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O,O-DIESTERS OF AMINO PHOSPHONIC ACIDS

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2 Claims. (Cl. 260—944)

This is a division of application Ser. No. 161,294, filed December 21, 1961, now abandoned.

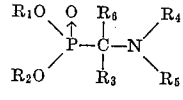
This invention relates to motor fuels characterized by their ability to suppress surface ignition in the operation of internal combustion engines. More particularly, the invention provides an improved motor fuel which is effective in suppressing surface ignition or "preignition."

Current emphasis on high compression ratios and other high-performance design features in gasoline engines of the internal combustion type has created a situation where random knock from surface ignition, often referred to as "preignition," has become a limiting factor in engine design and operation. Knock induced by surface ignition appears to be a result of the use of organo-lead compounds, particularly tetraethyl lead, as the anti-knock agent in high octane number fuels. When leaded motor fuels are burned in internal combustion engines, deposits of carbonaceous material and lead salts are continuously formed on the combustion chamber walls. Apparently surface ignition, that is, the ignition of the fuel-air mixture either before or after passage of the spark, is caused by glowing of carbon in the deposits. It is generally believed that the presence of lead compounds in the deposits causes the carbon to glow at a significantly lower temperature than the glow point of carbon alone.

It is well known that the addition of certain organic compounds of phosphorus, such as tricresylphosphate, to leaded fuels results in reducing surface ignition. Unfortunately, phosphorus compounds vary widely in effectiveness, and those that are most effective often have the undesirable property of lowering the octane number of the fuel. With petroleum refiners spending millions of dollars annually to raise the octane numbers of premium motor fuels, any substantial decrease in octane number is, of course, intolerable.

In accordance with the invention, an additive for use with leaded motor fuels has now been discovered which is extremely effective in reducing surface ignition or "preignition," yet, when employed in proper quantities, does not substantially reduce the octane number of the fuel.

Specifically, a new class of additives for spark ignition internal combustion motor fuel has been discovered. This new class of additives are preignition suppressors possessing other advantages as additives. The new class of additives are O,O-diesters of substituted amino-phosphonic acid having the formula:



wherein R_1 and R_2 are alkyl, aralkyl, alkaryl or aryl hydrocarbon groups and any of R_3, R_4, R_5 and R_6 may be hydrogen but R_4 and R_5 may not be hydrogen at the same time. Otherwise R_3 and R_6 and R_4 and R_5 may be a variety of organic groups. It is preferred that when either R_3 or R_6 are not hydrogen that they be alkyl, cycloalkyl, aryl, aralkyl, alkaryl hydrocarbon groups and when either R_4 or R_5 are not hydrogen that they be alkyl, cycloalkyl, aryl, aralkyl or alkaryl in nature. The foregoing O,O-diesters can be prepared as O,O-diesters of phosphorous acid with (A) an aldehyde or ketone and (B) an amine containing at least one replaceable hydrogen on an amino group especially (1) a primary or secondary monoamine, (2) an α-alkyol or β-alkyol amine, (3) an alkylidene diamine, (4) an arylene diamine, (5) an N-disubstituted amino methyl ether, or (6) an aldimine or ketimine derived from a primary amine. The preparation of certain of these esters is described by E. K. Fields in "The Synthesis of Esters of Substituted Amino Phosphonic Acid," J.A.C.S., 74, 1528 (1952).

In the foregoing formula, the portion of the diester:



is the residue of the ketone or aldehyde reactant. Thus, R_3 and R_6 are both hydrogen when formaldehyde and an amino compound are employed as reactants with a diester of phosphorous acid. Either R_3 or R_6 is hydrogen when an aldehyde other than formaldehyde is a reactant with the amino compound and the diester of phosphorous acid. When neither R_3 or R_6 are hydrogen, the reactant is, of course, a ketone. It is desirable that R_3 and R_6 be hydrogen or C_1 to C_8 alkyl hydrocarbon groups. Preferably R_6 is hydrogen and R_3 is a C_1 to C_4 alkyl hydrocarbon group or R_3 and R_6 are each alkyl hydrocarbon groups whose total carbon atoms is from 2 to 5 carbon atoms as derived from acetone (both R_3 and R_6 are methyl), methyl ethyl ketone (R_6 is methyl and R_3 is ethyl), diethyl ketone (R_3 and R_6 are both ethyl groups), methyl propyl ketone (R_6 is methyl and R_3 is propyl), ethyl propyl ketone (R_6 is ethyl and R_3 is propyl), methyl isobutyl ketone (R_6 is methyl and R_3 is isobutyl) and the like.

The nature of the substituents on the nitrogen in the foregoing formula R_4 and R_5, may vary widely and they need only be chosen with respect to compatability (miscibility) with hydrocarbons boiling in the gasoline range. Thus, when either or both R_4 and R_5 are not hydrogen they need only be alkyl or aryl in nature as are the alkyl, cycloalkyl, alkaryl, aralkyl and aryl hydrocarbon groups, amino alkylidene, amino arylene, hydroxyalkyl, alkoxyalkyl, alkoxy aryl, chloroaryl, or together R_4 and R_5 with the nitrogen atom may be a part of a heterocyclic ring as derived, for example, from morpholine and piperidine among others.

Illustrative of the additives of this invention include the following O,O-diesters of aminophosphonic shown in Table I wherein the various R groups are identified.

TABLE I

R_1 and R_2	R_3	R_4	R_5	R_6
Methyl	H	Methyl	Methyl	H.
Ethyl	H	Ethyl	Ethyl	H.
Do	H	i-Propyl	i-Propyl	H.
Do	H	Butyl	Butyl	H.
Do	H	Cyclohexyl	Cyclohexyl	H.
Do	H	Octyl	Octyl	H.
Do	H	Oxybisethylene [a]		H.
Do	H	Pentamethylene [b]		H.
Do	H	Ethyl	Phenyl	H.
Do	H	H	Butyl	H.
Do	H	H	β-Phenylethyl	H.
Do	H	Ethyl	Ethyl	Methyl.
Do	H	do	do	Ethyl.
Do	H	do	do	Propyl.
Do	Me	do	do	Methyl.
Do	H	do	do	α-Furyl.
Do	H	do	do	Vinyl.
Do	H	Butyl	Butyl	Propyl.
Butyl	H	Ethyl	Ethyl	H.
2-ethylhexyl	H	do	do	H.
Ethyl	H	H	Methyl	Methyl.
Do	H	H	Ethyl	Do.
Do	Me	H	do	Do.
Do	H	H	Methyl	Propyl.
Do	H	H	Butyl	Do.
Do	H	H	Ethyl	Ethyl.
Butyl	H	H	Methyl	Propyl.
Ethyl	H	H	Phenyl	Phenyl.
Do	H	H	Ethyl	α-Furyl.
Do	H	H	p-Methoxyphenyl	Phenyl.
Do	H	H	Bis [c] ethylene	Do.
Do	H	H	1-diethyl amino-4-pentyl	Propyl.
Do	H	H	do	p-Methoxyphenyl.
Do	H	H	Methyl	o-Chlorophenyl.
Do	H	H	2,4,4-trimethyl-2-pentyl	H.

[a] From morpholine.
[b] From piperidene.
[c] From dibenzalethylenediamine.

The O,O-diesters of amino alkyl phosphonic acid additives illustrated by the formula hereinbefore appearing, preferably those whose R_3 and R_6 are alkyl hydrocarbon groups or R_6 is hydrogen and R_3 is an alkyl hydrocarbon group and whose amine residue



is miscible with leaded hydrocarbons motor fuels boiling in the gasoline range at least to the extent of providing a mole ratio of phosphorus to lead (MR P/Pb) in the range of from about 0.01 to 1.0, preferably in the range of from about 0.1 to 0.5. The foregoing MR P/Pb ranges have been found to be suitable are preferred respectively for suppressing preignition. The motor fuel additives of this invention also possess the advantage of not appreciably depressing the octane number of the leaded motor fuel, i.e., possess low antiknock degradation. Additional advantages of the additives of this invention is that they do not contribute to gum formation in the motor fuel as measured by the Existent Gum Test (ASTM–D–381–587), hereinafter referred to as the D–381 Gum Test, and the function of the additives as induction system detergents.

It has further been discovered, contrary to experience with most other organic compounds of phosphorus, that the inventive additives do not cause fuel induction system deposits nor do they contribute to sticking of engine intake and exhaust valves.

The motor fuel of the invention may contain tetraalkyl lead equivalent to a concentration of from about 0.5 cc. to about 6 cc. or more per gallon of the hydrocarbon motor fuel; the concentration of tetraalkyl lead, e.g., tetraethyl and/or tetramethyl lead, may be varied as is usual with the engine and its use.

The hydrocarbon component which constitutes the base of the fuel will preferably be gasoline, but may be any other combustible liquid of suitable volatility commonly employed as fuel for internal combustion spark ignition engines, including paraffinic, naphthenic and aromatic hydrocarbons, pure hydrocarbons such as isooctane, and mixtures of isooctane with other suitable liquid hydrocarbons. These fuels may be derived, in whole or in part, by distillation of crude oil, catalytic or thermal cracking of gas oils, alkylation of isoparaffins with olefins, polymerization of olefins, etc. The boiling point of such fuels should be in the range of about 100° F. to about 500° F. and preferably in the range of about 100° F. to about 400° F. Motor fuels may also contain antioxidants, stabilizers, anti-icing agents, halogen-type lead scavenging agents and/or other compounds which are commonly employed in leaded motor fuels.

There can also be provided, in accordance with the invention, an additive concentrate suitable for incorporation into leaded motor fuels which contains a substantial amount (1–100%) of the hereinbefore described additives, O,O-diesters of amino-alkyl phosphonic acid. Concentrations of said additives of 5 to 85 weight percent are preferred. The additive concentrate may also contain an inert solvent, such as a refined hydrocarbon oil, and also desirable amounts of tetraethyl lead (to provide an MR P/Pb in the range of 0.01 to 1.0), halo-hydrocarbon lead scavenging agents, dyes, detergents, rust inhibitors and the like.

The defined additives may be prepared by the techniques described in detail by Fields in the J.A.C.S. article hereinbefore cited. As hereinbefore stated, an O,O-diester of hydrogen phosphonic acid is reacted with an aldehyde or ketone and an amine. The O,O-diesters may be prepared by reacting an alcohol or a phenolic compound or an ether alcohol with phosphorous trichloride in the presence of air or by the action of boiling water on a trialkyl or triaryl phosphite. The preferred additives contain as the R_1 and R_2 groups alkyl, aralkyl, alkaryl, aryl or alkoxyalkyl groups of from 1 to 18 carbon atoms. Typical of the R_1 and R_2 groups are those derived from the alkyl monoalcohols such as methanol, isopropanol, n-propanol, n-butylalcohol, 2-methyl-1-propanol, 2-butanol, 2-methyl-2-propanol, 1-pentanol, 3-methyl-1-butanol, 2-ethyl - 1 - pentanol, 2-pentanol, 3-pentanol, 2-methyl-2-butanol, 2,2-dimethyl-1-propanol, 2-methyl-3-butanol, n-hexylalcohol, 2-ethyl-hexanol, especially the heptyl, octyl and nonyl alcohols obtained through the oxo synthesis, and the like; such aralkyl alcohols as benzyl alcohol,

benzohydrol, phenethyl alcohol, α-ethyl benzyl alcohol, α-ethyl phenethyl alcohol, o,m and p-tolylcarbinols, and the like; such aryl monohydroxy (phenolic) compounds as phenol, o,m and p-cresols, 1- and 2-naphthols, and the like; and such alkoxyalkanols (ether monoalkanols) as methoxyethanol, ethoxyethanol, propoxyethanol, butoxyethanol, the methoxy-propanols ethoxy propanols, 2,3-dimethoxy-1-propanol, 2,3-diethoxy - 1 - propanol, 2,3-dipropoxy-1-propanol, 2,3-dibutoxy-1-propanol, and the like. R_1 and R_2 can contain 1 to 18 carbon atoms, with or without functional groups such as ether, alcoholic, amino, acidic groups.

The preferred ketone and aldehyde reactants providing the R_3 and R_6 groups have hereinbefore been illustrated. It is also desirable to employ benzaldehyde, acetophenone, tolualdehyde, o,m or p-methyl acetophenone, as well as 1-cyclohexyl-2-methyl-1-propane, and methyl cyclohexyl ketone among others.

To provide the amine residue there can be employed such primary alkyl amines as methyl amine, ethyl amine, n-propyl amine, isopropyl amine, butyl amine and octyl amine, such secondary alkyl amines as dimethyl amine, diethyl amine, dipropyl amine, dioctyl amine, didodecyl amine, benzyl amines, phenethyl amines; such aryl amines as aniline, diphenyl amine, toluidine, ditolyl amines, naphthyl amines, biphenyl amine; such alkylene diamines as ethylene diamine, 1,2-propanediamine, 1,2-butanediamine, 1,3-propanediamine, as well as N-alkyl derivatives of the alkylene diamines such as N-methyl ethylene diamine and the like; and such amines as N-ethyl phenylene diamine, furfuryl amine, cyclohexyl amine, ethane amine, diethane amine, methyl ethanol amine, isopropanol amine, diisopropanol amine, among others.

To determine surface ignition or "preignition" suppression effectiveness, the additive is added to a leaded (3 cc. TEL per gallon) fuel. This fuel with additive is used in a single cylinder, CFR–L head engine, having a 7 to 1 compression ratio. Typical operating conditions for surface ignition or "preignition" studies are:

Test duration ---------- hours	50
Coolant temperature, ° F. ----------	148
Oil temperature, ° F. ----------	160
Air to fuel ratio ----------	13 to 1

For this test the engine load and r.p.m. cycle is

Time	45 seconds	135 seconds.
R.p.m	600	900.
Load	None	Full.

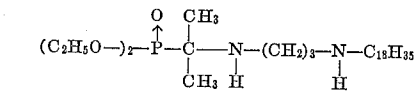
Surface ignition prevention effectiveness using a premium fuel having 3 cc. TEL per gallon and the following additives of this invention and other phosphorus compounds are conducted using the phosphorus containing additives on the same MR P/Pb concentration. The results of these tests are shown in Table II.

TABLE II.—EFFECTIVENESS IN SUPPRESSING SURFACE IGNITION CFR–L HEAD ENGINE

Additive	Concentration, MR P/Pb	Percent Effective
N,N-diethyl amino ethyl O,O-diethyl phosphonate	0.067	40
	0.13	87
Tricresyl phosphate	0.13	44
Commercial hydrocarbon dithiophosphate	0.13	61

An interesting additive of this invention is derived from O,O-diethyl hydrogen phosphite, acetone and N-octadecyl

1,3-propylene diamine. The additive is believed to have the following formula:



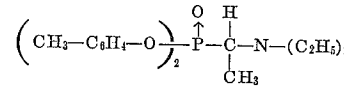
and is hereinafter referred to as N'-octadecyl 1,3-propylenediamine-acetone diethyl hydrogen phosphite derivative.

To demonstrate the advantage of the additives of this invention in not substantially reducing the octane number of high octane gasolines, the results of tests conducted in a CFR–L head engine at various MR P/Pb concentrations of several additives in gasolines of from 97 to 100 octane (RON) with from 2.5 to 3.0 cc. TEL per gallon and sulfur level of from 0.021% to 0.054% are shown in Table III. The additive concentrations are maintained at 0.2 and 0.4 MR P/Pb level and the values shown are the average octane number destruction obtained from a number of tests at the same MR P/Pb ratio with each premium gasoline.

TABLE III.—OCTANE NUMBER DEGRADATION

Additive	Concentration, MR P/Pb	
	0.13	0.26
N'-octyl-1,3-propylenediamine-acetonediethyl hydrogen phosphite derivative	0.0	
N,N-diethyl amino ethyl O,O-diethyl phosphonate	0.16	0.16
Commercial hydrocarbon dithiophosphate	0.40	0.60

When subjected to the same test for measuring octane number degradation N,N-diethyl 1-amino ethyl-1 O,O-ditolyl phosphonate;



has a negligible octane number degradation.

Additives of this invention are subjected to the D–381 Gum Test (ASTM D–381–58T). The results obtained can be illustrated by the following:

ASTM D-381-58T EXISTENT GUM TEST

Additive	0.13 MR P/Pb Hexane Wash		0.26 MR P/Pb Hexane Wash	
	Before	After	Before	After
Control, mg	4.4	2.9	4.4	2.9
N,N-diethyl amino ethyl O,O-diethyl phosphonate, mg	1.9	0.1	2.8	0.2

An additional benefit obtainable from the use of the additives of the present invention is the absence of prooxidant effect and thus do not contribute to gum formation in gasoline on long term storage. This can be demonstrated by testing motor fuels at accelerated storage conditions at 212° F. and 100 p.s.i.g. oxygen pressure and observing the time (induction period) before rapid oxygen consumption occurs. The following are results obtained in such a test with the leaded base fuel (no additive control) a commercial dihydrocarbon dithiophosphate and an additive of this invention all additives at 0.26 MR P/Pb.

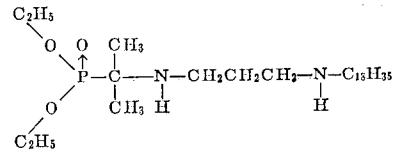
Additive:	Induction period, minutes
Control ----------	810
Commercial additive ----------	1113
N,N-diethyl aminoethyl O,O-diethyl phosphonate ----------	1440

Also of interest are certain members of the class of additives of this invention whose amine residue contain hydroxy-alkyl groups. These compounds prevent increase in gum formation and actually decrease the formation

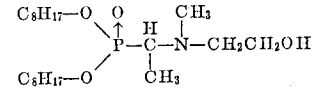
and/or deposition of gum precursors. For example, N-methyl N-beta-hydroxyethyl aminoethyl O,O-diisooctyl phosphonate as additives in gasoline subjected to an accelerated gum test, i.e., Rotogum Test at 415° F. The Rotogum Test is a test for detergency activity, i.e., the ability of a formulated gasoline to remove the deposits formed and is especially adaptable for testing detergency at high engine operation temperatures. The test employs a test apparatus which includes a rotating inclined glass tube through which a 100 ml. sample is flowed by gravity flow in the presence of air during a 42-minute test period. The apparatus used and an acceptable test procedure are described by Mickel in U.S. Ser. No. 25,577 filed April 29, 1960. The glass tube is maintained at a temperature of 415° F. during the test and the sample and air flow are maintained constant. After the test period, the glass tube is cooled to the touch, removed and washed with heptane while rotating until deposits cease to be removed. The remaining deposits are then removed by a strong triple solvent mixture and the solvent is evaporated therefrom by regular ASTM D–381 gum procedures yielding the "insoluble gum," i.e., those deposits which would not be removed by the hydrocarbon components of gasoline. The insoluble gum is reported in mg./100 ml. Using N-methyl, N-beta-hydroxyethyl aminoethyl O,O-diisooctyl phosphonate in a base motor fuel, a deposit of 2 to 3 mg. of insoluble gum is obtained whereas the gasoline without additive produced a gum deposit of 5 to 6 mg.

What is claimed is:

1. A compound of the formula:



2.



References Cited

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