferred. It is also preferred that at least one of the hydrocarbyl groups is an aryl radical, e.g., phenyl or cresyl.

The following are a few examples of suitable phosphorus compounds of the invention: tricresyl phosphate, tri(2,4 - methyl phenyl) phosphate, tri - (p-ethylphenyl) phosphate, tri-(2-methyl - 4 - isopropylphenyl) phosphate, tri(p-tert butylphenyl) phosphate, tri-(2,6-dimethyl-4-tert-butylphenyl) phosphate, tri-(4-methyl-1-naphthyl) phosphate, ethyl di-(p-cresyl) phosphate, 2,6-xylenyl di-(n-butyl) phosphate, triphenyl phosphate, cresyl diphenyl phosphate, dicresyl phenyl phosphate, xylyl dicresyl phosphate, trixylyl phosphate, dimethyl xylyl phosphate, dimethyl tolyl phosphate, dimethyl phenyl phosphate, methyl diphenyl phosphate, octyl diphenyl phosphate, trimethyl phosphate, triethyl phosphate, tri-n-butyl phosphate, tris(2-ethyl hexyl) phosphate, tri-p-(n-propyl) phenyl phosphate, tri-p-(1,1,3,3-tetramethyl butyl) phenyl phosphite, tri-(p-allyl phenyl) phosphite, isopropyl di-(2,5-dimethyl phenyl) phosphite, triisopropyl phosphite, S,S,S,-tri(2,5-dimethyl phenyl) trithiophosphate, O,S,S-tricresyl dithiophosphate, O,O,O-tri(2-methyl-4-isopropyl phenyl) thionophosphate, S,S-di(2,6-xylenyl-O-(m-butyl) dithiophosphate, 0,2-ethylhexyl - S,S - dicresyl dithiophosphate, S-alpha-methylbenzyl-O,O-diisopropyl thionophosphate, O-alpha-methylbenzyl-O,S-diisopropyl thionophosphate, etc., or mixtures thereof. Particularly preferred are mixtures of the phenyl phosphates which includes mixtures of two or more phenyl phosphate compounds such as triphenyl phosphate, cresyl diphenyl phosphate, dicresyl phenyl phosphate, tricryesl phospate, xylyl dicresyl phosphate, etc.

The base gasolines in which the antiknock compounds, scavengers, phosphorus compounds, and other additives are incorporated in accordance with the invention comprise high octane components including substantial concentrations of aromatic hydrocarbons, olefinic hydrocarbons, paraffins, naphthenes, or mixtures thereof, boiling in the gasoline range (i.e., from about 50° F. to about 450° F.). The base gasoline will normally contain at least 10% volume aromatics up to about 50% volume, but can contain as much as 80 or 90% volume. Similarly, olefins will often be present in amounts up to about 40% volume, usually about 5 to 30% volume. Usually the gasoline contains a total of about 20 to about 80 volume percent

of aromatics and olefins. The maximum amount of paraffins in the gasoline will be about 65% to 70% by volume, preferably less than 60% by volume. The gasoline compositions of the invention also contain in practice a minor amount of combined sulfur, generally from about 0.005% weight to about 0.2% weight sulfur, and more usually about 0.01% to about 0.1% weight sulfur.

The base gasoline is usually obtained by blending refinery streams such as straight-run gasoline and products in the gasoline boiling range from processes such as thermal cracking, catalytic cracking, hydrocracking, alkylation, isomerization, hydrogenation, polymerization, catalytic reforming, etc.

The gasoline composition of the invention contains a minor sufficiently effective antiknock amount of an organo-lead compound. This organo-lead antiknock agent is preferably a tetraalkyl lead compound. Tetraethyl lead is universally used as an antiknock agent, but other compounds such as tetramethyl lead, tetrabutyl lead, tetraamyl lead, tetrapropyl lead, etc., possess antiknock properties and can be used in the gasoline composition. The antiknock agent can also be physical and/or equilibrated mixtures of two or more organo-lead compounds.

The organo lead antiknock agent is present in concentrations of from about 0.1 cc. per gallon to about 4.5 cc. per gallon, preferably between about 0.5 cc. per gallon to about 3.0 cc. per gallon.

In the gasoline compositions of the invention, a halohydrocarbon scavenger such as ethylene dibromide or a mixture of ethylene dibromide and ethylene dichloride is suitably added in conjunction with the organo lead antiknock agent, especially in an amount of from about 0.2 to about 2.0 theories, particularly about 0.5 to about 1.5 theories, 1.0 theory being the amount necessary to provide two gram atoms of halogen per gram atom of lead in the lead antiknock agent present. However, special benefits are obtained in regard to corrosion, wear and/or octane requirement when the halohydrocarbon scavenger is excluded or limited to less than about 1.0 theory, for example 0.5 theory of bromine, e.g., as ethylene dibromide.

The fuel compositions of the invention can of course also contain anti-icant additives, anti-corrosion additives, anti-static additives, gum inhibitors, and the like.

In the compositions of the invention the ester and the phosphorus compound cooperate to provide improved engine cleanliness. The phosphorous compounds in question have boiling points which are relatively high compared with the average of the gasoline as a whole; moreover, their viscosities are relatively high and in fact some of them are commercially used as plasticizers, for example tricresyl phosphate. On the other hand, the substituted tertiary ester compounds of the invention are better solvents for gums and other resinous deposits encountered in internal combustion engines than are the conventional hydrocarbon components, especially the non-aromatic ones, of the gasoline. A possible explanation of this cooperative action can therefore be visualized as follows. When a gasoline engine operated with the present gasoline composition is started, the engine intake manifold is usually relatively cool and a substantial quantity of the ester compounds, even though they are relatively volatile, will appear in the liquid phase of gasoline on the walls of the intake manifolds. The phosphorous compound softens or plasticizes any existing deposits making it easier for the ester to penetrate the deposits and bring them into the liquid whereby they are carried through to the combustion chambers where they are burned. Subsequently-formed deposits which may occur during an extended operation of the engine at normal operating temperatures are then taken into solution during the next warm-up cycle of the engine.

An understanding of the benefits of the invention in regard to abnormal combustion noise requires further consideration of "rumble." Rumble appears to be a result of multiple flame fronts in the combustion chamber.

During each combustion cycle, there is normally a single flame front ignited by the spark plug in the internal combustion engine. Other flame fronts are known to be caused by the glowing of deposits. However, the kind of deposit is important, and I believe that sustained multiple flame fronts are uniquely related to the mechanical failure of certain lower layer deposits on combustion chamber surfaces.

The lower layer deposits are predominately mixtures of lead compounds in carbonaceous materials having a carbon to hydrogen ratio of about 1. These lower layer deposits have been cooled by the combustion chamber wall and insulated from the combustion flame by upper layer deposits. When structural failure of the deposit occurs, it usually occurs in the lower layer resulting in the lifting of the deposit from the combustion chamber wall.

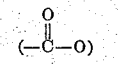
Lead oxides are either present initially or formed from the lead compounds in the lower deposits by means of a roasting process. As the lower layer peels away from the combustion chamber wall, the carbonaceous deposits are exposed to the hot combustion gases and the lead oxide acts as a catalyst for the combustion of the carbonaceous material. This causes the deposits to glow and burn while still attached to the combustion chamber wall. During subsequent combustion cycles, the compressed fuel/air mixture in the combustion chamber is ignited by these burning deposits and spurious flame fronts occur, producing rumble.

Phosphorus is of course known to supress the catalytic activity of lead salts by forming lead phosphate, a high melting non-catalytic material which is more powdery than lead oxides and which does not sinter into a cake. It has therefore been proposed to control rumble by adding larger than conventional amounts of phosphorus compounds to leaded gasoline for high compression ratio engines. But while increasing the amount of phosphorus in the gasoline will cut down on the frequency of rumble, the surface ignition potential can be greater due to the fact that the deposits are bulkier because of the presence of additional phosphorus, and being more porous can accumulate greater quantities of potentially flammable carbonaceous material. When these deposits do flake off, they can cause extremely early ignition of secondary flame fronts resulting in severe "bursts" of rumble. In addition, phosphorus is known to be lead antagonistic (i.e., capable of reducing the antiknock effectiveness of organo lead antiknock agents) in high concentrations. The bulkier deposits in the combustion chamber caused by the use of such expensive amounts of phosphorus, can also lead to higher octane number requirement increases.

It has now been found in accordance with the invention that when certain proportions of both the substituted tertiary esters and phosphorus compounds are added to leaded gasoline, rumble is effectively controlled at conventional and unharmful levels of phosphorus concentrations.

The unexpected cooperative effect between the substituted tertiary esters and the phosphorus compounds is probably because the esters enter into the overall chemical reactions sequence by which tetraethyl lead decomposes in the combustion chamber to form lead oxide, the ultimate antiknock species, in a way that results in a form of lead oxide which is more reactive with phosphorus compounds or their decomposition products or intermediates. This mechanism is consistent with the ability of certain of these esters to appreciate the effectiveness of organo lead compounds as antiknock agents. Moreover, it is consistent with the recent finding that the lead antagonism of very high concentrations of phosphorus compounds (e.g., 0.67 gram atom phosphorus per gram atom lead) is more pronounced in the presence of these substituted tertiary esters than in their absence.

Suitable concentrations of both esters and phosphorus compounds in the compositions of the invention depend upon the amount of organo lead antiknock agent present. The concentration of the esters should be such that the ratio of (a) the carbonyloxy gram equivalents



in the ester to (b) the gram atoms of lead in the organo lead antiknock agent present is from about 1:1 to about 50:1, and preferably from about 1.5:1 to about 25:1. Thus, in the case of an ester containing only one carbonyloxy equivalent per mol, such as 2-methyl-2-acetoxy-4-pentanone, the preferred concentration would be from about 1.5 to about 25 gram mols of the ester per gram atom of lead. On the other hand, in the case of an ester containing two carbonyloxy equivalents per mol, such as 2-methyl-2,4-diacetoxy pentane, the preferred concentration would be from about 0.75 to about 12.5 moles of the ester per gram atom of lead.

The concentration of the phosphorus compounds should be such that the ratio of the gram atoms of phosphorus to the gram atoms of lead is from about 0.03:1 to about 0.4:1, more preferably from about 0.07:1 to about 0.3:1.

The following are illustrative examples of compositions suitable for use according to the present invention:

Example I

Tetraethyl lead
Ethylene dibromide, 1.0 gram atom bromine per gram atom lead present
Ethylene dichloride, 2.0 gram atoms chlorine per gram atom lead present
2-methyl-2-acetoxy-4-pentanone, 25 gram mols per gram atom lead present
Tricresyl phosphate, 0.3 gram atom phosphorus per gram atom lead present

Example II

Tetraethyl lead
Ethylene dibromide, 1.0 gram atom bromine per gram atom lead present
Ethylene dichloride, 2.0 gram atoms chlorine per gram atom lead present
2,4-diacetoxy-2-methyl pentane, 12.5 gram mols per gram atom lead present
Cresyl diphenyl phosphate, 0.3 gram atom phosphorus per gram atom lead present

Example III

Tetramethyl lead
Ethylene dibromide, 2.0 gram atoms bromine per gram atom lead present
2,4-diformyloxy-2-methyl pentane, 25 gram mols per gram atom lead present
S,S,S-tri(2,5-dimethyl phenyl) trithiophosphate, 0.03 gram atom phosphorus per gram atom lead present

Example IV

Tetramethyl lead
Ethylene dibromide, 1.2 gram atoms bromine per gram atom lead present
Ethylene dichloride (2.0 gram atoms chlorine per gram atom lead present
2,4-dibutyryloxy-2-methyl pentane, 0.75 gram mol per gram atom lead present
S-alpha methyl benzyl-O,O-diisopropyl thionophosphate, 0.03 gram atom phosphorus per gram atom lead present

Example V

Tetramethyl lead
Ethylene dibromide, 1.0 gram atom bromine per gram atom lead present
Ethylene dichloride, 2.4 gram atoms chlorine per gram atom lead present
2-methyl-2-acetoxy - 4 - propionyloxyheptane, 0.75 gram mol per gram atom lead present
S,S,S-tricresyl trithiophosphate, 0.03 gram atom phosphorus per gram atom lead present

Example VI

Tetramethyl lead
Ethylene dibromide, 2.0 gram atoms bromine per gram atom lead present
2-methyl-2-acetoxy-4-heptanone, 1.0 gram mol per gram atom lead present
Octyl diphenyl phosphate, 0.03 gram atom phosphorus per gram atom lead present

Example VII

Tetraamyl lead
2-methyl-2-acetoxy-4-pentanone, 50 gram mols per gram atom lead present
Trimethyl phosphate, 0.4 gram atom phosphorus per gram atom lead present

Example VIII

Tetramethyl lead and tetraethyl lead present in mol ratio of 1:3
Ethylene dibromide, 1.0 gram atom bromine per gram atom lead present
Ethylene dichloride, 2.0 gram atoms chlorine per gram atom lead present
2,4-diacetoxy-2-methylhexane, 12.5 gram mols per gram atom lead present
Triisopropyl phosphite, 0.07 gram atom phosphorus per gram atom lead present

Example IX

Tetramethyl lead
Ethylene dibromide, 2.0 gram atoms bromine per gram atom lead present
2-methyl-2-acetoxy-4-pentanone, 1.5 gram mols per gram atom lead present
Dimethyl xylyl phosphate and dimethyl tolyl phosphate, 0.07 gram atom phosphorus per gram atom lead present

Example X

Tetramethyl lead
2-methyl-2-acetoxy-4-pentanone, 9 gram mols per gram atom lead present
Cresyl diphenyl phosphate, 0.07 gram atom phosphorus per gram atom lead present

Example XI

Tetraethyl lead
2,4-diacetoxy-2-methylpentane, 0.75 gram mol per gram atom lead present
Tricresyl phosphate, 0.07 gram atom phosphorus per gram atom lead present

Example XII

Motor gasoline:
- 3 cc. tetraethyl lead per gallon gasoline
- 0.01536 gram atom bromine as ethylene dibromide per gallon gasoline
- 0.192 gram mol 2-methyl-2-acetoxy-4-pentanone per gallon gasoline
- 0.0031 gram atom phosphorus as tricresyl phosphate per gallon gasoline

Example XIII

Motor gasoline having composition:
- 0.6 gallon aromatics
- 0.1 gallon olefins
- 0.3 gallon paraffins and naphthenes
- 1 cc. tetramethyl lead per gallon gasoline
- 0.0075 gram atom bromine as ethylene dibromide per gallon gasoline
- 0.0150 gram atom chlorine as ethylene dichloride per gallon gasoline
- 0.093 gram mol 2,4-diacetoxy-2-methyl pentane per gallon gasoline

- 0.003 gram atom phosphorus as cresyl diphenyl phosphate per gallon gasoline

Example XIV

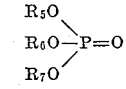
Full range motor gasoline:
- 1.5 cc. tetraethyl lead per gallon gasoline
- 1.03 cc. tetramethyl lead per gallon gasoline
- 0.031 gram atom bromine as ethylene dibromide per gallon gasoline
- 0.023 gram mol 2-methyl-2-acetoxy-4-pentanone per gallon gasoline
- 0.0015 gram atom phosphorus as a mixture of 10% v. triphenyl phosphate, 35% v. cresyl diphenyl phosphate, 37% v. dicresyl phenyl phosphate, 15% v. tricresyl phosphate and 3% v. xylyl dicresyl phosphate per gallon gasoline

Example XV

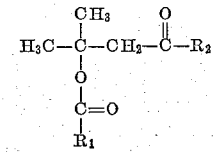
Gasoline having the following composition:
- 0.65 gallon catalytic reformate
- 0.20 gallon light catalytic cracked gasoline
- 0.05 gallon alkylate
- 0.05 gallon butane
- 0.05 gallon isopentane
- 2 cc. tetraethyl lead per gallon gasoline
- 0.127 gram mol 2-methyl-2-acetoxy-4-pentanone per gallon gasoline
- 0.002 gram atom phosphorus as cresyl diphenyl phosphate per gallon gasoline

I claim as my invention:

1. A fuel composition for internal combustion engines consisting essentially of gasoline, a minor sufficiently effective antiknock amount of a tetraalkyllead antiknock compound, a trihydrocarbon phosphate having the formula

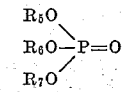


wherein R_5, R_6 and R_7 are hydrocarbyl groups having from 1 to 15 carbon atoms and a substituted tertiary ester containing carbon, hydrogen and oxygen and having the formula



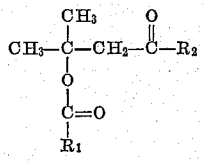
wherein R_1 is selected from the group consisting of hydrogen and low molecular weight alkyl radicals containing up to 4 carbon atoms and R_2 is a low molecular weight alkyl radical containing up to 4 carbons, said trihydrocarbon phosphate being present in an amount such that the gram atom ratio of phosphorus to lead in the antiknock compound present is from about 0.03:1 to about 0.4:1 and said ester being present in an amount such that the ratio of gram equivalents of carbonyloxy in the ester to gram atoms lead in the antiknock compound present is from about 1:1 to about 50:1.

2. A gasoline additive composition consisting essentially of a tetraalkyllead antiknock compound, a trihydrocarbon phosphate having the formula



wherein R_5, R_6 and R_7 are hydrocarbyl groups having from 1 to 15 carbon atoms, and a substituted tertiary ester

containing carbon, hydrogen and oxygen and having the formula



wherein R_1 is selected from the group consisting of hydrogen and low molecular weight alkyl radicals containing up to 4 carbon atoms and R_2 is a low molecular weight alkyl radical containing up to 4 carbon atoms, said trihydrocarbon phosphate being present in an amount such that the gram atom ratio of phosphorus to lead in the antiknock compound present is from about 0.03:1 to about 0.4:1 and said ester being present in an amount such that the ratio of gram equivalents of carbonyloxy in the ester to gram atoms lead in the antiknock compound present is from about 1:1 to about 50:1.

3. A fuel composition in accordance with claim **1** wherein at least one of R_5, R_6 and R_7 is an aryl radical.

4. A fuel composition in accordance with claim **3** wherein the gram atom ratio of phosphorus to lead in the antiknock compound present is from about 0.07:1 to about 0.3:1 and the ratio of the gram equivalents of carbonyloxy in the ester to gram atoms lead in the antiknock compound present is from about 1.5:1 to about 25:1.

5. A fuel composition in accordance with claim **1** wherein the organo-lead antiknock compound is tetraethyl lead.

6. A fuel composition in accordance with claim **1** wherein the organo-lead antiknock compound is tetramethyl lead.

7. A fuel composition in accordance with claim **3** wherein the phosphorus compound is tricresyl phosphate.

8. A fuel composition in accordance with claim **3** wherein the phosphorus compound is cresyl diphenyl phosphate.

9. A fuel composition in accordance with claim **1** wherein the substituted tertiary ester is 2-methyl-2-acetoxy-4-pentanone.

10. A gasoline additive composition in accordance with claim **2** wherein the phosphorus compound is a trihydrocarbyl phosphate at least one hydrocarbyl radical of which is an aryl radical.

11. A gasoline additive composition in accordance with claim **10** wherein the phosphorus compound is cresyl diphenyl phosphate.

12. A gasoline additive composition in accordance with claim **10** wherein the phosphorus compound is tricresyl phosphate.

13. A gasoline additive composition in accordance with claim **2** wherein the substituted tertiary ester compound is 2-methyl-2-acetoxy-4-pentanone.

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