vapor pressure study at high temperatures. However, a strong indication that the α-and β-forms are both anhydrous is provided by analysis of the α-acetate as it picks up moisture. Exposure to air for a few days showed a gradual increase in water content with a change in the x-ray diffraction pattern to mixtures of the α-anhydrous acetate and half-hydrate; no β-form appeared. If the β-form were a hydrate, it is likely that it would have been present. Apparently, the β-form is metastable and can be made only by heating the hydrates.

The behavior of the monohydrate in the thermobalance showed that the weight lost at temperatures above 220° C. accounts for essentially all the water present in the monohydrate. Table III illustrates this and shows what happens when the acetate samples were exposed to air at room temperature after being heated. On cooling, these samples behaved as previously reported (*7*). They picked up moisture at different rates to form the half-hydrate; the amorphous-anhydrous form reacted most quickly. In this study no decomposition was observed, even up to 390° C. The decomposition observed by Walter-Levy may have been due to longer exposure at the high temperatures.

Differential thermal analysis showed major heat absorption in the temperature ranges where other experiments showed phase changes occurring. The following tabulation summarizes these observations.

Temp. Ranges of Heat Absorption, ° C.	Phase Formed
80–150	Half-hydrate
195–215	Amorphous and β-anhydrous forms
240–275	α-anhydrous form
400–430	Decomposition to $CaCO_3$

The x-ray diffraction patterns of all the crystalline forms of calcium acetate agree with those published by Walter-Levy (*7, 8*). The pattern for the monohydrate is similar to that reported earlier by Hanawalt (*3*), but different from that shown in the ASTM x-ray powder data file (*6*). The latter pattern is similar to that observed for the half-hydrate. Hanawalt's x-ray pattern for anhydrous calcium acetate (*3*) is also different from that observed in this study. The detailed x-ray patterns with the relative numerical intensities are shown in Table IV.

Two of the hydrates and the three anhydrous forms of calcium acetate now appear to be well characterized and their behavior on heating is understood. The anhydrous forms can be obtained directly by heating the hydrates. Some further work is planned to determine whether calcium acetate dihydrate truly exists, and if so, to characterize it as well as possible and to obtain its x-ray diffraction pattern.

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Effect of Phosphorus Deposit Modifiers on Gasoline Octane Quality

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ORGANOPHOSPHORUS compounds are widely used in leaded gasoline to control surface ignition and spark plug misfiring. Of the many factors influencing the choice of a specific compound, its effect on gasoline octane quality is one of the most important. Nevertheless, except for the patent literature (*5*), there has appeared little, if any, discussion of the factors which affect the action of phosphorus compounds on octane number. This series of studies was undertaken to define the mechanism of the proknock action of phosphorus compounds and to relate such action, if possible, to the chemical structures of the phosphorus additives and the properties of the fuels in which they are used.

EXPERIMENTAL CONDITIONS

All studies of additive structure, whether inorganic or organic, were conducted using a motor gasoline composed of 91.5% light virgin naphtha and 8.5% heavy catalytic naphtha. Its octane characteristics were as follows:

	Octane Number	
	Research	Motor
Unleaded	71.0	69.5
With 3 cc. TEL/Gal.	87.0	85.0

The high lead susceptibility of this fuel magnifies any interaction of additive and TEL (tetraethyllead), and its low sensitivity allows a ready comparison of effects on motor and research octane numbers. While this fuel is not typical of the composition or quality of those in which phosphorus additives are commonly used, the trends observed in it have been confirmed in representative commercial gasolines.

Except where noted, all determinations were made with fuels containing 3 cc. TEL and 1.0 theory of phosphorus per gallon [1.0 theory of phosphorus is that amount required to convert all the TEL to $Pb_3(PO_4)_2$, assuming complete combustion of fuel and additives, and quantitative reaction of lead and phosphorus. Thus, 2 moles of a phosphate are added for each 3 moles of TEL]. Whenever possible, octane numbers were obtained using the direct match procedure, although some additives caused octane losses of such magnitude that this procedure was not applicable.

UNLEADED FUEL TESTS

None of the additives, organic or inorganic, had any significant effects on the octane quality of the unleaded test fuels. Thus all the octane losses described below are the results of some form of lead antagonism. In the case of the organophosphorus compounds, this can also be taken to mean that no appreciable quantities of peroxygenated free radical are produced from the additives, since such radicals are notoriously proknock whether TEL is present or not.

INORGANICS IN THE LEADED FUEL

As shown in Figure 1, lead antagonism by inorganic compounds is a function of the substituents and the structure of any given compound (*9, 11*). For instance, note the sequence of octane loss $PCl_3 > PSCl_3$, $POCl_3 > (PNCl_2)_n$. This parallels the lability of the halogen, as P—Cl bond structure is first altered by the change from tervalence to quinquevalence and finally by the aromaticity of $(PNCl_2)_n$. This undoubtedly represents the degree of reactivity of these compounds toward TEL.

The reaction, $(C_2H_5)_4Pb + PCl_3 \rightarrow (C_2H_5)_3PbCl +$ structure is first altered by the change from tervalence to quinquevalence and finally by the aromaticity of $(PNCl_2)_n$. This undoubtedly represents the degree of reactivity of the PCl_3 additive fuel showed such a loss, but it was not enough to account for the total change in octane number. Prepared by an alternate route (*6*), $(C_2H_5)_3$ PbCl was then found to have no antiknock properties, even in a highly susceptible primary reference fuel.

The general behavior of the inorganics thus seems to be a conversion of TEL to ethyllead derivatives, which may be lost by precipitation, or which have no antiknock properties. The halogens, pseudohalogens, and sulfides appear to enter such reactions readily, although structure can still alter reactivity. [Compare $P(SCN)_3$ *vs.* $P(NCO)_3$ and P_4S_3 *vs.* $P_4S_4O_6$]. Other than their structural contributions, oxygen and hydroxyl appear to have no effect.

ORGANICS IN THE LEADED FUEL

Early in this series of tests, it became apparent that organophosphorus additives gave greater losses in the motor octane number determination than they did in the research method. This phenomenon is explored further below. Throughout this section most of the discussions are thus based on motor octane number results, since the larger values appear to offer more valid comparisons.

Lead antagonism has been further demonstrated by saturating the test fuel with an organic (Figure 2). When more unleaded octane value is reached, additive has no effect.

EFFECT OF STRUCTURE

The data in Table I indicate that TEL is attacked by the substituents rather than the phosphorus, and the more highly esterified the organophosphorus compounds, the greater the octane loss.

A reaction similar to the one for halogen may be occurring: $(C_2H_5)_4Pb + RO\text{-}PX_2 \rightarrow (C_2H_5)_3PbOR + C_2H_5PX_2$ In this case, the product would be an ethyllead alkoxide, which might be expected to have little antiknock property, since it is structurally analogous to the ethyllead halide. However, there is no proven example of the above reaction in the literature, although the reaction of TEL and sodium ethoxide is formally similar (*2*) and demonstrates the reaction in principle.

Since the larger motor octane losses indicate a thermally activated process, the known behavior of phosphorus esters under such conditions warrants discussion. Thermal cracking yields olefins and a residue of phosphorus acids in an ionic mechanism (*1*):

$$(RO)_3P \longrightarrow R^+ + (RO)_2PO^-$$
$$\quad\;\; \longrightarrow (RO)_2P^+ + RO^-$$

In a motor gasoline, such a process (and subsequent attack on TEL) probably occurs in the liquid phase, since the higher boiling components enter the engine as liquids (*3*). The cations above would not attack the electropositive lead center. Either of the two anions might, but if we compare $(C_4H_9)_2P(O)OC_4H_9$ and $(C_4H_9)_2P(O)OH$ in Table I, we see a large octane loss only for the former, despite the fact that the anion $(C_4H_9)_2P(O)\bar{O}$ would be produced from either. It appears reasonable to assign the role of TEL antagonist to the alkoxy group, inasmuch as the other reactive species may be logically eliminated.

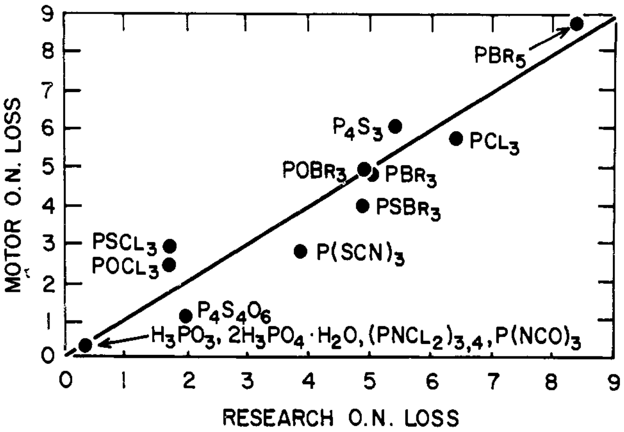

Figure 1. Inorganic phosphorus compounds reduce octane number

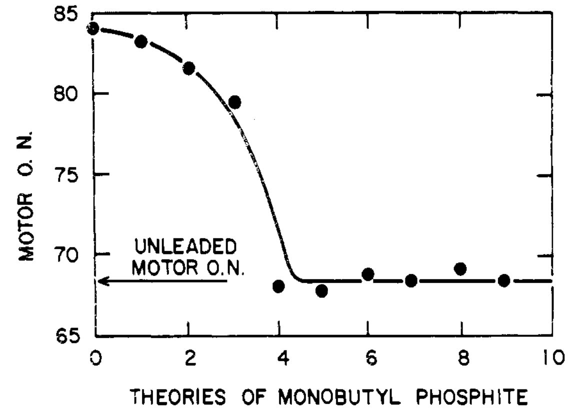

Figure 2. High phosphorus concentrations reduce fuel octane number to unleaded value

Table I. Lead Antagonism by *n*-Butyl Phosphorus Compounds

No. of Alkoxy Groups	Structure	Formula	Change in Motor O.N.
0	Phosphonic acid	$C_4H_9P(O)(OH)_2$	−0.4
	Phosphinic acid	$(C_4H_9)_2P(O)OH$	−0.4
	Phosphine oxide	$(C_4H_9)_3PO$	−0.8
	Phosphine	$(C_4H_9)_3P$	−1.1
1	Metaphosphate	$(C_4H_9OPO_2)n$	−0.6
	Monobutyl phosphate	$C_4H_9OP(O)(OH)_2$	−0.7
	Monobutyl phosphite	$C_4H_9OP(OH)_2$	−0.8
	Phosphinate	$(C_4H_9)_2P(O)OC_4H_9$	−1.5
	Monobutyl butanephosphonate	$C_4H_9P(O)(OC_4H_9)OH$	−1.8
2	Pyrophosphate	$[(C_4H_9O)_2PO]_2O$	−1.5
	Dibutyl phosphate	$(C_4H_9O)_2P(O)OH$	−2.0
	Dibutyl butanephosphonate	$C_4H_9P(O)(OC_4H_9)_2$	−2.5
	Dibutyl phosphite	$(C_4H_9O)_2POH$	−3.2
3	Tributyl phosphate	$(C_4H_9O)_3PO$	−3.3
	Tributyl phosphite	$(C_4H_9O)_3P$	−3.6

Further structural trends fit this sequence. Thus, the quinquevalent phosphates are, within any group in Table I, less reactive than the tervalent phosphates, paralleling the lability of the alkoxy groups as structure changes.

Losses from compounds such as the phosphines, where no ester structure is initially present, may be the result of oxidation to esters in the hot air-fuel mixture. Esters are among the oxidation products of such compounds.

In the inorganic tests above, thiono sulfur and oxygen appeared equivalent ($PSCl_3$ *vs.* $POCl_3$, $PSBr_3$ *vs.* $POBr_3$). An additional test indicates the same holds true for organophosphates and phosphorothionates, $(C_2H_5O)_3PS$ and $(C_2H_5O)_3PO$ giving motor octane number losses of 3.5 and 3.4, respectively. However, the effect of R—S—P bonds has not been investigated in this work.

EFFECT OF SUBSTITUENT VARIABLES

Aliphatic Structure. Both chain length and branching can have a profound effect on antagonistic properties of phosphorus esters. The results from a series of phosphites are shown in Figures 3 and 4. Note in Figure 3 that the effects are directionally the same, regardless of the octane determination method. The peak in the *n*-alkyl curve and the relative position of the branched derivatives are the same as those obtained in other reaction systems where the structure of the alkoxy group is a critical factor (*4, 8*). Figure 5 plots the data of one such study, using the reciprocal of reaction rate as a measure of the basicity of RO^-. The excellent correspondence of these results with our own is the strongest single piece of evidence for attributing the lead antagonism to the alkoxy substituent.

The peak in the *n*-alkoxy curve probably represents the inductive effect (increasing reactivity) being overcome by the steric effect of greater chain length. Branching may affect both of these factors, leading to either the extreme activity of the *tert*-butoxy ester, or merely increasing bulk at long chain lengths. (Note: Tri-*tert* butyl phosphite is not readily synthesized. The value shown here was obtained by extrapolation, using a series of dialkyl phosphites for the base curve. Di-*tert* butyl phosphite still gave the highest octane loss obtained in this study, 8.1 O.N.).

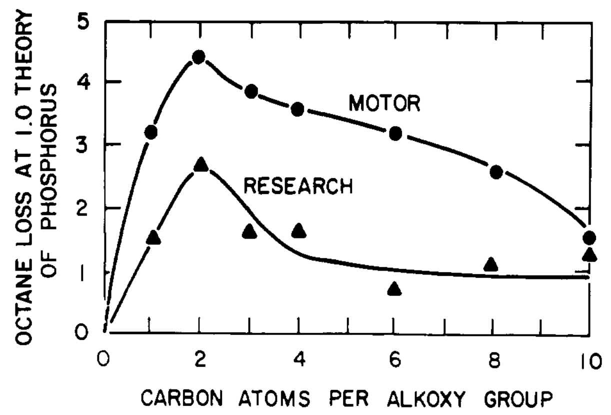

Figure 3. Octane loss with tri-*n*-alkyl phosphites varies with chain length

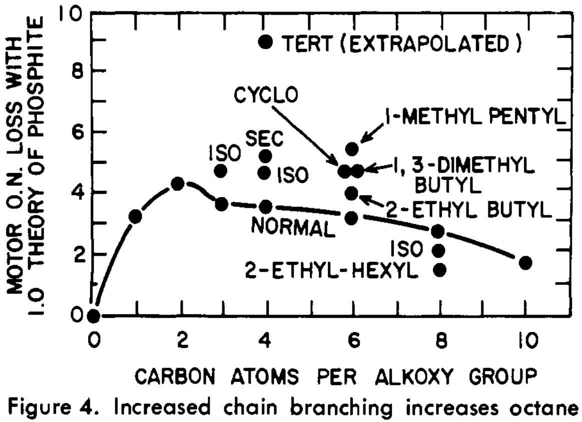

Figure 4. Increased chain branching increases octane loss with tri-alkyl phosphites (alkyl less than C_8)

Aryl Groups. Aryl substitution reduces lead antagonism. As shown in Figure 6, successive replacement of alkyl groups by phenyl groups gives successively lower losses. The inertness of the aryl esters is consistent with the mechanism: aryl esters are more resistant to cracking than alkyl esters, and aryl ionic intermediates, if formed, would be resonance stabilized and thus less reactive.

Other Substitutions. Substitution on the aryl rings does not have a marked effect on the extent of octane loss. Table II presents the results from a series of aryl phosphites. The last two of these, one with strong ortho, para-directing methoxy groups and one with the strong meta-directing acetyl groups, were tested to see if effects transmitted through the ring could alter the reactivity. However, both had negligible effects.

In contrast to the preceding results, substituent effects are observed in alkyl esters. Substitution of a chlorine atom on the beta-carbon atom decreases the electron density on the oxygen atom in the alkoxy radical $ClCH_2CH_2O$ Thus the octane losses with tris-beta-chloroethyl phosphate are less than with triethyl phosphate in an experimental premium grade fuel.

	Change in Motor O.N.	
Phosphate	0.2 Theory	0.4 Theory
$(C_2H_5O)_3PO$	−0.6	−2.0
$(ClCH_2CH_2O)_3PO$	−0.3	−0.8

FUEL FACTORS

To develop information of wider applicability, the investigation was extended to other fuels. In this study 18 different fuels, and four different additives were used. Octane determinations were made by both the research and motor methods. Results of these studies showed that—in

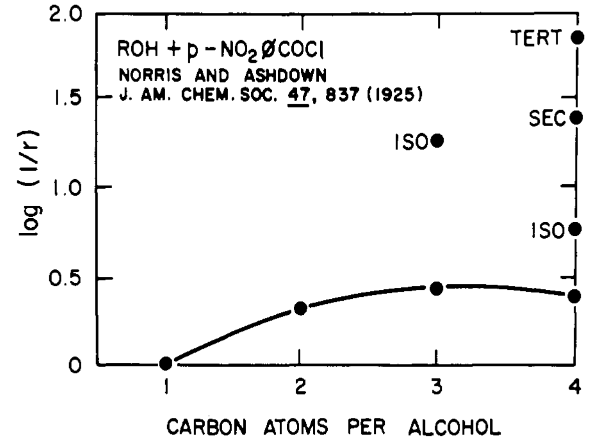

Figure 5. Reactivity of alcohols depends on chain length and branching

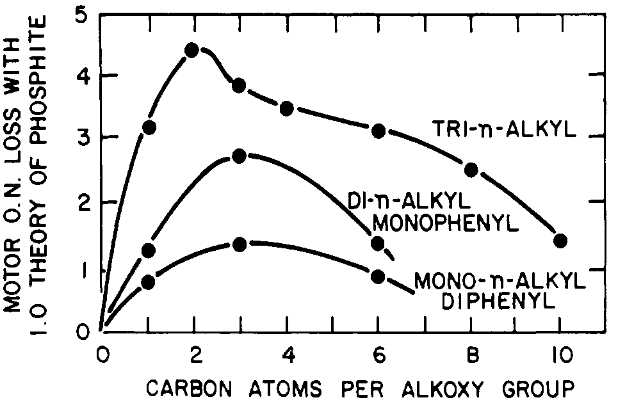

Figure 6. Aryl substitutions reduce octane number loss

Table II. Aromatic Phosphites Give Small Octane Losses

Aryl Phosphite	Research O.N.	Motor O.N.
$P(OC_6H_5)_3$	0	0
$P(OC_6H_4CH_3)_3$	+0.3	−0.5
$P(OC_6H_4C_9H_{19})_3$	0	−0.2
$P(OC_6H_4OCH_3)_3$	+0.2	−0.4
$P(OC_6H_4\overset{\overset{O}{\|}}{C}{-}CH_3)_3$	−0.2	−0.2

Table III. Effect of Phosphorus Additives on Laboratory Octane Quality as a Function of Aromatic Content in Fuel

	Change in Octane Number[a]	
% Arom.	Research	Motor
65	−0.9	−2.5
31	−0.7	−2.2
13	−0.5	−1.3

[a] Average values for four additives.

Table IV. Temperature Sensitivity of Phosphorus Esters in Cold Motor O.N. Test

	Change in Octane Number		
Additive	Research	Motor	Cold motor
$[(C_4H_9O)_2PO]_2O$	−0.6	−1.5	−1.6
$C_4H_9P(OH)(OC_4H_9)OH$	0	−1.8	−1.4
$(C_4H_9O)_2POH$	−1.6	−3.2	−1.5
$(C_4H_9O)_3PO$	−1.2	−3.3	−1.4
$(C_4H_9O)_3P$	−1.6	−3.6	−1.6

addition to additive structure—fuel composition and properties and TEL content are important in determining the magnitude of octane loss.

TEL Concentration. Increasing TEL content led to higher losses at the same phosphorus concentration in theories (phosphorus content increased with increasing TEL content, Figure 7). In this figure, straight lines showing TEL loss as a function of TEL content extrapolate to the origin as expected, since losses are not found in an unleaded fuel. (TEL loss is the apparent loss in TEL which is equivalent to the measured octane number loss. It is determined from the TEL, susceptibility curve of the fuel.) The effect was independent of the additive employed, the method of octane determination, or the fuel in which the effect was measured. (Fuels *A*, *B*, and *C* had aromatic contents of 13, 31, and 65%, respectively.)

Aromatic Concentration. Octane losses were higher in fuels of higher aromatic content.

The greater losses observed in aromatic fuels may be due to their abilities to form more polar solutions and thus promote charge separation. This point is not clear however, and a difference in the character of the knock reaction between aromatics and paraffins may be the cause.

Octane Level. Motor octane losses increased as the octane level increased, but the effect was reversed in the research method. It would seem consistent with the proposed mechanism that losses should increase as octane level is increased, since rating at higher octane levels involves a higher temperature environment, thus increasing the rate of reaction. Perhaps the anomalous research octane results may exist because the highest octane fuels were over 100 research O.N., thus requiring the use of different reference fuels (leaded isooctane) and a somewhat different octane scale (the Coordinating Research Council extension).

METHOD OF OCTANE DETERMINATION

A regression equation developed from results on four additives in 18 fuels is the following:

$$\text{Research O.N. loss} = 0.62\ (\text{motor O.N. loss}) - 0.57$$

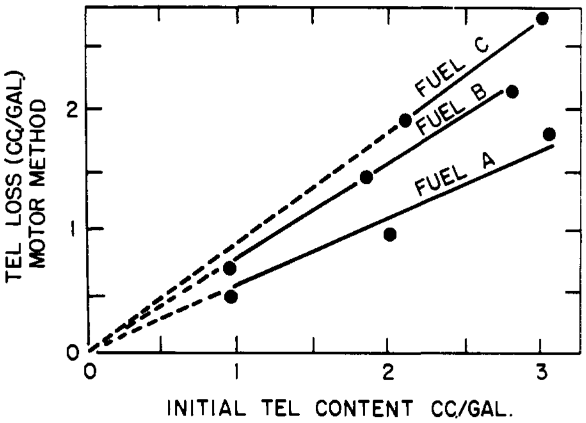

Figure 7. TEL loss increases with TEL content (average effect of 4 additives at 1.0 theory)

The difference between the two ratings can be explained on the basis of the temperature dependence of the phosphorus ester reactions. With the inorganic compounds, (Figure 1) the losses in the two methods are about the same, implying that the reaction with the inorganic compounds is not temperature sensitive. In the research method, the air-fuel temperature is not controlled, and is usually in the order of 100° F. The motor method heats the air-fuel mixture to 300° F. by passing it over a blade heater, the surface temperature of which may reach 700° F. To demonstrate the importance of temperature on octane loss, some phosphorus additives selected from the structure study series were given an additional octane rating by motor method, conducted in the usual manner with the exception that the heater blade was turned off. The results are shown in Table IV. In all but two cases, the loss was substantially reduced, and in three out of the five cases, the loss came down to the same level as observed for the research method. While such a test does change some other engine operating variables, temperature is the major one; it is significant that the base fuel gave the same octane rating (85.0 motor O.N.) by cold motor method as it did by standard procedure.

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