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SURFACE IGNITION SUPPRESSION

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This invention relates to a hydrocarbon fuel for internal combustion engines and, more particularly, to an improved gasoline for use in spark ignition engines containing additives that improve the performance of the engine by reducing certain harmful effects due to engine deposits that form in the operation of modern high compression engines. This application is a division of Serial No. 624,507, filed November 27, 1956, and now abandoned.

The progressive increase in compression ratios in recent years has led to certain problems in engine operation. One difficult problem has been that of surface ignition with accompanying rough operation, which tends to occur particularly during rapid acceleration at sustained high power output and results primarily from premature ignition caused by incandescent deposits (mostly lead compounds and carbon) which form in the upper cylinder area are as unburned residues of the fuel.

Engine "knocking" may result from any of several causes. The knocking phenomenon known as "detonation" normally results when combustion chamber deposits have built up in the engine to such an extent that the engine octane requirement exceeds the octane rating of the gasoline used. Detonation can be reduced or eliminated by increasing the octane rating of the gasoline by any of many known methods.

The knocking caused by surface ignition is more difficult to remedy, because it results from abnormal combustion of the fuel in the combustion chamber, due to ignition of the fuel by incandescent surface deposits at a time prior to normal firing by the spark plug. Such abnormal firing of the charge by surface ignition usually results in a loss of power and rough operation of the engine.

It is an important object of this invention to provide an internal combustion engine fuel containing an additive material which, in relatively low concentration in the fuel, is effective to inhibit surface ignition.

Another important object of the invention is to provide a novel composition of matter with marked ability to suppress surface ignition, probably by increasing the temperature at which the surface deposits become incandescent.

Another object of the invention is to provide a novel fuel additive that suppresses pre-ignition of leaded gasoline.

A further important object is to provide a fuel containing both an anti-detonating agent in amount effective to inhibit detonation and another additive in amount sufficient to inhibit surface ignition.

The phenomenon of surface ignition in gasoline engines appears to be a result of the use of tetraethyllead as an anti-knock agent. Early in the experience with tetraethyllead as an anti-knock compound, it became apparent that some means had to be provided to prevent excessive deposition of lead compounds in the engine. It was then found that certain bromine and chlorine compounds (such as a mixture of ethylene dichloride and ethylene dibromide) were reasonably effective in reducing such deposits, by reacting with the lead to produce volatile lead compounds that were passed out through the exhaust, although these active chemicals had to be employed in

concentrations which would not cause engine damage. The resulting deposit control was acceptable as long as compression ratios remained relatively low. Recently, with compression ratios reaching values of 9 to 1 and 10 to 1 and still rising, the presence of lead halides and carbon in combustion chamber deposits has resulted in lowering the temperature at which the carbon deposits become incandescent, and these glowing deposits caused premature ignition of the next charge of fuel.

The use of these bromine and chlorine compounds is still important, and they are used in the leaded fuel of this invention because otherwise excessive deposits would be built up. The point is, however, that in modern high-compression automobile engines deposits of lead chloride and lead bromide are built up in the combustion chamber and they lower by several hundred degrees the temperature at which the carbon deposits become incandescent, so that incandescence occurs under normal engine operating conditions; when they become incandescent, surface ignition results.

Attempts have been made to remove these deposits by detergents added to the gasoline, but the results have not been very successful. Usually they reduce the deposits in one part of the engine, only to redeposit them elsewhere. Research continues to produce cleaner gasolines, and these help, but so far no leaded gasoline has been produced that does not produce substantial amounts of combustion-chamber deposits that soon lead to surface ignition conditions.

A more recent attack on the problem has been to include in the leaded gasoline an additive that chemically modifies the combustion-chamber deposits so as to reduce this harmful effect. Various organic and metallo-organic compounds have been tried with varying degrees of success, but heretofore none of them has solved the problem. They failed of complete success because none of them fulfilled all of the following important properties:

(1) Be chemically reactive with existing combustion chamber deposits to reduce their tendency to ignite the fuel.
(2) Be soluble in gasoline under all practical conditions.
(3) Have no adverse effect on gasoline stability.
(4) Have enough volatility to reach the combustion chamber.
(5) Produce no undesirable deposits.
(6) Cause no damage to engine parts.

Certain organic phosphorus compounds, such as tricresyl phosphate, have heretofore proved beneficial in controlling surface ignition, and these compounds have satisfactorily met conditions 1–4, by supplying phosphorus in a reactive form to combine with the lead. Lead phosphate apparently helps suppress surface ignition because it does not substantially lower the incandescence temperature of the carbon deposits. Tricresyl phosphate is particularly effective in this regard. However, all compounds, including tricresyl phosphate, heretofore shown to be effective surface ignition control agents, have failed to meet the fifth and sixth conditions; they have produced adverse deposits, especially in the induction system of automotive engines, and they have caused damage to parts of the engine. The deposits caused by these prior-art additives themselves have often interfered with the smooth operation of the intake valves, and their build-up on critical engine parts has eventually resulted in rough engine operation and power loss. Thus, the very additives designed to overcome one engine deposit problem have themselves, heretofore, been the source of another deposit problem.

Thus, another important object of the invention is to provide a modifier for combustion-chamber deposits, practicable for use in leaded gasolines, that not only reacts

with these deposits so as to reduce their tendency to cause surface ignition, but also does not itself lead to the production of substantial adverse deposits and does not tend to damage the engine.

Another object is to provide an additive for leaded gasolines that is a clean-operating surface-ignition suppressor.

Another object is to suppress the tendency of surface deposits to become incandescent and pre-ignite the fuel by a chemical that modifies the deposits and does not cause other adverse deposits.

Another object of the invention is to provide a high-octane leaded gasoline with reduced tendency toward building up deposits in the combustion chamber and with a reduced tendency of the deposits that do build up to cause surface ignition.

Another object is to provide a gasoline of the type described that obtains the beneficial results described without loss of power, anti-knock depreciation, change in stability, or increased fuel consumption.

Other objects and advantages of the invention will become apparent from the following description of some preferred embodiments thereof.

I have now found a class of organic phosphorus compounds that, in dilute admixture with gasoline, is outstanding both in its ability to suppress pre-ignition resulting from surface deposits and in its ability to pass through the intake system of an internal combustion engine without adding to the induction system deposits.

My preferred class of compounds has the apparently unique behavior of: (*a*) providing phosphorus in a reactive form for the desired chemical modification of combustion chamber deposits; (*b*) contributing no induction system deposits; and (*c*) not relocating induction system deposits from their normal locations.

THE COMPOUNDS OF THE INVENTION BROADLY

The compounds are phosphate esters of certain polypropylene glycol monoalkyl ethers. Specifically, the compound is tris(1-alkoxypolyoxypropylene glycol) phosphate, in which there are from three to six oxypropylene groups. Preferably, the alkoxy group has between 1 and 4 carbon atoms. Specific examples of the class are tris(1-methoxytripropylene glycol) phosphate and tris(1-butoxyhexapropylene glycyl) phosphate.

The class may also be defined by the following general formula:

$$[R(OC_3H_6)_nO]_3PO$$

in which

—OC_3H_6 represents the oxy 1,2 propylene unit, as in a polypropylene glycol;

n is a number lying between 3 and 6 and refers to a degree of polymerization;

R represents an end group which is preferably a small alkyl radical; and

PO refers to the phosphate radical of these orthophosphate esters.

THE POLYPROPYLENE GLYCOL GROUP (—OC_3H_6—)

Phosphate esters prepared from polypropylene glycol monoalkyl ethers have proven to be far superior in engine cleanliness to the corresponding esters of other oxyalkylene glycol ethers that have been tested, such as the phosphate esters of polyethylene glycol monoalkyl ethers. Later in the specification are the results of tests showing comparisons of some typical compounds.

THE DEGREE OF POLYMERIZATION (*n*)

The number (*n*) of oxy 1,2 propylene units in the polypropylene glycol monoalkyl ether has been found to be an important determinant in the engine cleanliness characteristics of the phosphate ester prepared therefrom. Very effective activity both in suppression of surface ignition and in engine cleanliness has been shown where *n* equals 3. A somewhat less effective but still good additive obtains when *n* equals 6, where engine cleanliness was substantially the same as the base gasoline. The ester corresponding to *n* equals 1 (as with propylene glycol monomethyl ether) gave a depreciated engine test and was considered unsuitable. It is believed that the range between *n* equals 3 and *n* equals 6 comprises the usable polymers. In commercial use *n* need not be an integer but may stand for the average degree of polymerization; however, the components should not include substantial amounts outside the indicated range.

THE END GROUP (R)

R may be an alkyl or phenyl (lower aryl) radical, but preferably R is a small alkyl radical with between 1 and 4 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl. The use of higher alkyl end groups tends to reduce the cleanliness of the ester in the engine, and such esters are less economical because they contain a smaller weight percent of phosphorus. Polar radicals produce compounds unsuited to this invention, and so do higher aryls.

THE PHOSPHATE RADICAL (PO)

The presence of the phosphate radical is essential in this invention. Compounds analogous to the best ones disclosed above, but where a phosphite radical has been substituted for the phosphate radical, proved deleterious to engine cleanliness and entirely unsuited to the objects of this invention. No other radicals are known that are comparable to the phosphate radical.

Preferred compounds of this invention are shown in Table 1.

Table 1.—Chemical composition of typical polypropylene glycol monoalkyl ether phosphates

Phosphate Ester	*n*	R	Percent P
1. Tris(1-methoxytripropylene glycol) phosphate	3	CH_3—	5.0
2. Tris(1-butoxyhexapropylene glycol) phosphate	6	C_4H_9—	2.3

METHOD OF PREPARING THE PHOSPHATE ESTERS

A preferred method of synthesis consists in reacting the appropriate polypropylene glycol monoether with phosphoryl chloride in the presence of a hydrogen chloride acceptor. The latter (normally, but not necessarily, pyridine) was added to prevent the undesirable side reaction of acid-catalyzed ether cleavage from lowering the otherwise high product yields.

EXAMPLE I.—PREPARATION OF TRIS(1-METHOXYTRIPROPYLENE GLYCOL) PHOSPHATE

Reagents	Wt., g.	Moles
Tripropylene glycol monomethyl ether	1,256	6.10
Phosphoryl chloride	153	1.85
Pyridine	460	5.82

The reaction was conducted in a 3-liter flask fitted with a sealed stirrer, reflux condenser, thermometer and dropping funnel. Reagents and apparatus were thoroughly dried before use. The phosphoryl chloride was added in about 3.5 hours to the stirred solution of glycol ether and pyridine. The exothermic reaction was maintained at 5–15° C. by external cooling. A copious quantity of salt-like pyridine hydrochloride was formed as a by-product to the main reaction. The use of pyridine or some other well known acid acceptor prevents an undesirable side reaction acid-catalyzed ether cleavage).

Stirring of the reaction mixture was continued, after the halide addition, for a period of 3 hours, as the temperature was raised to 80° C. by external heating. The

contents were cooled, and 750 ml. of pentane were added to dissolve the product, and 300 ml. of water were added to dissolve the by-product. The two layers were then separated, and the aqueous layer was set aside for pyridine recovery. The product layer was water-washed twice, dried over annydrous sodium sulfate, and filtered in the presence of diatomaceous earth to remove trace turbidity. The pentane solvent was removed by vacuum evaporation to yield 1213 grams of clear pale yellow liquid (99% of theoretical based on $POCl_3$). This phosphate ester is essentially insoluble in water but completely soluble in pentane, benzene or gasoline.

Analysis showed the empirical formula $C_{30}H_{63}O_{16}P$. This compound had a refractive index of n_D^{20} 1.4419, a density of d_4^{20} 1.039, an acid No. (ASTM–D974–55T) of 4.2, a saponification No. (ASTM–D94–55T) of 48.2, and showed 5.0% P (calculated 4.7%).

EXAMPLE II.—PREPARATION OF TRIS(1-BUTOXYHEXAPROPYLENE GLYCOL) PHOSPHATE

Reagents	Wt., g.	Moles
Hexapropylene glycol monobutyl ether (Carbide & Carbon Chem. Co., UCON LB-70X)	455	1.05
Phosphoryl chloride	51	0.33
Pyridine	90	1.14

This reaction was conducted as in Example I, except that benzene (250 ml.) was also placed in the reaction flask with the glycol ether and pyridine, merely to facilitate stirring of the contents. Halide addition required only one hour at the reaction temperature of 5–10° C. Stirring was continued for several hours at room temperature and at 100°–110° C. for five hours. Product isolation was carried out as before except that pentane dilution was omitted since benzene was already present. The product was obtained as 394 grams (89% of theoretical) of an amber oil. This ester was also completely soluble in pentane, benzene and gasoline but insoluble in water.

Found for tris(1-butoxyhexapropylene glycol) phosphate Sap. No. 16, 2.3% P (calculated 2.3%), 0.30% Cl (calculated nil).

PRE-IGNITION SUPPRESSION

Performance tests have shown that the inclusion of the phosphate esters of the present invention in leaded gasoline produces substantial improvement both in suppressing pre-ignition and in engine cleanliness, as compared to the same fuel without the additive and to the same fuel containing a well-known phosphorus-containing additive (viz. tricresyl phosphate).

Pre-ignition suppression is, of course, not the sole criterion of success, since engine cleanliness is also very important. However, the best results appear to coincide. Preferably the leaded gasoline of this invention contains at least 1 theory of bromine and/or chlorine and between 0.15 theory and 0.6 theory of my phosphate ester. The term "theory" is used in this art to indicate the theoretical stoichiometric amount of the active ingredient (e.g., Br, Cl, or P) needed to react with the lead (Pb) content. In other words, 1 theory of tris(1-methoxytripropylene glycol) phosphate is enough of the compound to supply the stoichiometric amount of phosphorus for complete combination with the lead content of the fuel. Since the effectiveness of the phosphate ester as a pre-ignition suppressor depends directly on the amount of the lead in the gasoline, a quantitative formula is best expressed in "theories." If all the lead combined with the phosphorus and all the phosphorus combined with the lead, $Pb_3(PO_4)_2$ would be the sole resultant compound. Actually, such a reaction is neither feasible nor desirable. Usually, ethylene dibromide and ethylene dichloride are present in an amount totaling about 1.5 to 1.8 theory, since much of them pass through the engine unreacted. A typical product uses 1.0 theory of chlorine in ethylene dichloride and 0.6 theory of bromine in ethylene dibromide. Even so, an additional amount of phosphate ester lying in the range of 0.15 to 0.6 theory is necessary to suppress surface ignition. The excess over the stoichiometric amount of the three elements, Br, Cl, and P, is present because conditions inside the engine are not ideal for a stoichiometric reaction of the lead.

The gasoline employed in these tests discussed hereinafter for purposes of illustration was composed of (1) about 45% catalytic reformate having a boiling range of about 180°–310° F., (2) about 35% light cracked (catalytic) naphtha having a boiling range of about 100°–300° F., (3) about 8% light straight-run naphtha having a boiling range of about 95°–250° F., (4) about 7% natural gasoline having a boiling range of about 85°–350° F., and (5) about 5% medium cracked (catalytic) naphtha having a boiling range of about 250°–400° F. This blend contained as additives about 2.10 ml. per gallon of tetraethyllead (including ethylene dibromide and ethylene dichloride, as described below) and an amine inhibitor in normal amounts. The gasoline blend had a Motor Octane No. of 8 and a Research Octane No. of 97. Gum was present at about 2–3 mg. per 100 ml. in the ASTM test and at about 13–26 mg. per 100 ml. in the copper dish test. The gasoline had the following volatility specifications (Engler distillation): 10% evaporated at 135°–142° F., 50% at 218°–222° F., and 90% at 322° F. The approximate composition of the gasoline was:

	Percent
Paraffins and naphthenes, about	48
Olefins, about	24
Aromatics, about	28
Sulfur, about	0.06
Nitrogen, about	0.001

To the gasoline were added separate samples of the two phosphate esters given above as examples of this invention. The results were compared both with the same gasoline without these additives and with the same gasoline without these additives but containing tricresyl phosphate.

As blended into the gasoline the additives contained 1.5% by weight each of an antioxidant (phenylalphanaphthylamine) and an acid acceptor (nonylamine), the former to assure against possible oxidation in storage and blending operations and the latter to neutralize any trace acidity present.

EXAMPLE III.—SURFACE IGNITION OF GASOLINE WITHOUT ADDITIVES

The fuel blend described above was used to operate a test engine esepecially adapted for detecting surface ignition. This engine is a CFR L-head engine fitted with a conventional spark plug which acts as an ionization gap and is electrically connected during the test runs to an Ethyl Corporation type deposit ignition counter. The counter is connected and operated in such a manner as to count all explosions occurring within the cylinder except those which happen as a result of the firing of the ignition spark plug. Such explosions are detected by the deposit ignition counter as a result of current flowing across the gap in the modified spark plug through ionized gases, caused by the surface-ignition firing of the combustion charge. With this equipment, the number of surface ignitions per unit time can be accurately measured during operation of the engine.

The above-described single cylinder engine had a compression ratio of 8.5 to 1 with a spark setting at top dead center of the piston travel. During each test run the engine was operated on the test fuel for a period of 50 hours under cycling conditions while maintaining the temperature of the water cooling jacket and the intake air each at 150° F. The crankcase lubricant employed was a refined non-additive Pennsylvania oil of 495 SUS viscosity at 100° F.

In order to aproach normal driving conditions for automobile engines the test engine was operated throughout each run under idling conditions (750 r.p.m.) for 50 seconds and high duty conditions (4.9 horsepower at 1150 r.p.m.) for 150 seconds. The air-to-fuel ratio was adjusted to 11 to 1 during the idle cycle and 13 to 1 during the full load cycle. The low duty cycle permitted the engine to build up deposits in order to encourage surface ignition during the subsequent high duty cycle, the latter being under high power output conditions at which the engine containing such deposits would be more likely to exhibit surface ignition.

In conductance of the engine tests referred to herein, deposits were removed from the combustion chamber of the test engine before commencing each run in order that all runs were started under similarly clean engine conditions.

The above-described engine was operated in a 50 hour test under the above stated conditions, using the commercial leaded gasoline described earlier. The average number of surface ignition counts per hour indicated by the deposit ignition counter was 400 (the spread of five runs was 340–430). This run constituted a standardization run for the base gasoline containing no phosphorus additives.

EXAMPLE IV

There was dissolved into the above-specified base gasoline (the same as that used in Example III) 2.5 g./gal. of tris(1-methoxytripropylene glycol) phosphate. This amount was equivalent to 0.5 theory based on the lead content.

The test engine was operated for 50 hours with this fuel under the conditions set forth above. The average number of surface ignitions registering on the counter during this run was 90 counts per hour.

EXAMPLE V

There was dissolved into the base gasoline of Example III, 1.4 g./gal. of tricresyl phosphate, an amount equivalent to 0.5 theory based on the lead content of the gasoline.

The test engine was again operated for 50 hours with the fuel under the conditions set forth above. The average number of surface ignition counts was 90 counts per hour.

EXAMPLE VI

Similar tests were made with smaller amounts of these additives with the following results:

Additive	Theories of P	Counts Per Hour
Tris(1-methoxytripropylene glycol) phosphate	0.165	320
Tricresyl phosphate	0.165	240

The above tests show that, while smaller amounts of tris(1-methoxytripropylene glycol) phosphate are somewhat less effective than tricresyl phosphate, larger amounts are just as effective. Moreover, as later will be shown, my phosphate is clean acting in the engine, instead of dirty like the tricresyl phosphate.

EXAMPLE VII

There was dissolved into the above-specified base gasoline of Example III, 4.5 grams per gallon of tris(1-butoxyhexapropylene glycol) phosphate, equivalent to 0.44 theory based on the lead content of the gasoline.

The test engine was operated for 75 hours with this fuel under the conditions set forth above. The average number of surface ignitions registering on the counter during this run was 100 counts per hour.

The base fuel surface ignition counts were checked before and after the additive tests were completed.

Thus, the phosphorus esters of this invention have been shown to perform effectively as pre-ignition control compounds under conditions where pre-ignition can occur.

ENGINE CLEANLINESS

Moreover, the phosphorus esters of this invention have been shown to impart a desirable effect on engine cleanliness, said effect being particularly evident in the induction system of an automotive engine. This beneficial effect has not been observed with other phosphorus-containing additives. This finding is even more surprising in view of the fact that compounds closely related to those of this invention (even homologs only a few carbon atoms different) have failed to display this beneficial effect.

EXAMPLE VIII

Laboratory tests have shown that the present invention can produce improvement in engine cleanliness, as compared to the same fuel not containing the additive. The test procedure is a modified Coordinating Research Council Designation FL–2 procedure which has proven to correlate with field performance. In this test a 216.5 cubic-inch, six-cylinder Chevrolet engine is run continuously for forty hours at a speed of 1900 r.p.m. (plus or minus 25 r.p.m.) under an engline load of 36 B.H.P. (plus or minus 1 B.P.H.). The jacket inlet coolant temperature is kept at 155° F. minimum, the jacket outlet coolant temperature is kept within two degrees of 190° F. The air-fuel ratio is 14.5 (plus or minus 0.5 to 1) to 1. The spark advance is 35° (plus or minus 3°). The spark plug gap, ignition cam angle, valve clearance, exhaust back pressure and other similar conditions are also maintained at predetermined values. Before the test the engine is disassembled and cleaned, and a new set of piston rings is installed. The engine is given a standard two-hour break-in before the actual test is begun. Again, the crankcase lubricant employed was the refined non-additive Pennsylvania oil of 495 SUS viscosity at 100° F., used in Example III.

After the test run of 40 hours, the engine is dismantled and inspected, and is rated on ten items, as follows:

(1) Piston skirt varnish rating.
(2) Cylinder wall varnish rating.
(3) Intake valve stem deposit rating.
(4) Intake valve tulip deposit rating.
(5) Intake port deposit rating.
(6) Overall engine sludge rating.
(7) Overall engine varnish rating.

On each of these first seven items, the rating runs between 0 for dirty to 10 for clean.

(8) Corrosion or rust rating (10 for none, 9 for light, 8 for medium, and 7 for heavy corrosion).

(9) Stuck ring rating (10 minus 0.5 demerit for each 99° ring stuck in the groove).

(10) Tight ring rating (10 minus 0.5 demerit for each tight ring).

A perfectly clean engine will thus rate 100. A total rating of 85 is considered acceptable if the piston skirt varnish is 7.5 or better.

Table 2 shows the results of such tests where 0.75 cc./gal. of the phosphate esters of this invention are used, in comparison both with the same gasoline (that of Example III) without these additives and the same gasoline without these additives but containing other phosphorus additives.

Table 2.—Comparison of pre-ignition control compounds based on engine test ratings

Additive	Test Result
None (control gasoline)	87.5
Tris(1-methoxytripropylene glycol) phosphate	89.0
Tris(1-butoxyhexapropylene glycol) phosphate	86.0
Tricresyl phosphate	82.0
Tris(butylcarbityl) phosphate (described in U.S. Patent 2,723,237)	80.5
Tris(1-methoxytripropylene glycol) phosphite	81.5
Tris(1-methoxymonopropylene glycol) phosphate	83.5

From the above table it will be seen that tris(1-methoxytripropylene glycol) phosphate improved engine cleanliness, as compared with the control gasoline, as well as suppressing surface ignition. The related compound tris(1-butoxyhexapropylene glycol) phosphate not only suppressed surface ignition but left the engine almost as clean as the control gasoline.

In contrast, tricresyl phosphate left the engine much dirtier, and so did three other phosphorus compounds which might appear to be so similar to the compounds of this invention that no substantial difference in behavior would normally be expected. Thus, the same compound as the preferred one of this invention except for the substitution of the phosphite radical for the phosphate radical, was very dirty and shows the criticality of the phosphate radical. Similarly, the compound identical to the preferred one of this invention except that it has only one oxypropylene group instead of three to six groups, was also a failure.

Table 3 shows a breakdown of some of the items in the same test as Table 2.

Table 3

	Piston Varnish	Intake Valve Stems	Intake Valve Tulips	Intake Valve Ports	Overall Varnish
None (control gasoline)	8.0	9.0	9.5	9.0	8.0
Tris(1-methoxytripropylene glycol) phosphate	8.0	9.0	9.0	9.5	9.0
Tris(1-butoxyhexapropylene glycol) phosphate	8.0	9.0	9.5	10.0	9.0
Tricresyl phosphate	7.5	8.0	8.5	9.0	8.0
Tris(1-methoxytripropylene glycol) phosphite	8.0	8.5	7.5	8.5	7.5
Tris(butylcarbityl) phosphate	8.0	7.0	5.0	7.0	8.5
Tris(1-methoxymonopropylene glycol) phosphate	7.5	8.5	9.0	8.5	8.0

It is also significant that in the above test, no substantial change in power output of the engine was noted with the gasoline containing the phosphate esters of this invention, whereas the power output dropped noticeably with some of the other samples.

The fuel incorporating the additives of this invention showed no anti-knock depreciation, as measured by the research method, ASTM–D–908–47T. Nor did it show a change in stability as measured by the U.O.P. (Universal Oil Products) induction test. Nor was any increase in fuel consumption noted.

EXAMPLE IX

Tests like those in Example VIII were performed under the same conditions and procedure, but with a different gasoline. The gasoline employed in these tests was composed of (1) about 38% catalytic reformate having a boiling range of about 180°–310° F., (2) about 40% light cracked (catalytic) naphtha having a boiling range of about 100°–300° F., (3) about 10% light straight-run naphtha having a boiling range of about 95°–250° F., (4) about 6% medium cracked (catalytic) naphtha having a boiling range of about 250°–400° F., and (5) about 6% hydrogenated heavy cracked (catalytic) naphtha having a boiling range of about 250–400° F. This blend contained as additives about 2.72 ml. per gallon of tetraethyllead (including ethylene dibromide and ethylene dichloride, as described above) and an amine inhibitor in normal amounts. The gasoline blend had a Research Octane No. of 97. Gum was present at about 2 mg. per 100 ml. in the ASTM test and at about 13 mg. per 100 ml. in the copper dish test. The gasoline had the following volatility specifications (Engler distillation): 10% evaporated at 129° F., 50% at 218° F., and 90% at 332° F.

Table 4 shows the results of the tests of Example IX, where the control gasoline above and the same gasoline with 2.67 grams per gallon of tris(1-methoxytripropylene glycol) phosphate were tested in different runs. The 2.67 grams of additive corresponds to 0.4 theory band on the lead content of the control gasoline.

Table 4

Additive	Piston Varnish	Intake Valve Stems	Intake Valve Tulips	Intake Valve Ports	Overall Varnish
None (control gasoline)	8.5	9.5	9.0	9.5	8.5
Tris(1-methoxytripropylene glycol) phosphate	8.0	9.5	9.5	9.5	8.5

EXAMPLE X

A road test was also made using a high quality leaded gasoline containing 0.15 theory of phosphorus, added as tris(1-methoxytripropylene glycol) phosphate. For this test a 1956 Pontiac was run 4817 road test miles. No knocking was observed, and inspection at the end of the test indicated a reduction in the amount of combustion chamber deposits, as compared with the same gasoline without additive, and in a previous run. A minimum of deposit was formed on the valves and in the intake ports. The intake manifold and carburetor were clean. The overall appearance of the test parts was good.

The combustion chamber deposits were weighed. The reference run showed deposits of 32.9 grams and the run with the fuel containing the new additive showed deposits of 27.9 grams.

The octane requirement increase for this test was 3.5 road octane numbers, as compared with an octane requirement increase of 4.0 for the reference run (which appears to have been done under conditions less likely to build up surface ignition deposits).

The phosphate esters of this invention, being freely miscible with gasoline, may be added and mixed in any manner desired, either directly or from a concentrate, usually of the ester dissolved in gasoline in any convenient concentration. The ester or its concentrate may or may not contain other desirable materials, such as anti-oxidants or stabilizers of known type.

I claim:

1. A gasoline fuel for internal combustion engines containing tetraethyllead in anti-knock amounts, halide scavengers in normal amounts in excess of 1.0 theory, and between 0.15 and 0.6 theory of a compound having the formula

$$[R(OC_3H_6)_nO]_3PO$$

wherein n is an integer of 3 to 6, inclusive, and R is a lower alkyl radical.

2. The fuel of claim 1 wherein the phosphate is tris (1-methoxytripropylene glycol) phosphate.

3. The fuel of claim 1 wherein the phosphate is tris (1-butoxyhexapropylene glycol) phosphate.

4. A leaded gasoline containing effective amounts of an additive for suppressing surface ignition, characterized by cleanliness in the engine, said additive consisting essentially of tris(1-alkoxypolyoxypropylene glycol) phosphate, each individual glycol group having between three and six oxypropylene groups, the alkyl group being a lower alkyl radical.

5. A leaded gasoline containing effective amounts of an additive for suppressing surface ignition, said additive

consisting essentially of tris (1-methoxytripropylene glycol) phosphate.

6. A gasoline fuel for internal combustion engines, comprising a major portion of gasoline, tetraethyllead in antiknock amounts, halide scavengers in normal amounts in excess of 1.0 theory, and tris(1-alkoxypolyoxypropylene glycol) phosphate having a lower alkyl radical and each glycol group having from three to six oxypropylene groups, in an amount between 0.15 and 0.6 theory.

7. A method of suppressing the tendency of surface deposits in the combustion chambers of internal combustion engines to become incandescent and pre-ignite leaded gasoline while also aiding in maintaining engine cleanliness comprising adding to the leaded gasoline between 0.15 and 0.6 theory of a compound having the formula

$$[R(OC_3H_6)_nO]_3PO$$

wherein n is an integer of 3 to 6, inclusive, and R is a lower alkyl radical.

8. The method of claim 7 wherein the compound is tris (1-methoxytripropylene glycol) phosphate.

9. The method of claim 7 wherein the compound is tris (1-butoxyhexapropylene glycol) phosphate.

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