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2,984,551

PHOSPHINE-ALDEHYDE DERIVATIVES AS GASOLINE ADDITIVES

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8 Claims. (Cl. 44-63)

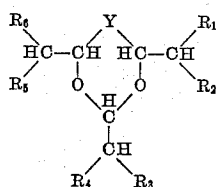
The present invention relates to improvements in motor fuels, specifically gasoline-type fuels containing tetraethyl lead.

It is common practice to add to motor fuels a composition generally known as "ethyl fluid" consisting principally of tetraethyl lead and a small amount of an alkyl halide, such as ethylenedibromide, ethylenedichloride, or the like, in order to increase the anti-knock value of the motor fuel. Most of the gasoline now being sold contains some of this fluid, the amount varying generally from about 1 cubic centimeter to 3 cubic centimeters per gallon of gasoline. Fuel for special purposes, such as for use as aviation gasoline, may contain even more.

While the addition of tetraethyl lead is highly beneficial, the use of such an additive generally involves concomitant difficulties. For example, the presence of tetraethyl lead in gasoline used in modern high-compression engines not too infrequently causes misfiring and rough running of engines due to pre-ignition. Surface ignition, as it is also known and as the name implies, is the tendency for gasoline containing lead to ignite independently of the spark plug as a result of surface hot spots or glow points in the combustion chamber. This has the effect of disrupting the ignition timing of the engine and, as would be expected, causes rough running, knock and buildup of extreme pressures and temperatures in the combustion chamber.

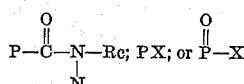
According to the present invention, however, it has been found that by the addition of a small amount of a 2,4,6-trisecundary-alkyl-1,3-dioxo-5-phosphacyclohexane of the type contemplated herein to motor fuels, such as gasoline, containing tetraethyl lead, pre-ignition is suppressed to a significant degree and the advantages accompanying such suppression are realized.

The additives contemplated herein correspond to the formula

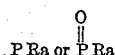


wherein R_1 to R_6 represent alkyl chains of 1 to 10 carbon atoms and, as will be seen hereinafter, R_1 , R_2 , R_3 , R_4 , R_5 and R_6 may be the same or different radicals;

Y represents PH ; PRa ; $\text{P}-\text{Ra}$; $\text{P}-\text{OH}$; $\text{P}-\text{ORb}$; $\text{P}-\text{OM}$



When Y is



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the Ra group represents substituted and unsubstituted, saturated and unsaturated, branched and straight chain aliphatic hydrocarbon radicals; substituted and unsubstituted aryl radicals; saturated and unsaturated, substituted and unsubstituted alicyclic radicals; said substituted radicals carrying substituents including halogen, carbamyl, cyano, amino, hydroxyl, acyloxy, carbalkoxy, carboxy, alkoxy, aryl, aryloxy, and the like.

When Y is



the ester derivative of



Rb represents a hydrocarbon radical including methyl, ethyl, propyl, octyl, phenyl, and the like. By the same token, when Y is

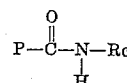


the salt derivative of



M represents mono- and polyvalent metals, including the alkali metals (Na, K, and the like), the alkaline earth metals Ba, Ca, and the like), zinc, mercury, and the like.

When Y is



the alkyl carbamyl and arylcarbamyl derivatives of the compounds contemplated herein are intended, Rc including phenyl, chlorophenyl, ethyl, butyl, chloroethyl, and the like.

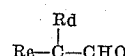
When Y is PX, a radical representing the halogenated phosphacyclohexanes of the instant discovery is intended, in which X includes Cl, Br, and the like. Similarly, other halogenated derivatives of the present invention are contemplated when Y is



X including Cl, Br, and the like.

The amount of additive employed in gasoline according to the instant discovery is generally from 5 to 200 percent by weight of the theoretical amount required and calculated to convert all of the lead in the gasoline to lead phosphate $\text{Pb}_3(\text{PO}_4)_2$. Preferably, from 10 to 50 percent of the theoretical amount is employed.

The suppressors or additives contemplated herein may be prepared by reacting an alkylaldehyde having an alkyl branch in the alpha position, such as isobutyraldehyde, and corresponding to the formula



in which Rd and Re represents alkyl chains of 1 to 10 carbon atoms, with phosphine in the presence of an aqueous mineral acid solution to produce the corresponding 2,4,6-trisecundaryalkyl-1,3-dioxo-5-phosphacyclohexane, such as 2,4,6-trisopropyl-1,3-dioxo-5-phosphacyclohexane. If desired, a water-soluble, inert organic solvent may be present, such as tetrahydrofuran, dioxane, a lower aliphatic monohydric alcohol, the dimethyl ether of ethylene glycol, and the like.

The additive compounds contemplated herein are described and claimed in copending application of Sheldon

A. Buckler, U.S. Serial No. 766,656 filed October 13, 1958, which is hereby incorporated by reference.

As will be seen in greater detail hereinafter, the 2,4,6-trisecundaryalkyl - 1,3 - dioxo - 5 - phosphacyclohexanes thus produced may be converted to their corresponding acids (POOH) by oxidation with air, for example. These acids may then be reacted to produce their respective esters and salts. For example, 2,4,6-triisopropyl-1,3-dioxo-5-phosphacyclohexane-5-inoic acid produced by the oxidation of 2,4,6 - triisopropyl - 1,3-dioxo-5-phosphacyclohexane may be reacted with NaOH as contemplated herein to yield the corresponding sodium 2,4,6-triisopropyl - 1,3 - dioxo - 5 - phosphacyclohexane-5-inate.

Likewise, the 2,4,6-trisecundaryalkyl-1,3-dioxo-5-phosphacyclohexanes may be reacted with para-chlorophenylisocyanate to produce the corresponding 5-(para-chlorophenylcarbonyl) - 2,4,6 - trisecundaryalkyl - 1,3-dioxo-5-phosphacyclohexanes.

Other typical additives within the purview of the present invention are prepared by reacting a 2,4,6-trisecundaryalkyl-1,3-dioxo-5-phosphacyclohexane with 1-octene or COCl_2 to produce, respectively, the corresponding 2,4,6-trisecundaryalkyl - 5 - octyl - 1,3-dioxo-5-phosphacyclohexane or 2,4,6 - trisecundaryalkyl-5-chloro-1,3-dioxo-5-phosphacyclohexane. In addition, 2,4,6 - trisecundaryalkyl-5-octyl-1,3-dioxo-5-phosphacyclohexane may be reacted with H_2O_2 to produce 2,4,6-trisecundaryalkyl-5-octyl-1,3-dioxo-5-phosphacyclohexane-5-oxide.

Similarly, a 2,4,6 - trisecundaryalkyl-1,3-dioxo-5-phosphacyclohexane-5-inoic acid may be reacted under the conditions contemplated herein with SOCl_2 to produce the corresponding 2,4,6 - trisecundaryalkyl-1,3-dioxo-5-phosphacyclohexane-5-inoyl chloride.

The aqueous mineral acid employed in the reaction of phosphine with an alkyl aldehyde as defined above doubles as catalyst and solvent. Among the mineral acids contemplated herein are HCl , HBr , HI , H_2SO_4 , H_3PO_4 , and the like. While concentrated mineral acids are preferred, concentrations in the range of 0.1 to 12 normal are suitable.

In general, the reactions contemplated herein are carried out at temperatures in the range of 0°C . to 80°C ., preferably 15°C . to 60°C .

Among the numerous alkyl aldehydes suitable for the preparation of the additives of the present invention, in addition to isobutyraldehyde, are 2-ethylhexaldehyde, 2-ethylbutyraldehyde, 2-methyloctaldehyde, 2-propylpentaldehyde, 2-methylheptaldehyde, and the like.

The amount of aldehyde employed in the reaction with respect to phosphine is, generally, at least 3 molar equivalents of aldehyde per molar equivalent of phosphine. However, excesses of either constituent as great as 10:1, aldehyde to phosphine, or phosphine to aldehyde, or even greater, are suitable.

The following examples illustrate several methods of preparing additives of the type contemplated herein:

EXAMPLE I

2,4,6-triisopropyl-1,3-dioxo-5-phosphacyclohexane

A one-liter, three-necked reactor flask was equipped with a gas inlet tube, an addition funnel, a mechanical stirrer and a gas bubbler device so disposed that all exit gases from the flask passed upwardly therethrough, the bubbler device comprising a column containing a two-inch head of water. The reactor flask was charged with a solution mixture at ambient temperature (21°C .- 23°C .) of 200 milliliters of a concentrated aqueous solution of hydrochloric acid containing 37.7 percent HCl by weight and 200 milliliters of tetrahydrofuran.

Subsequently the flask system and the charge were purged substantially free of oxygen-containing gas with nitrogen gas, and then a total of 108 grams (1.5 moles) of isobutyraldehyde and 17 grams (0.5 mole) of gaseous phosphine, at ambient temperature (21°C .- 23°C .), was

slowly and continuously introduced into the charge over a period of 30 minutes.

A reaction mixture resulted which, after settling for 30 minutes, left an upper organic layer or phase which was separated from the remaining reaction mixture and distilled under reduced pressure. A total of 91 grams (78 percent of theory) of product 2,4,6-triisopropyl-1,3-dioxo-5-phosphacyclohexane was thus collected as a colorless liquid having a boiling point of 100°C .- 101°C . at 8 millimeters pressure. The material had a pungent odor and a refractive index of $n_D^{25}=1.4602$.

Analysis.—Calculated for $\text{C}_{12}\text{H}_{25}\text{O}_2\text{P}$; C, 62.04; H, 10.85; P, 13.34. Found: C, 61.82; H, 10.78; P, 13.26.

EXAMPLE II

The procedure described in Example I was repeated with the exception that the tetrahydrofuran was omitted. The same product and yield (equivalent to 78 percent of theory) were obtained.

EXAMPLE III

2,4,6-tris(3-heptyl)-1,3-dioxo-5-phosphacyclohexane

The reactor flask in Example I was charged instead with a mixture of 125 milliliters of a concentrated aqueous solution of hydrochloric acid containing 37.7 percent HCl by weight and 125 milliliters of tetrahydrofuran, and a total of 66.5 grams (0.52 mole) of 2-ethylhexaldehyde and 6.2 grams (0.18 mole) of phosphine at ambient temperature (21°C .- 23°C .) was added uniformly with agitation in the course of 30 minutes. A reaction mixture resulted having an upper organic phase which was separated from the remaining reaction mixture and distilled under reduced pressure. A total of 61.1 grams (90 percent of theory) of 2,4,6-tris(3-heptyl)-1,3-dioxo-5-phosphacyclohexane as a colorless liquid product was recovered having a boiling point of 148°C . to 153°C . at 0.025 millimeter pressure and having a refractive index of $n_D^{24}=1.4709$.

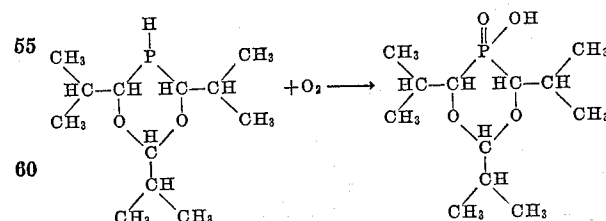
Analysis.—Calculated for $\text{C}_{24}\text{H}_{48}\text{O}_2\text{P}$; C, 71.95; H, 12.33; P, 7.73. Found: C, 71.87; H, 12.62; P, 7.57.

EXAMPLE IV

The procedure described in Example III was repeated except that the reactor was charged instead with 200 milliliters of a concentrated aqueous solution of hydrochloric acid containing 37.7 percent HCl by weight and no tetrahydrofuran was employed. A total of 59 grams (85 percent of theory) of the product was obtained.

EXAMPLE V

2,4,6-triisopropyl-1,3-dioxo-5-phosphacyclohexane-5-inoic acid



A solution of 30 grams (0.13 mole) of 2,4,6-triisopropyl-1,3-dioxo-5-phosphacyclohexane, produced as in Example I, above, in 125 milliliters of isopropyl alcohol was prepared and a stream of air passed into this solution at the rate of 75 milliliters per minute for 4 hours at ambient temperature (21°C .- 23°C .). The resulting solution was then concentrated to 100 milliliters and 25 milliliters of water was added thereto. A solid precipitated which was collected and dried to give 20.1 grams of product 2,4,6-triisopropyl-1,3-dioxo-5-phosphacyclohexane-5-inoic acid having a melting point of 158°C .- 160°C . Recrystallization from a water-isopropyl alcohol

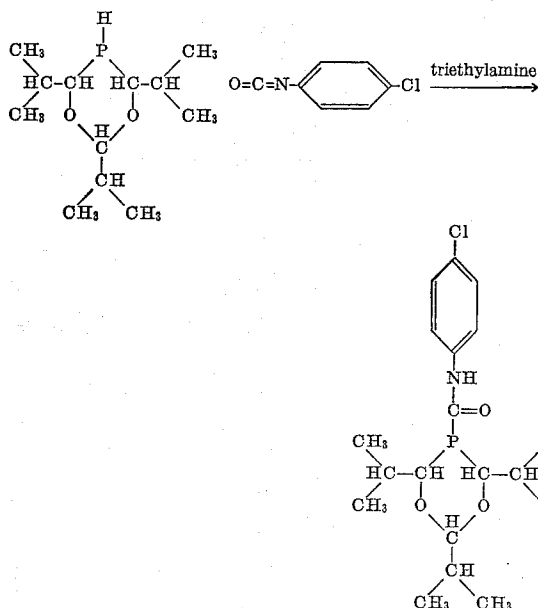
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mixture gave a product having a melting point of 159° C.-160° C.

Analysis.—Calculated for $C_{12}H_{25}O_4P$: C, 54.53; H, 9.53; P, 11.72. Found: C, 54.51; H, 9.44; P, 11.95.

EXAMPLE VI

5-(*para*-chlorophenylcarbonyl)-2,4,6-triisopropyl-1,3-dioxo-5-phosphacyclohexane

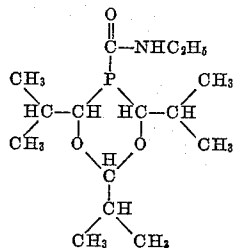


A solution of 11.6 grams (0.05 mole) of the product of Example I, above, and 7.67 grams (0.05 mole) of *p*-chlorophenyl-isocyanate in dry benzene was prepared and a small catalytic amount of triethylamine added thereto. The resulting mixture was then heated under reflux for 23 hours, cooled, evaporated and the resulting product recrystallized from methanol to give 8.6 grams of 5-(*p*-chlorophenylcarbonyl)-2,4,6-triisopropyl-1,3-dioxo-5-phosphacyclohexane having a melting point of 158° C.-160° C., a yield equivalent to 42 percent of theoretical. Recrystallization of the product from ethanol gave a melting point of 162° C.-162.5° C.

Analysis.—Calculated for $C_{19}H_{29}ClNO_5P$: C, 59.14; H, 7.58; P, 8.03. Found: C, 58.88; H, 7.89; P, 8.14.

EXAMPLE VII

5-ethylcarbonyl-2,4,6-triisopropyl-1,3-dioxo-5-phosphacyclohexane



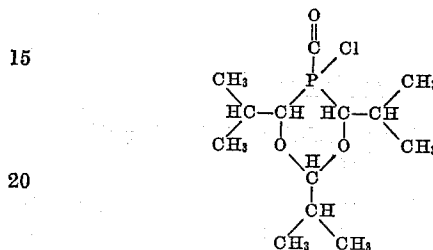
A solution of 11.6 grams (0.05 mole) of 2,4,6-triisopropyl-1,3-dioxo-5-phosphacyclohexane, produced as in Example I, above, 3.56 grams (0.05 mole) of ethyl isocyanate, and 0.1 gram of triethylamine in 20 milliliters of toluene is prepared and heated under reflux for 48 hours. The toluene and triethylamine are then removed by evaporation leaving the product 5-ethylcarbonyl-2,4,6-triisopropyl-1,3-dioxo-5-phosphacyclohexane as residual solid material.

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EXAMPLE VIII

2,4,6-triisopropyl-1,3-dioxo-5-phosphacyclohexane-5-inoyl chloride

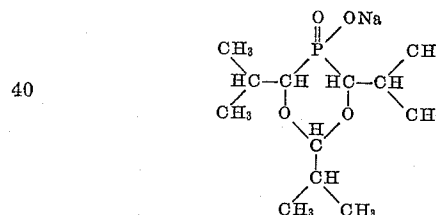
- 5 Thirteen and two-tenths grams (0.05 mole) of the phosphinoic acid produced as in Example V, above, is combined with 35 milliliters of thionyl chloride and heated under gentle reflux for 1 hour. The excess thionyl chloride is then removed by distillation, leaving the product 2,4,6-triisopropyl-1,3-dioxo-5-phosphacyclohexane-5-inoyl chloride as a residual oil and having the structural formula



EXAMPLE IX

25 Sodium 2,4,6-triisopropyl-1,3-dioxo-5-phosphacyclohexane-5-inate

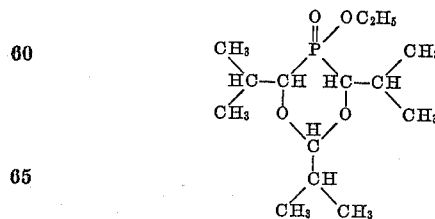
- Thirteen and two-tenths grams (0.05 mole) of the phosphinoic acid produced as in Example V, above, is suspended in 100 milliliters of water and a solution of 2.0 grams (0.05 mole) of sodium hydroxide in 10 milliliters of water is added. The mixture is stirred until all the acid is dissolved and the resulting solution is evaporated to give the product sodium 2,4,6-triisopropyl-1,3-dioxo-5-phosphacyclohexane-5-inate in solid form and having the structural formula



EXAMPLE X

Ethyl 2,4,6-triisopropyl-1,3-dioxo-5-phosphacyclohexane-5-inate

- 50 Fourteen and one-tenth grams (0.05 mole) of the phosphinoic acid, produced as in Example VIII, above, is added continuously during a period of 30 minutes and at ambient temperature (21° C. to 23° C.) to 50 milliliters of anhydrous ethyl alcohol. The resulting solution is refluxed gently for an additional 30 minutes and then evaporated to give the product as solid residual matter and having the structural formula



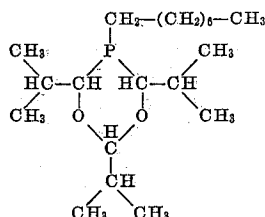
EXAMPLE XI

2,4,6-triisopropyl-5-octyl-1,3-dioxo-5-phosphacyclohexane

- 70 A solution of 23.2 grams (0.1 mole) of 2,4,6-triisopropyl-1,3-dioxo-5-phosphacyclohexane, produced as in Example I, above, 11.2 grams (0.1 mole) of 1-octene, and 1.64 grams (0.01 mole) of α,α' -azobisisobutyronitrile in 100 milliliters of benzene is prepared and heated at 85°

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C. for 1 hour. Distillation of the thus-heated reaction solution yields the product

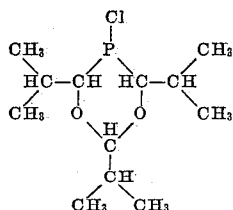


in liquid form.

EXAMPLE XII

2,4,6-triisopropyl-5-chloro-1,3-dioxo-5-phosphacyclohexane

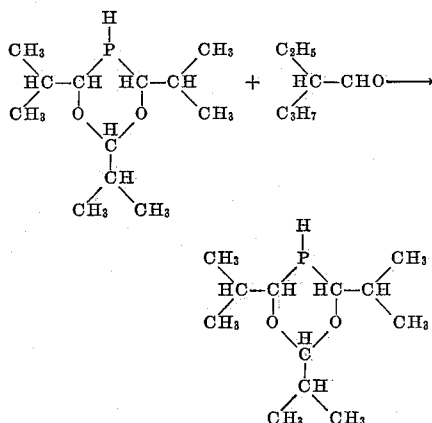
A solution of 11.6 grams (0.05 mole) of 2,4,6-triisopropyl-1,3-dioxo-5-phosphacyclohexane, produced as in Example I, above, in 50 milliliters of hexane is prepared and phosgene is passed into this solution at ambient temperature (21° C-23° C.) until no further reaction occurs. Distillation of the resulting reaction solution yields the product



in liquid form.

EXAMPLE XIII

2-(3-hexyl)-4,6-diisopropyl-1,3-dioxo-5-phosphacyclohexane

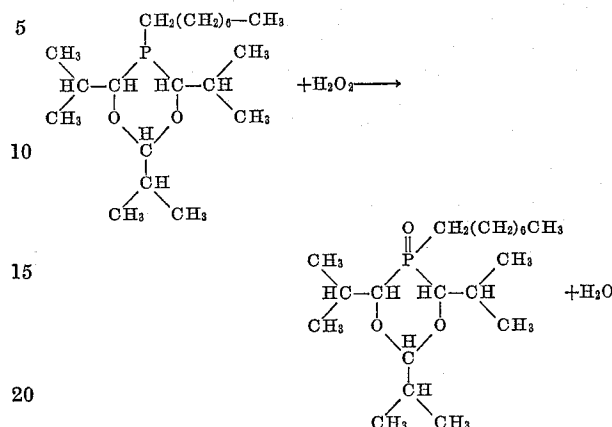


A solution of 11.6 grams (0.05 mole) of 2,4,6-triisopropyl-1,3-dioxo-5-phosphacyclohexane, produced as in Example I, above, 11.4 grams (0.1 mole) of 2-ethylpentanal and 1 milliliter of a concentrated aqueous solution of hydrochloric acid containing 37.7 percent HCl by weight is prepared and heated to boiling in an apparatus arranged for slow distillation. Isobutyraldehyde is thus formed and collected slowly over a period of 2 hours and the product desired 2-(3-hexyl)-4,6-diisopropyl-1,2-dioxo-5-phosphacyclohexane, is then recovered from the remaining solution in liquid form by fractional distillation at a reduced pressure.

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EXAMPLE XIV

2,4,6-triisopropyl-5-octyl-1,3-dioxo-5-phosphacyclohexane-5-oxide



A solution of 17.2 grams (0.05 mole) of 2,4,6-triisopropyl-5-octyl-1,3-dioxo-5-phosphacyclohexane (produced as in Example XI, above) in 50 milliliters of acetic acid is prepared and 1.7 grams (0.05 mole) of hydrogen peroxide is added. The solution is heated at 60° C. for 1 hour, and the product is then recovered as a residue by evaporation of the solution.

The products produced according to Examples I through XIV may be employed, as explained hereinabove, in lead-containing gasoline according to the following examples which, although detailed, are not to be considered as restricted to the details contained therein, since it will be obvious to one skilled in the art that numerous modifications within the purview of the invention are possible, and by the same token, are contemplated herein:

EXAMPLE XV

Products produced according to Examples I, V, and XI, above, are evaluated for their effectiveness in reducing pre-ignition in a modern high-compression engine.

A 1957 Oldsmobile V-8 engine is instrumented, according to known techniques, with electrical pressure pickups and electrical ionization gap pickups so that occurrences of abnormal ignition and pressure rise within the combustion chamber are relayed to and recorded on an electronic counter. Using a catalytically-cracked and reformed gasoline (98 octane) containing 3.0 cubic centimeters of tetraethyl lead per gallon, the engine is run for 100 hours on a cycle simulating 1.5 hours at 55 miles per hour, 2.5 hours at 30 miles per hour, and 6 hours of stop and go driving below about 30 miles per hour, i.e. 30 percent of the six hours is spent in idling, 30 percent in acceleration to 30 miles per hour, 30 percent in deceleration to idling speed, and 10 percent in running at about 30 miles per hour.

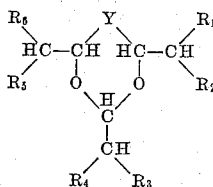
This 10-hour cycle is repeated 10 times for a total of 100 continuous hours and pre-ignition is measured and recorded twice, once upon completion of 50 hours of running and, secondly, at the end of 100 hours.

Three separate 100-hour runs are made. In the first run the product of Example I, above, is admixed with the lead-containing gasoline, in the second run the product of Example V, above, is added, and in the third run the product of Example XI, above, is added. These additives are present in their respective runs in the concentration corresponding to 20 percent by weight of the theoretical amount required to convert all of the lead in the gasoline to lead phosphate, $Pb_3(PO_4)_2$.

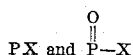
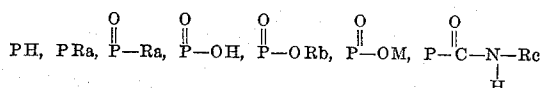
As compared to a standard, i.e., a run in which no additive of the type contemplated herein is present, the runs in which products of Examples I, V, and XI are present in the gasoline in the concentration just given manifest a substantial decrease in the percentage of firings during which pre-ignition occurs.

We claim:

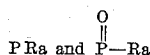
1. A motor fuel comprising predominantly gasoline, tetraethyl lead in a minor amount yet sufficient to impart anti-knock properties to said motor fuel, and from 5 to 200 percent by weight of the amount theoretically required to convert all of said tetraethyl lead in the gasoline to lead phosphate $Pb_3(PO_4)_2$ of an organophosphorus compound corresponding to the formula



wherein R_1 - R_6 represent alkyl chains of 1 to 10 carbon atoms; Y represents a radical selected from the group consisting of



P represents phosphorous;



represent derivatives of the above formula in which Ra is a member selected from the group consisting of alkyl having 1 to 8 carbon atoms and substituted alkyl having 1 to 8 carbon atoms, said substituents being selected from the group consisting of halogen, cyano, amino and hydroxyl;



represents the ester group derived from



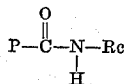
Rb being selected from the group consisting of alkyl having from 1 to 8 carbon atoms and phenyl;



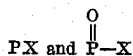
represents the salt group derived from



M being selected from the group consisting of alkali metal, alkaline earth metal, zinc and mercury;



represents the carbamyl derivatives of the compounds represented above by the general formula, Rc being selected from the group consisting of lower alkyl, phenyl, chloro-substituted lower alkyl and chloro-substituted phenyl;



represent moieties of the above general formula, X representing a halogen atom.

2. The gasoline fuel composition of claim 1 in which the organophosphorus compound is present in the amount corresponding to 10 to 50 percent by weight of the amount theoretically required to convert all of the lead in the gasoline to lead phosphate $Pb_3(PO_4)_2$.

3. A motor fuel comprising predominantly gasoline, tetraethyl lead in a minor amount yet sufficient to impart anti-knock properties to said motor fuel, and from 5 to 200 percent by weight of the amount theoretically required to convert all of said tetraethyl lead in the gasoline to lead phosphate $Pb_3(PO_4)_2$ of a 2,4,6-trisecundaryalkyl-1,3-dioxo-5-phosphacyclohexane in which the alkyl moiety contains from 1 to 10 carbon atoms.

4. A motor fuel comprising predominantly gasoline, tetraethyl lead in a minor amount yet sufficient to impart anti-knock properties to said motor fuel, and from 5 to 200 percent by weight of the amount theoretically required to convert all of said tetraethyl lead in the gasoline to lead phosphate $Pb_3(PO_4)_2$ of 2,4,6-trisopropyl-1,3-dioxo-5-phosphacyclohexane.

5. A motor fuel comprising predominantly gasoline, tetraethyl lead in a minor amount yet sufficient to impart anti-knock properties to said motor fuel, and from 5 to 200 percent by weight of the amount theoretically required to convert all of said tetraethyl lead in the gasoline to lead phosphate $Pb_3(PO_4)_2$ of a 2,4,6-trisecundaryalkyl-1,3-dioxo-5-phosphacyclohexane-5-inoic acid in which the alkyl moiety contains from 1 to 10 carbon atoms.

6. A motor fuel comprising predominantly gasoline, tetraethyl lead in a minor amount yet sufficient to impart anti-knock properties to said motor fuel, and from 5 to 200 percent by weight of the amount theoretically required to convert all of said tetraethyl lead in the gasoline to lead phosphate $Pb_3(PO_4)_2$ of 2,4,6-trisopropyl-1,3-dioxo-5-phosphacyclohexane-5-inoic acid.

7. A motor fuel comprising predominantly gasoline, tetraethyl lead in a minor amount yet sufficient to impart anti-knock properties to said motor fuel, and from 5 to 200 percent by weight of the amount theoretically required to convert all of said tetraethyl lead in the gasoline to lead phosphate $Pb_3(PO_4)_2$ of a 2,4,6-trisecundaryalkyl-5-octyl-1,3-dioxo-5-phosphacyclohexane in which the alkyl moiety contains from 1 to 10 carbon atoms.

8. A motor fuel comprising predominantly gasoline, tetraethyl lead in a minor amount yet sufficient to impart anti-knock properties to said motor fuel, and from 5 to 200 percent by weight of the amount theoretically required to convert all of said tetraethyl lead in the gasoline to lead phosphate $Pb_3(PO_4)_2$ of 2,4,6-trisopropyl-5-octyl-1,3-dioxo-5-phosphacyclohexane.

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OTHER REFERENCES

65	"Organo-phosphorus Compounds," page 15 (1950), by Kosolapoff, John Wiley and Sons, Inc.
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UNITED STATES PATENT OFFICE
CERTIFICATION OF CORRECTION

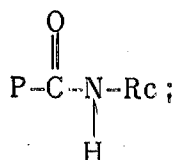
Patent No. 2,984,551

May 16, 1961

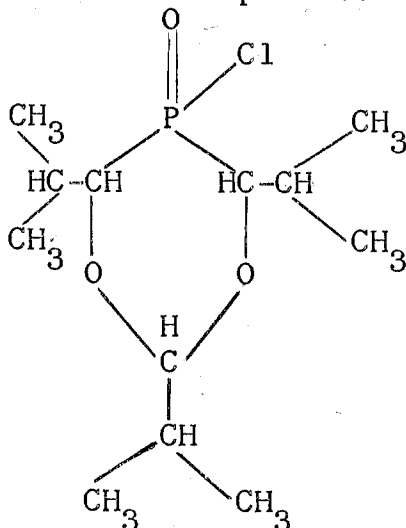
Clyde S. Scanley et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, lines 65 to 68, the left-hand portion of the formula should appear as shown below instead of as in the patent:



column 6, lines 13 to 23, the formula should appear as shown below instead of as in the patent:



column 7, line 72, for "-1,2-dioxa-" read -- -1,3-dioxa- --.

Signed and sealed this 31st day of October 1961.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

DAVID L. LADD

Commissioner of Patents