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Review

Phosphate Esters, Thiophosphate Esters and Metal Thiophosphates as Lubricant Additives

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Abstract: Phosphate esters, thiophosphate esters and metal thiophosphates have been used as lubricant additives for over 50 years. While their use has been extensive, a detailed knowledge of how they work has been a much more recent development. In this paper, the use of phosphate esters and thiophosphate esters as anti-wear or extreme pressure additives is reviewed with an emphasis on their mechanism of action. The review includes the use of alkyl phosphates, triaryl phosphates and metal containing thiophosphate esters. The mechanisms of these materials interacting with a range of iron and steel based bearing material are examined.

Keywords: phosphate ester; anti-wear additive; extreme pressure additive; ZDDP; TCP

1. Introduction

Phosphate esters have found numerous industrial applications due to their overall stability, especially in the presence of oxygen [1]. The general structure, (Figure 1) shows the fully oxidized phosphorus at the core. The ability to exchange oxygen for sulfur and to easily include a variety of substituent groups has led to a wide range of applications. Some of the initial applications were as fire retardants, especially for the films industry [2]. Other significant applications are as environmentally degradable pesticides due to their toxicity to a wide range of insects and their relatively short residence time in the environment [3]. The phosphate esters have also found application as surfactants and as brighteners in detergents [4]. The multiple industrial uses have led to the commercial availability of a

wide range of phosphate esters with different properties and reactivities. The available esters include aromatic phosphate esters such as tricresyl phosphate, alkyl phosphate esters such as tributyl phosphate, thiophosphates and metal containing phosphate esters such as zinc dialkyldithio-phopsphates (ZDDP) [5]. The purpose of this paper is to review the use of the various types of phosphate esters as lubricant additives and to illustrate what is known about how they function as lubricant additives.

Figure 1. Structure of a phosphate ester, a thiophosphate ester and a dialkyldithio phosphoric acid.

Phosphate Ester   Thiophosphate Ester   Dithiophosphate
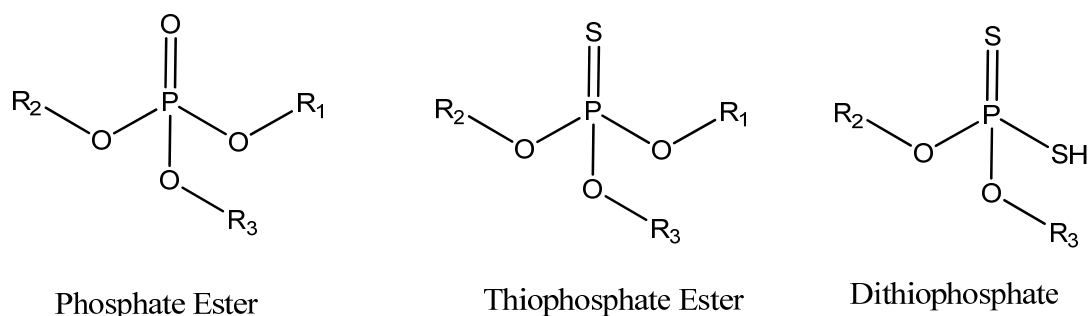
Phosphate esters have been used as lubricant additives for more than 80 years, beginning with the early patents on the use of tricresyl phosphate and tri-*n*-butyl phosphate in lubricants [6]. As the temperature, pressure and sheer stress requirements for lubricants have increased, more additives have been developed. In addition, environmental requirements have created the need for metal free additives and additives with little or no phosphorus or sulfur content. While containing phosphorus, many organic and metal containing phosphate esters have been developed to fill a number of these roles. As the allowed phosphorus concentration has decreased, the search for phosphate esters that are effective at lower and lower concentrations and for non phosphorus additives has increased. Some studies, however, have indicated that phosphorus concentration in the oil and oil volatility do not predict phosphorus emissions [7] and some additives that contain phosphorus, do not contribute to phosphorus in the exhaust stream depending on their molecular structure [8]. There are, however concerns about long term toxicity of many of these compounds and their degradation products remain. The different aspects of phosphate ester lubricants, including their efficiency as anti-wear/extreme pressure additives with various substrates, mechanisms of action and toxicities of the classes of compounds will be examined in the sections below.

2. Zinc Dialkyldithiophosphate and Other Metal Containing Phosphate Esters

The formal introduction of lubricant additives containing zinc, phosphorus and sulfur traces back to a series of patents by Lubri-zol (the name was changed to Lubrizol in 1943) [9], American Cyanamid [10] and Union Oil [11] in 1941, claiming the mixtures, now known to be zinc dialkyldithiophosphates, ZDDPs to function as corrosion and oxidation inhibitors. Zinc dialkyldithiophosphates were originally prepared by the reaction of phosphorus pentasulfide (P_2S_5) and one or more different alcohols to give the dialkyldithiophosphoric acid, which was neutralized by the addition of zinc oxide to give the product as is shown in Figure 2 [12]. The ability to use a mixture of alcohols, resulting in a statistical mixture of products allows the chemical and physical properties of the resulting additive to be varied significantly

and the resulting mixture has a wider liquid range that would be observed for a pure compound. The properties can also be varied based on the ratio of zinc oxide to the dialkyl dithiophosphoric acid resulting in acidic, neutral and basic ZDDPs, each having a different reactivity [13]. This method of preparation is still in use industrially today.

Figure 2. Method for the preparation of zinc dialkyldithio-phopsphates (ZDDP).
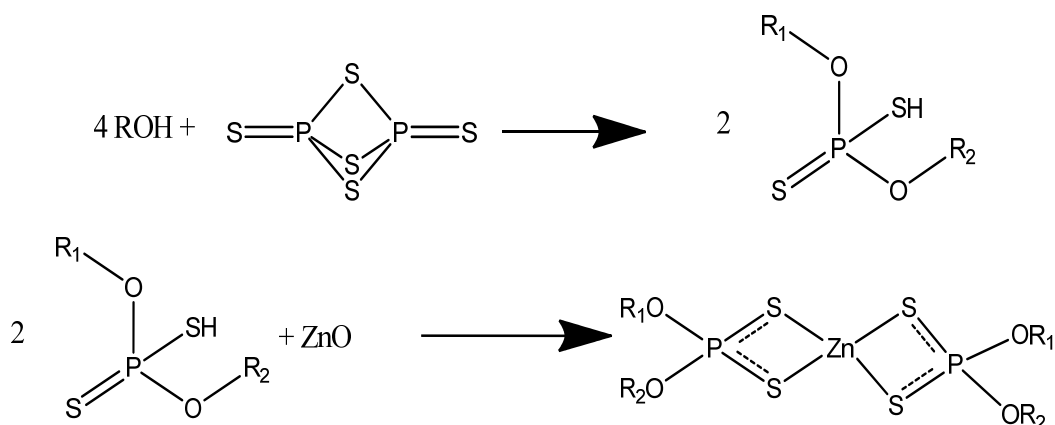
The initial application of ZDDP in lubricating oils was as an antioxidant. The mechanism of ZDDP's action as an antioxidant appears to be through reaction with peroxy radicals [14]. It was not until 1955 that it was demonstrated that ZDDP was an effective anti-wear additive [15], which led to its rapid adoption by the automobile industry [16]. Current environmental limits on phosphorus and sulfur in lubricant formulations as well as the concern regarding heavy metal emissions, threatens the use of ZDDP in engine oil and has brought an increase in research to find replacements that do not contain phosphorus. The history of ZDDP and of much of the early research on ZDDP has been reviewed by Spikes [17].

2.1. The Structure of ZDDP in Solution

The nature of ZDDP in solution forms an important basis for its interaction with metal surfaces and its use as an anti-wear additive. In solution, ZDDP acts effectively as an anti-oxidant adding to the complexity of its chemistry and also its utility as an additive [18]. ZDDP appears to exist primarily as an equilibrium between monomers and dimers based on NMR and vibrational spectroscopy, with the dimer being predominant in toluene or chloroform solution [19]. Quantum mechanical models of the conversion from a monomeric ZDDP to a dimeric structure is thought to go through two distinct transition states, the first containing a four membered ring with 2 bridging sulfur atoms, and the second containing a six membered ring [20]. Basic ZDDP exists as a tetrameric form that could be formulated as three molecules of ZDDP with a zinc oxide, giving it the formula $Zn_4O(dialklydithiophosphate)_6$. Polymeric forms are also observed based on the formation of polymers in the solid state [21] and dynamic light scattering results that indicate significantly larger molecules are present in solution [22]. The structures of some of these forms are shown in Figure 3.

Figure 3. Structures of various forms of ZDDP.

Monomeric ZDDP

Dimeric ZDDP

Basic ZDDP (tetrameric)

Polymeric ZDDP
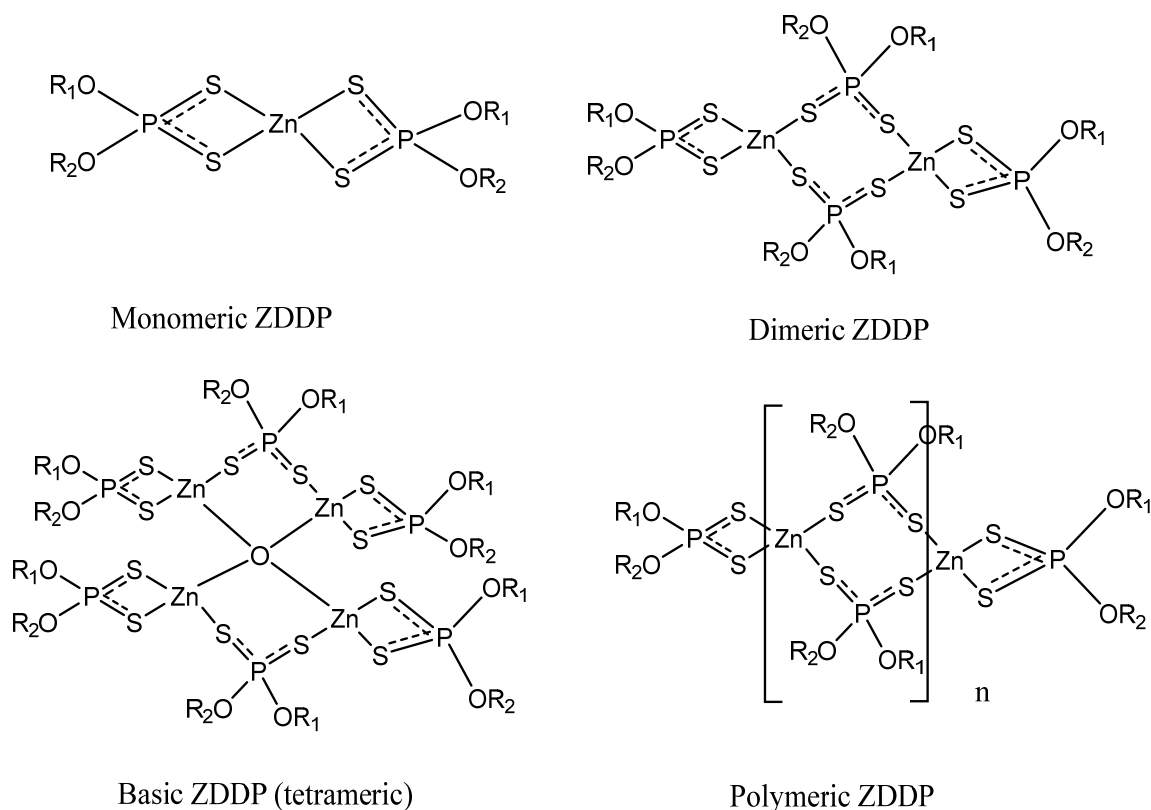
The nature of ZDDP in solution also depends on the ratio of zinc to the dialkyl-dithiophosphate. In solutions with an excess of zinc oxide (basic ZDDP), a tetrameric structure is formed with an oxide ion located in the center of the four zinc atoms [23]. It appears, however, that under high temperature conditions, the basic ZDDP converts to neutral ZDDP and zinc oxide, giving identical wear test performance [24], and the oxidation of thiophosphate to phosphate was a part of the degradation mechanism [25].

2.2. The Reaction of ZDDP at Surfaces

The fundamental mechanism of all anti-wear additives is that they form a protective film at the bearing surface and that that film protects the surface, principally at periods of start-up and in the elastohydrodynamic and boundary lubrication regime. In these regions, the contact between asperities is the major cause of wear [26]. The nature of the surface films formed and how the reactivity of different ZDDPs can be modified has been the object of substantial research.

An initial model for the structure of ZDDP films formed might be obtained from an examination of the solid state structure of ZDDP. Several structures have been determined by X-ray crystallography showing that polymeric complexes [27] and binuclear complexes [28,29] exist, depending upon the alkyl groups used in the ZDDP. Additional studies, based on solid state NMR have indicated that ZDDP can exist in structures not seen in crystalline solids and different from those seen in solution [30]. The application of X-ray absorption techniques indicates the decomposition of species in solution is a possible precursor to the formation of films. X-Ray absorption near edge structure

spectroscopy and solution ^{31}P NMR were correlated to the formation of a surface film and that if no phosphorus remained in solution, films continued to form [31].

When metal are immersed in a ZDDP solution in a lubricant or other non-polar solvent, a thermal film rapidly forms at the metal surface. It is apparent that these films are not simply zinc phosphate, zinc phosphide or iron phosphate [32]. These films have compositions similar to films formed in tribological junctions. Best results for the reduction of wear were obtained when a thermal film was deposited first, followed by rubbing in an oil containing ZDDP to generate the tribofilm [33]. The outer layer of the thermal film consists of a thin layer of polyphosphate, which gradually changes to pyro or ortho phosphate in the bulk of the film [34]. A significant difference, however is that the tribofilms frequently show iron in the film instead of zinc [35].

Tribofilms formed from ZDDP have been studied when formed under a wide range of conditions, differing substrates and using a number of different techniques. A number of observations have been reported, including the necessity of phosphate being present in the oil to form a wear resistant surface, and the observation that once the phosphate is removed from the solution, the sulfur causes corrosion within the wear scar [36]. Other techniques have shown that ZDDP prevents the reduction of surface oxides by the lubricant basestock, leaving an easily sheared surface layer that prevents direct contact between the surfaces [37]. It is commonly thought that ZDDP forms a series of pads on the surface of the bearing. The initial reaction occurs in solution to form a linkage isomer [38], which then adsorbs to the metal surface [39]. The reactions that form the pads eliminate most of the alkyl groups and much of the sulfur from the ZDDP leaving a surface of zinc polyphosphate. Moving from the surface layer towards the metal, the composition converts to a glassy, mixed iron and zinc phosphate. The ratio of iron to zinc is increased closer to the metal surface [40]. The pads are fixed to the surface by a thin layer of a mixture of iron and zinc sulfide [41]. The films tend to grow to a thickness of 50–150 nm and then stabilize [42]. A schematic representation of the structure of the films is shown in Figure 4. A particularly interesting property of the films is the increase in the modulus with an increase in pressure, a property referred to as smart material behavior [43].

The applicability of ZDDPs as an anti-wear additive relies on the reactivity of ZDDP at the operating temperatures achieved in automobile engines. Efforts to reduce the ZDDP content in oils in order to meet environmental requirement for reduced phosphorus, sulfur and heavy metals has led to an interest in the addition of catalysts such as FeF_3 which would allow a lower ZDDP content in the oil [44]. Studies indicate that in the presence of FeF_3, decomposition is faster and that detergents also accelerate the deposition reaction [45]. Under extreme loading conditions, a mixed catalyst containing FeF_3 and TiF_3 and polytetrafluoroethylene (PTFE) and ZDDP resulted in a lower reaction temperature needed to induce film formation [46] and reduced wear scars compared to ZDDP alone [47]. Iron(III) fluoride, when heated with ZDDP, in addition to acting as a catalyst, reacts with ZDDP to form fluorinated phosphate esters based on the presence of an P–F signal in both the ^{19}F and ^{31}P NMR spectra. The presence of P–F containing species arises from either the direct reaction of ZDDP with FeF_3 or a decomposition product of ZDDP with FeF_3 [48]. The reactivity itself leads to concern because of the similarity of the fluorinated phosphates to nerve agents Sarin and Soman [49].

Figure 4. Layered structure of surface film formed from ZDDP.
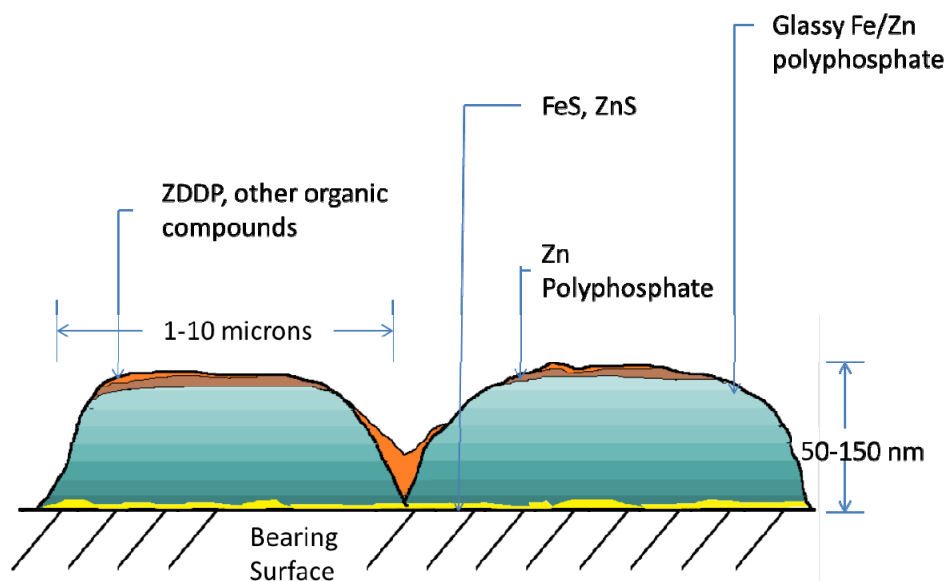
3. Dithiophosphate Ester and Phosphorothionate Ester Additives

Modern engines frequently use exhaust treatment filters or catalysts as a means of meeting current environmental emissions requirements for particulate emissions [50]. It is well known that phosphorus, sulfur and metals in the exhaust stream can block filters and poison catalysts [51]. Recently, lubricants and lubricant additives have been identified as an important contributor to all of these components on the exaust stream. Efforts to reduce ash, while still maintaining the effectiveness of a ZDDP like additive with similar reaction temperature have led to the investigation of a number of substituted thiophosphate ester and phosphorothionate ester based anti-wear additives [52].

The development of "ashless" anti-wear additives for automotive applications has focused *O,O′*-dialkyl-dithiophosphoric acids (Figure 5), which can be viewed as ZDDP with the zinc removed. To reduce the acid number, the dialkyl dithiophosphoric acid can be further reacted with an amine to neutralize the additive [53]. The degree of substitution on the amine leads to potential for property optimization. These additives often offer the highest load carrying capability, however suffer from reduced hydrolytic stability and higher resulting acidity when compared to other additives [54]. A common class of ashless additives can be prepared by the addition of amines to an appropriate thiophosphoyl chloride to form the amidothiophosphate [55]. Other additives can be prepared by the addition of the sulfur atom across the double bond of acrylic acid or an acrylate ester, among other possibilities [56]. An alternate approach relies on hydrogen peroxide to oxidize and dimerize the dialkylthiophosphate [57].

A number of ashless dialkyldithiophosphates have been studied, indicating that they form thermal films at temperatures of approximately 150 °C. The films consist of a mixture of iron(II) polyphosphate and iron(II) sulfate [58]. In tribological testing, the ashless additives gave thicker surface films and better overall performance than ZDDP under similar conditions. The films formed from the ashless additive consisted of shorter chain iron(II) polyphosphates than ZDDPs but with thicker films, with an average film thickness of 400 nm [59].

Figure 5. Structure of some ashless dithiophosphate additives.

Dialkyldithiophosphoric Acid   Amino Dialkyldithiophosphate salts   Amidodialkyldithiophosphate
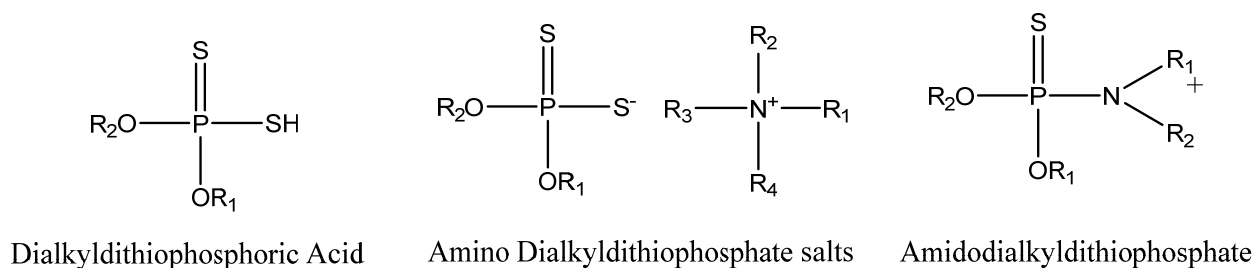
Another class of molecules that have received significant attention as antiwear additives are the triarlyphosphorothionates. Structurally, these molecules are similar to the phosphate esters, except the doubly bound oxygen is replaced with a sulfur atom. The parent in the series, triphenyl phosphorothionate has received the most study. Triphenylphosphorothionate is oxidized thermally in solution to eventually form triphenyl phosphate, with no oil insoluble products identified [60]. In the presence of iron or steel, however metal catalyzed reaction produces triphenyl phosphate and results in the production of a multilayered solid film on iron or iron oxide [61]. In tribological studies, wear debris was found by transmission electron microscopy to contain Fe_3O_4 particles and amorphous material. A wear mechanism was proposed that included wear particles trapped within the phosphate tribofilm. The antiwear additives that contained the fewest iron oxide particles had the best performance [62].

4. Phosphate Esters

Aromatic and aliphatic phosphate esters have been used as antiwear additives for more than 60 years. They were initially developed for aircraft engines; however they have also become indispensable in automotive applications as well. Trialkyl phosphates, such as tri-butylphosphate were preferred in many early studies because of their higher reactivities [63], however their higher reactivity limited their use to mild lubrication conditions [64]. As early as 1940, the effectiveness of tricresyl phosphate in reducing friction and wear in the boundary lubrication regime had been established [65]. With the advent of synthetic neopentyl polyol ester base stocks, triarylphosphates such as tricresyl phosphate became more critical because the film formed on the metal also reduces the reactivity of the base stock [66]. Triaryl phosphate esters continue to be used today, in spite of the requirements to reduce phosphorus in emissions and concerns about the toxicity of certain isomers of aromatic phosphate esters. When used with synthetic polyolester base stocks, the film formed by phosphate esters passivated the metal surface, reducing base stock degradation [67]. These concerns have led to the use of more highly substituted materials, such as butylated triphenyl phosphate (BTPP) (Figure 6) as a replacement for tricresyl phosphate.

Figure 6. The structure of the four components of commercial butylated triphenylphosphate additives.
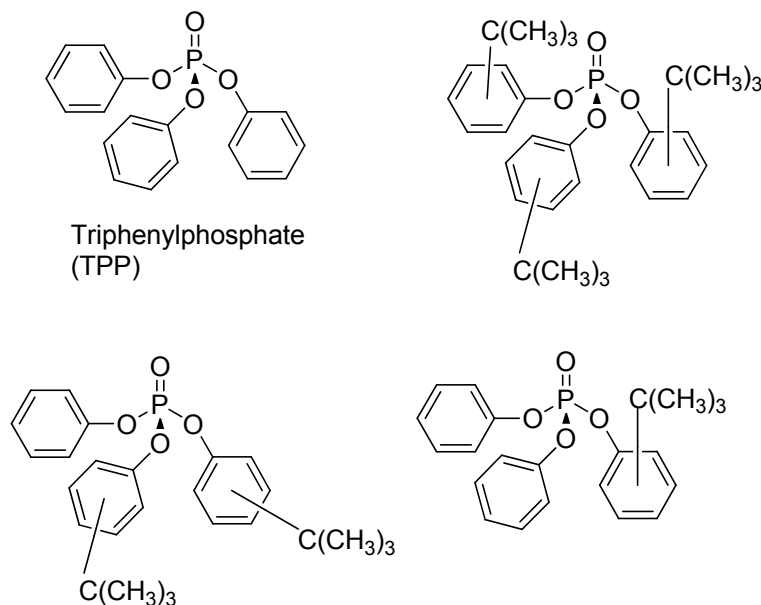

4.1. Mechanism of Phosphate Ester Modification of Metal surfaces

The reactions of trialkyl and triaryl phosphates at metal surfaces has been studied using a wide range of techniques, including Fourier transform infrared spectroscopy (FT-IR) [68], nuclear magnetic resonance (NMR), X-ray photoelectron spectroscopy and many other surface methods [69]. Much of what is known about the reactions of phosphate esters with iron surfaces starts with the work of Klauss on vapor phase lubrication [70]. It was shown that tricresyl phosphate forms a multilayer film on steel balls, which acts as a lubricious polymer. Later work by Forster indicated that iron diffusion through the phosphate layer was a likely mechanism for preservation of the lubricious coating [71]. The diffusivity of iron is estimated at 1–3×10^{-16} cm^2/s and appears to be the rate determining step in film growth [72]. The details of the mechanism resulting in the formation of the lubricious coating have been somewhat more difficult to determine.

Phosphate esters have been shown to react much more rapidly with iron oxides than normal iron or steel surfaces [73]. In the presence of oxygen at the surface, the initial step appears to be addition of the oxide to the phosphate ester, which results in a bound dialkyl phosphate and the production of the appropriate substituted phenol. The phosphate ester loses the remaining phenols resulting in a bound iron polyphosphate. The amine antioxidants commonly found in the formulated lubricants were found to negatively impact the fatigue and wear resistance [74]. The most common mechanism for film formation with phosphate esters involves initial adsorption of the phosphate ester on the oxide surface of the iron. One of the alkyl groups is displaced by breaking the P–O bond to give a bound phosphate which reacts further to produce an iron polyphosphate film. If oxygen at the metal surface is limited, breakage of the C–O bond occurs giving the same bound phosphate and the aryl group adds to another aryl group [75]. Under both thermal and tribological conditions, immediately adjacent to the iron surface is found a layer which has been characterized as either amorphous carbon or low order graphite. On top of that layer is found an iron polyphosphate layer which extends to the surface. An

auger depth profile, showing the different layers of the structure is shown in Figure 7. The immediate surface, as shown by X-ray photoelectron spectroscopy, however has a thin layer of organic carbon consistent with the presence of residual aryl groups or alkyl groups (Figure 8). In contrast, if an excess of oxygen is present, the carbon layer is absent but an iron phosphate film is formed that is bound to the bearing surface.

Figure 7. Auger depth profile of a film formed by the deposition of butylated triphenyl phosphate (BTPP) onto an iron foil at 425 °C under nitrogen (sputter rate 1.5 nm/min) [76].
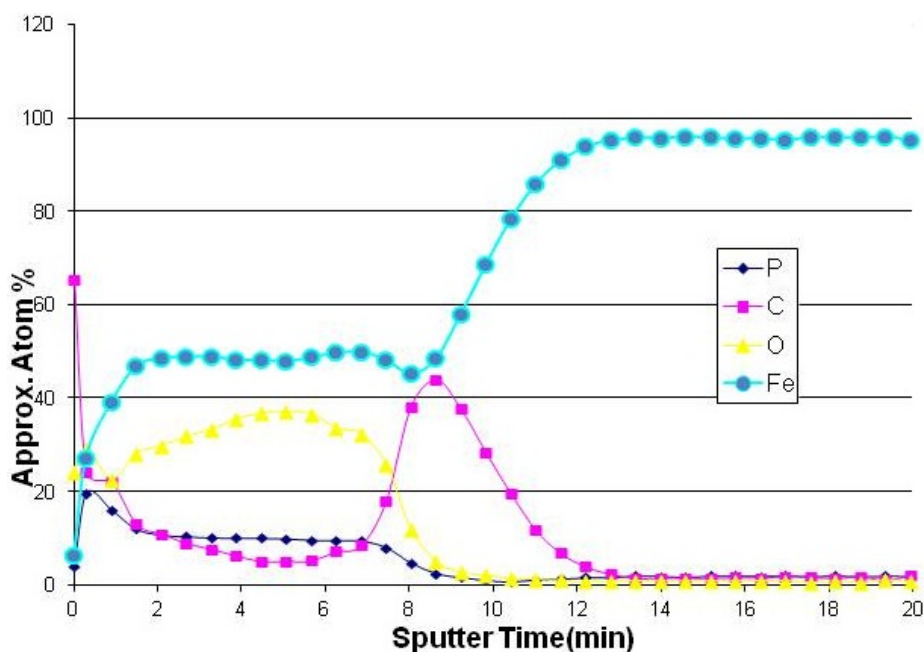
Advances in the performance of modern aircraft engines have required more advanced bearing materials [77]. In general, these materials have resulted in changes in the surface chemistry from primarily iron oxide to a mixture of carbides. A critical question has been the ability of phosphate esters to form a lubricious film on carbide surfaces. Tricresyl phosphate was shown to be beneficial in all of the advanced bearing alloys [78]. The advanced alloys under current study are all carburized stainless steels. In the carburization process the steel is heat treated in the presence of a carbon source to convert many of the surface hydroxyl groups to carbide, in the process forming an extremely hard surface coating. A study of the reactivity of metal carbides with tricresyl phosphate showed that the phosphate esters did not decompose even at high temperatures in the presence of carbides alone, but in the presence the phosphate ester and an ester based lubricant, rapid reaction occurred [79]. The reaction appeared to go through a trans-esterification mechanism that resulted in the less stable alkyl phosphate esters [80]. The formation of phosphate containing films similar to other metals on stainless steel samples has been recently demonstrated [81].

Figure 8. The layered structure of the film formed under reduced oxygen conditions based on X-ray photoelectron spectroscopy and auger depth profiling [75].
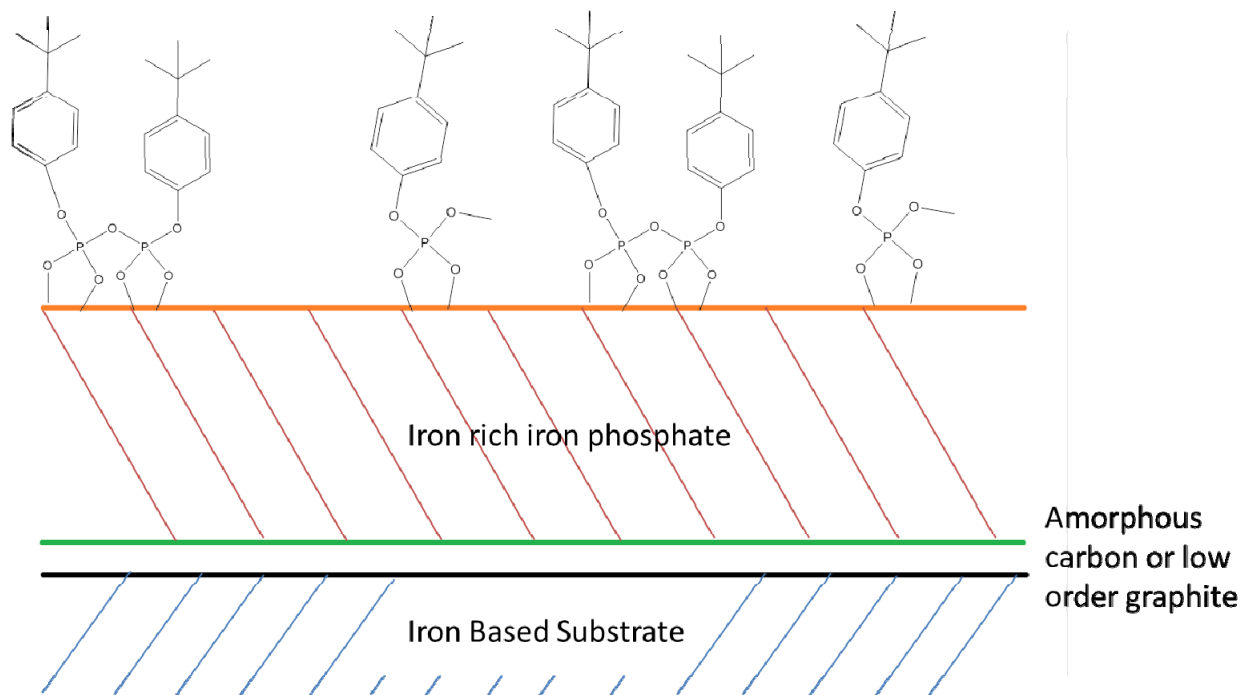

4.2. Safety of Phosphate Esters

One of the major advantages of triaryl and trialkyl phosphates has been their perceived safety. They are non-flammable [82] and have been shown to exhibit low order toxicity with median lethal doses (the dose of a toxic material which results in the death of 50% of an animal population) in the range of 10–20 g/kg [83]. There are, however significant concerns about delayed neurotoxicity of some isomers of triaryl phosphates as well as the products that might be derived from high temperature decomposition of triaryl phosphates in the presence of other additive and the lubricant basestock. In particular, the development of organophosphate-induced delayed neuropathy (OIDN) has been reported as a paralytic condition [84]. A more recent concern has been the possibility of triaryl phosphate entering the cabin of jet turbine aircraft as a part of the bleed air [85]. This has accelerated the search for safer phosphate ester additives [86].

The general toxicity of organo phosphates has been associated with organophosphate inhibition of acetylcholine esterase [87]. This form of acute toxicity is associated with chemical warfare agents and organophosphorus insecticides. Organophosphorus lubricant additives, based on their high LD-50 do not appear to react by this pathway but have other toxicological mechanisms. Organophosphate-induced delayed neuropathy (OIDN) is an alternate form of toxicity which results in lack of coordination, cramping and can progress to paralysis in a period of 7–14 days after exposure to organophosphorus agents. Recovery is very slow and is seldom complete. Of the compounds commonly seen in lubricant additives, tri-*O*-cresyl phosphate (*O*-TCP) is of particular concern in the development of OIDN. Well known exposures to *O*-TCP in adulterated Jamaica Ginger [88] and cooking oil adulterated with jet engine oil containing *O*-TCP have led to greater concern over *O*-TCP [89]. Recent studies on OIDN and aerotoxic syndrome have focused on *O*-TCP frequently present as one of the isomers in the TCP

lubricant additive. The *O*-TCP is oxidized at the benzylic position by cytochrome P450 which is then allows the cyclization with the release of *O*-cresol shown in Figure 9 catalyzed by serum albumin. The product 2-(*O*-cresyl)-4*H*-1,3,2-dibenzodioxaphosphoranone (CBDP) is an irreversible inhibitor of human butyrylcholinesterase and human acetylcholinesterase [90].

Figure 9. Conversion of tri-*O*-cresyl phosphate (*O*-TCP) to 2-(*O*-cresyl)-4*H*-1,3,2-dibenzodioxaphosphoranone (CBDP), and irreversible inhibitor of human butyrylcholinesterase and human acetylcholinesterase.
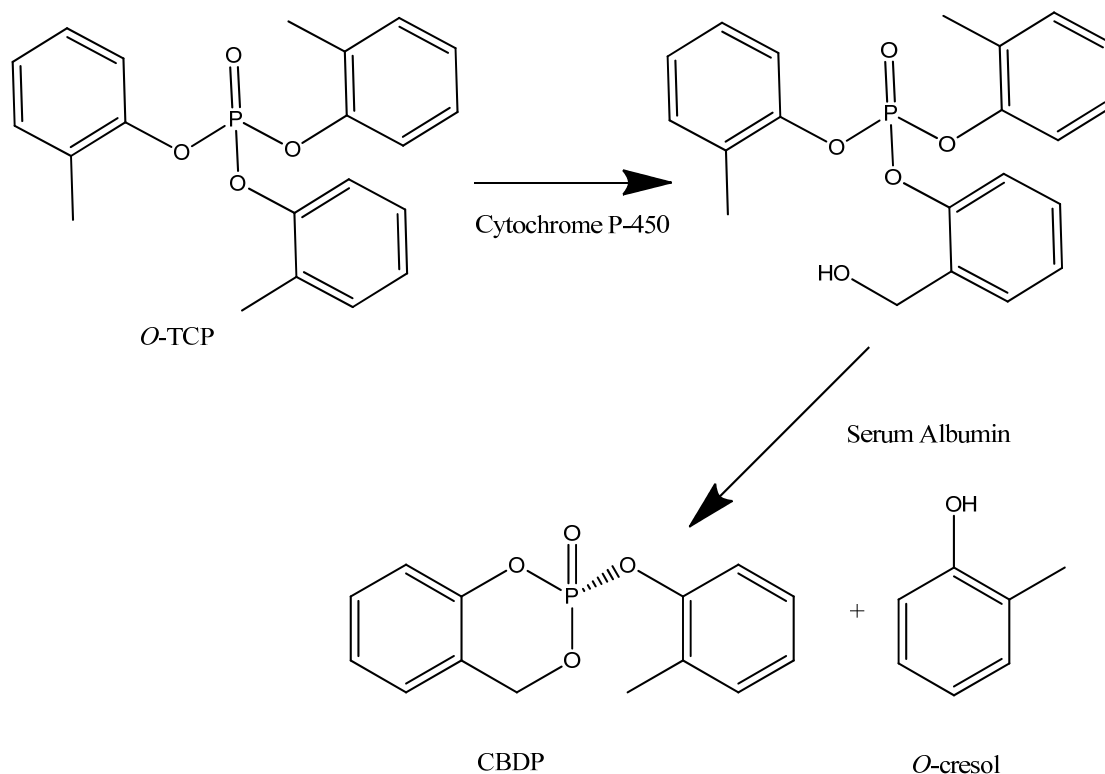
Beyond the concern associated with ortho isomers of TCP and potentially other organophosphorus additives with ortho substitution, there is also concern about products formed when formulated lubricant components react with each other under extreme conditions [91]. The authors noted that the conditions were well above the temperature encountered within engines, but might be encountered in vapor phase lubrication [92]. In particular, the reaction of trimethyolopropane esters with *O*-TCP to form neurotoxic compounds in fires has been studied [93].

The general concern with the toxicity of the triaryl phosphate appears to be with ortho methylated aromatic rings. To avoid this isomer, compounds based on butylated triphenyl phosphate and other aryl phosphates where the ortho isomer or the possibility of oxidation at the benzylic position of an ortho isomer is absent have been developed.

5. Conclusions

Phosphate esters, possibly with sulfur and metals added, have found wide application because of their ability to form films on a wide range of materials. The films are all similar in composition with iron phosphate or iron polyphosphate being a major component. The films adhere strongly to the

substrate, are durable and continue to form as long as there is additive remaining. An important feature is that films can form by different mechanisms depending on the amount of oxygen present. An important aspect of the films formed is that their modulus increases in response to stress, allowing the films to maintain their integrity under extreme loads [43].

While the details of the film and the conditions of film formation are somewhat different for the different additives, the films form an effective coating which reduces friction and wear at the surface. The ability to replace oxygen atoms with sulfur and the possibility of incorporating metals and the presence of a range of organic groups allow for the fine tuning of the additive reactivity to match different lubrication problems. Although environmental and toxicity concerns are present, additives based on the chemistry of phosphate esters are likely to find application well into the future.

Conflicts of Interest

The authors declare no conflict of interest.

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