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The Tribology and Chemistry of Phosphorus-Containing Lubricant Additives

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Abstract

Phosphate esters, thiophosphate esters and metal thiophosphates have been used as lubricant additives for over 50 years. Recently, phosphorus-containing ionic liquids have emerged as a new class of lubricant additives. While the use of phosphorus compounds has been extensive, a detailed knowledge of how they work has been a much more recent development. In this chapter, the use of phosphate esters, thiophosphate esters, metal thiophosphates and phosphorus-containing ionic liquids as antiwear or extreme pressure additives is discussed. The primary emphasis will be on how they form a protective film, which is both durable and reduces friction. The first part of the chapter discusses the use of alkyl phosphates, triaryl phosphates and metal-containing thiophosphate esters with primarily iron- and steel-based bearing materials. The second part of the chapter examines phosphorus-containing ionic liquids and the challenges posed by new bearing materials with different surface chemistries.

Keywords: phosphate ester, thiophosphates, ZDDP, zinc dialkyldithiophosphate, antiwear additive, turbine engines, refrigeration

1. Introduction

Lubricant additives are a critical part of all lubricant systems because they impart properties to the formulated lubricant that the basestock does not possess. Additives allow longer lubricant lifetimes by eliminating certain modes of basestock decomposition. For example, when a lubricant is used, it is exposed to temperatures much higher than the bulk oil temperature for short periods of time. This occurs in the presence of oxygen, which can cause oxidation of the lubricant. Additives can reduce the decomposition of the basestock by

scavenging free radicals formed in the initial stages of the reaction. Aircraft lubricants typically contain the following groups of additives:

- Boundary lubrication additives (antiwear, lubricity and extreme pressure)

- Antioxidants

- Anticorrosion additives

- Antifoaming additives

- Metal deactivators

- Viscosity index improvers

Choices of additives are frequently limited based on the thermal stability of the additive, needs for long lifetimes and tendencies of the additives to form deposits [1].

Organophosphorus compounds are found in a range of formal oxidation states from -3 to +5. Of these oxidation states, compounds in the -3, +3 and +5 oxidation states have particularly important industrial applications [2]. The structures of some of these compounds are shown in **Figure 1**.

| Phosphonium ion P(-3) | Phosphite P(+3) | Phosphate (+5) |
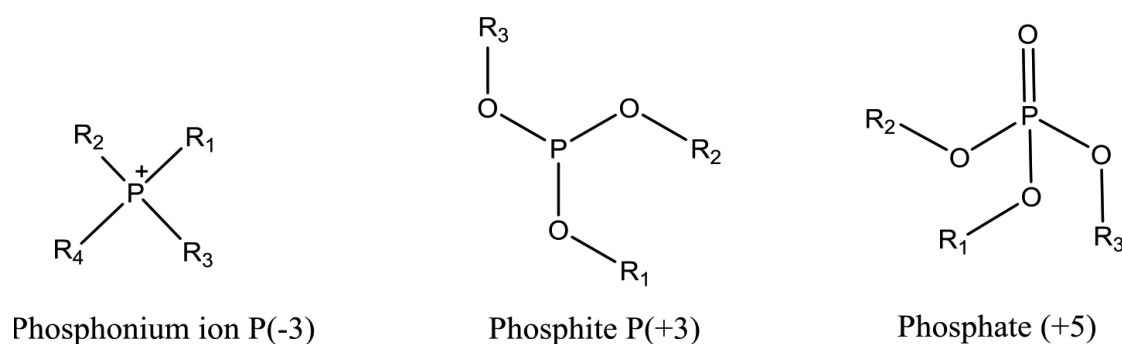
Figure 1. Phosphorus compounds in various oxidation states.

The thermal and oxidative stability of phosphorus compounds, particularly phosphorus in the +5 oxidation state, has led to a number of important industrial applications [3]. The structure of phosphates, for example (**Figure 1**), shows a fully oxidized phosphorus at the center of the molecule. The possibility of exchanging the oxygen atom for either a sulfur or a nitrogen atom greatly increases the variety of compounds as does the ability to include various organic groups attached to the oxygen, nitrogen or sulfur atoms. While organophosphites and organophosphonium ions have important applications, by far the phosphates have found the greatest use.

Initial industrial applications of organic phosphates include fire retardants, especially for the film industry [4] and environmentally degradable pesticides due to their toxicity to insects, but not animals and their relatively high reactivity in the environment [5]. Phosphate esters have been used as surfactants and as brightening agents in detergents [6]. Phosphate esters with a variety of structures and reactivities are commercially available and have found important industrial application. Commonly available compounds include aromatic phos-

phate esters, alkyl phosphate esters, thiophosphates and a number of metal-containing phosphate esters, including zinc dialkyldithiophosphates (ZDDP) [7].

The development of lubricant additives began in response to the need for higher performance lubricants. Many of the initial hydrocarbon lubricating oils contained sulfur and phosphorus-containing species that in hindsight were naturally occurring antioxidants and antiwear agents. These naturally occurring additives however varied substantially as the crude oil sources changed. When it was initially suggested that synthetic additives should be added, they were regarded as an expensive component of unknown use. As time progressed, phosphorus-containing additives became a required part of formulated lubricants in order to meet more stringent specifications [8]. The purpose of this chapter 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.

2. Zinc dialkyldithiophosphates and other metal dithiophosphates

Lubricant additives containing zinc, phosphorus and sulfur originate with a series of patents filed in the 1940s by Lubrizol [9], American Cyanamid [10] and Union Oil [11] claiming a composition that functioned as an antioxidant and a corrosion inhibitor. These additives, now known as ZDDPs, were originally prepared by the reaction of phosphorus pentasulfide (P_4S_{10}) with one or more alcohols to give the appropriate dialkyldithiophosphoric acid. The acid was then neutralized by the addition of zinc oxide to give the product as shown in **Figure 2** [12].
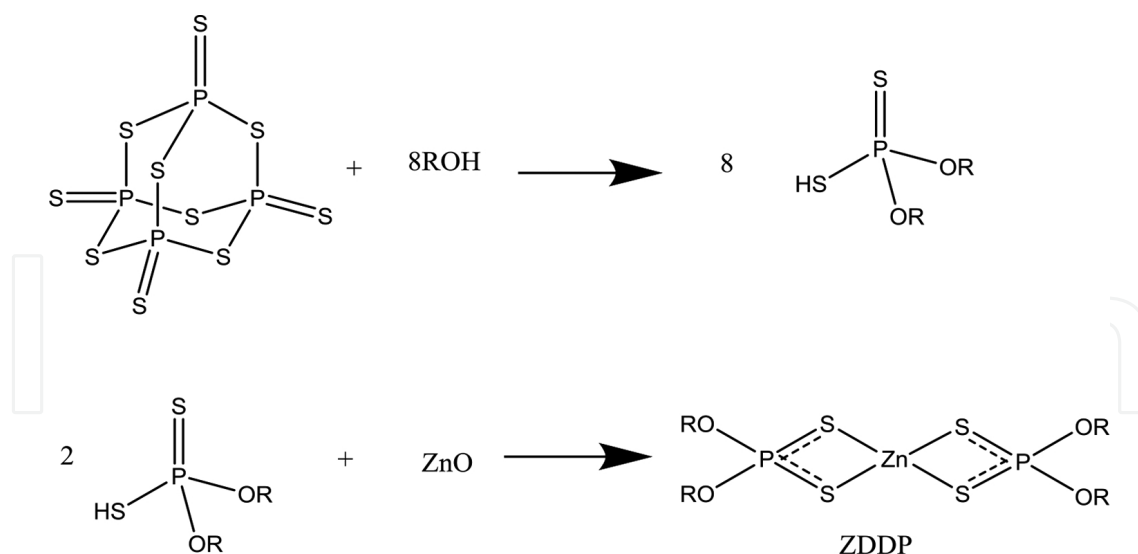

Figure 2. Method for the preparation of ZDDP.

ZDDPs have been prepared with a wide variety of alcohols in order to tune physical properties, including oil solubility and viscosity and chemical reactivity of the resultant additive. In addition, the chemical properties can be adjusted by altering the ratio of zinc oxide to the dialkyldithiophosphoric acid resulting in acidic, neutral and basic ZDDPs [13].

ZDDP was initially applied in industrial oils as an antioxidant. ZDDP appears to react rapidly with peroxy radicals in the oils [14]. In 1955, it was shown that ZDDP could also act as an antiwear additive [15], which led to its primary use in the automotive industry [16]. The use of ZDDP in aerospace and refrigeration industries did not develop because of their need for an ashless additive which made ZDDP unsuitable [17].

2.1. The structure of ZDDP in solution

The interaction of ZDDP with metal surfaces is closely related to its structure in solution. In solution, ZDDP can act as an antioxidant [18], increasing its utility, but the primary use is as an antiwear additive. In solution, acidic and neutral ZDDP exists as an equilibrium between a monomeric and a dimeric form, with the dimer being dominant in toluene or chloroform solution [19]. Quantum mechanical models have suggested a mechanism for the interconversion with two different transition states. The first transition state contains a four-membered ring with two bridging sulfur atoms and the second contains a six-membered ring which leads to the final product that contains an eight-membered ring [20]. Basic ZDDP, in contrast to acidic and neutral ZDDP, incorporates excess zinc oxide into a structure that contains three ZDDP molecules and a zinc oxide [21]. Polymeric forms are observed in the solid state [22], and larger molecules are observed in solution by dynamic light scattering [23]. The structures of these forms are included in **Figure 3**.
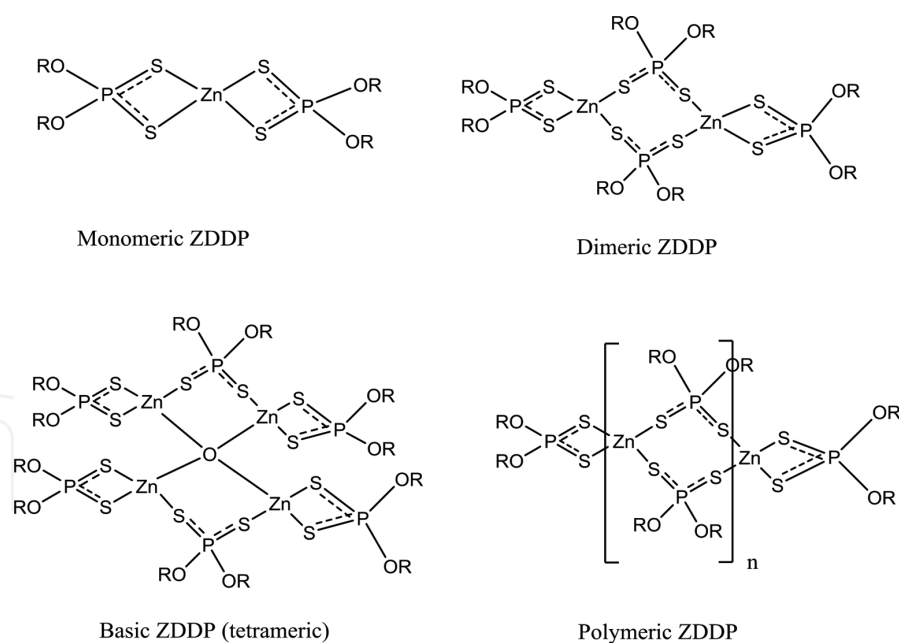
Figure 3. Structures of some of the observed forms of ZDDP.

While there are several structures observed in low-temperature solution, it appears that at high temperatures, basic ZDDP converts to the same structure as neutral ZDDP and gives identical wear test performance [24]. It is also thought that oxidation of the thiophosphate to phosphate is a part of the degradation mechanism [25].

2.2. The reactions of ZDDP at metal surfaces

All antiwear additives operate by forming a protective film on the bearing surface. That film acts to protect the surface during periods of elastohydrodynamic and boundary lubrication when asperity-asperity contact is a major cause of wear. The same film also protects the surface during start-up when there is no lubricant flowing through the system [26]. The composition of the surface film, how it forms and how it can be modified, has been the object of a great deal of research.

An initial model for the species found on metal surfaces begins with the study of the solid state structures of ZDDP. Several structures have been observed, including polymeric [27] and binuclear [28] structures depending on the alkyl groups present in the ZDDP. Solid state nuclear magnetic resonance (NMR) studies have indicated that structures not seen crystallographically exist and that these structures differ from the solution structure [29]. X-ray absorption near-edge spectroscopy (XANES) and 31-P NMR indicated the formation of a surface film and even when there was no phosphorus remaining in solution, the film continued to form. This is an indication that the decomposition of a species in solution precedes the formation of the film [30].

Metal coupons, when they are immersed in a solution of ZDDP dissolved in a lubricant or nonpolar solvent rapidly form a thermal film on the surface of the coupon. Analysis of the films by several techniques indicates that they are not simple zinc or iron compounds such as zinc phosphate, zinc phosphide and iron phosphate [31]. The thermally generated films have similar compositions to the coatings formed inside tribological junctions. Wear reduction is found to be the greatest when a thermal film is formed first, followed by friction between the surfaces (i.e., rubbing motions of a pin on disk) in a ZDDP containing oil to generate the tribofilm [32]. The outermost layer of the thermally generated film is zinc polyphosphate, which is converted to zinc pyrophosphate or zinc orthophosphate deeper in the film [33]. The tribofilms differ from the thermal films because a significant amount of the zinc is replaced by iron [34].

A number of different techniques have been used to study the tribofilms formed by ZDDP. Studies have demonstrated that phosphate must be present in the oil for a wear-resistant surface and once the phosphate is depleted, sulfur causes corrosion inside the wear scar [35]. ZDDP has also been shown to stop the reduction of surface metal oxides the lubricant, forming an easily sheared layer that prevents direct contact between the two surfaces [36]. A commonly proposed mechanism for the reduction of wear involves the formation of pads that cover most of the surface of the bearing. The formation of a linkage isomer [37] that ultimately binds to the metal surface [38] is the initial step, followed by a series of reactions that eliminates the majority of the alkyl substituents and most of the sulfur. These reactions leave a deposit of zinc polyphosphate at the surface. Iron diffusion into this layer gives a mixed zinc polyphosphate/ iron polyphosphate layer with increased iron closer to the surface [39]. The pads appear to be bound to the surface through a thin layer of mixed zinc and iron sulfide [40]. The film thickness eventually stabilizes at a thickness of 40–150 nm [41]. The film is shown schematically in **Figure 4**. The film itself has the interesting property of responding to increased pressure

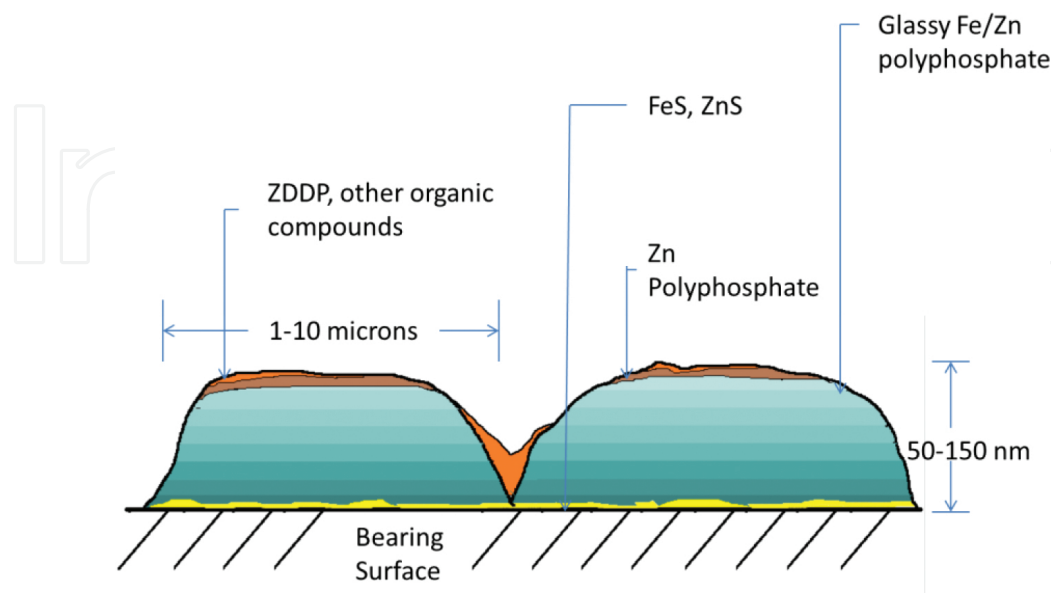through an increase in the modulus of elasticity, which is referred to as smart material behavior [42].

Figure 4. Layered structure of surface film formed from ZDDP.

3. Dithiophosphate esters and related materials

Current environmental standards have significantly reduced the allowed particulate emissions for diesel engine. Metal containing additives frequently clog filters and phosphorus additives can poison catalysts. Lubricants and lubricant additives have been identified as a possible contributor to metals, phosphorus and sulfur in the exhaust stream. In order to reduce particulate emissions, but still take advantage of the advantages of ZDDP like additives, a number of compounds based on thiophosphate and phosphorothionate compounds have been developed as ashless lubricant additives [43]. The structures of some of the ashless thiophosphate-based additives are shown in **Figure 5**.
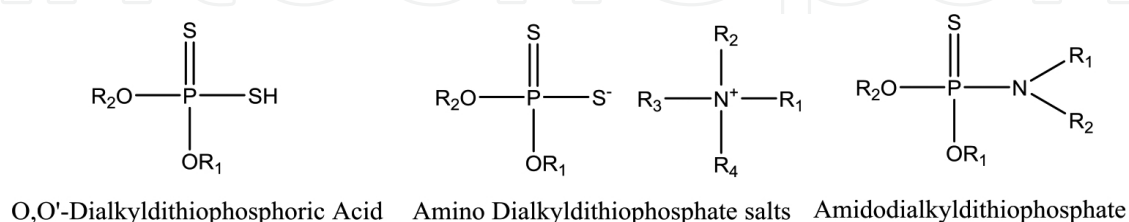

O,O'-Dialkyldithiophosphoric Acid   Amino Dialkyldithiophosphate salts   Amidodialkyldithiophosphate

Figure 5. Structures of some ashless dithiophosphate additives.

A number of lubricant additives have been developed for automotive applications based on O,O'-dialkyldithiophosphoric acids. These compounds are simply ZDDP without the zinc. A

major concern with these additives is the acidity of the S-H group. In order to reduce the total acid number of the additive, the compound can be neutralized with a quaternary ammonium hydroxide forming the ammonium salt [44]. The degree of substitution on the ammonium ion gives good solubility in the oil and leads to potential for property optimization. These amine phosphate additives, actually a type of ionic liquid discussed later, offer some of the highest load carrying capabilities, however suffer from reduced hydrolytic stability and higher resulting acidity during use compared to other additives [45].

Another common class of additives is the amidothiophosphates. They are prepared by the addition of amines to an appropriate thiophosphoryl chloride [46]. Other additives are prepared by the addition of sulfur across the double bond of acrylic acid or an acrylate ester [47]. An alternate approach is to use hydrogen peroxide to oxidize and then dimerize the alkyldithiophosphate [48].

Thermal films form from dialkyldithiophosphates at about 150°C. The films consist of a mixture of iron (II) polyphosphate and iron (II) sulfate [49]. Under tribological conditions, the ashless compounds form thicker films and give better overall performance than ZDDP under the same conditions. The ashless additives also gave shorter chain polyphosphates than ZDDP, but an average film thickness of 400 nm [50].

Triaryl phosphorothionates are another class of molecules that have received significant attention as antiwear additives. These molecules are structurally similar to the phosphate esters, except a doubly bound sulfur atom replaces the oxygen atom. Triphenyl phosphoro-thionate, the parent compound in the series, has received the most study. In solution, triphenyl phosphorothionate is oxidized thermally to form triphenyl phosphate which reacts rapidly with the bearing surface. There appear to be no solid products formed from this reaction [51]. In the presence of iron or steel, a metal catalyzed reaction converts triphenylphosphorothionate to triphenyl phosphate, and the decomposition of triphenylphosphate results in the production of a multilayered solid film on iron or iron oxide [52]. The wear debris analyzed by transmission electron microscopy was found to include a mixture of Fe_3O_4 particles and amorphous material. A mechanism for the reduction of wear included solid particles trapped within the tribofilm. Antiwear additives that produced a film with the smallest number of iron oxide particles resulted in the greatest reduction of wear [53].
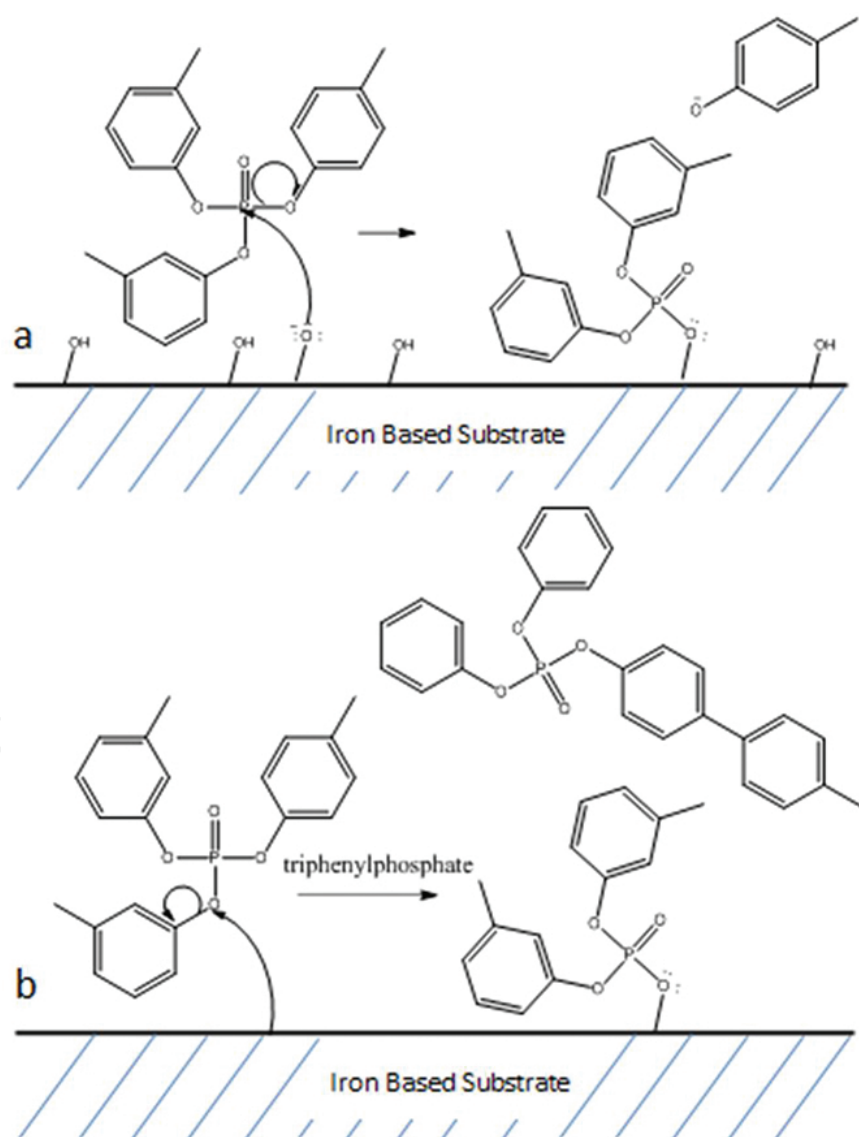
4. Phosphate esters

The initial application of phosphate esters as lubricant additives was more than 60 years ago. While initially developed as antioxidants for aircraft engines, phosphate esters have found increasing use in both automobile engines [54] and refrigeration compressors [55]. Trialkyl phosphates were initially preferred because of their high reactivity [56], but the reactivity also limited their use to moderate temperatures and mild lubrication conditions [57]. Triaryl phosphates and particularly tricresyl phosphate have been known to reduce friction and wear under boundary lubrication conditions since the 1940s [58]. With many applications, especially aviation, moving to synthetic basestocks, the need for effective antiwear additives increased.

In the case of neopentyl polyol basestocks, the formation of a surface film was more important because its presence also reduced the reactivity of the basestock [59]. Although concerns about the volatility and toxicity of the triaryl phosphates have come to light, triaryl phosphates continue to be used. These concerns however have brought about the development of more highly substituted phosphate esters such as butylated triphenyl phosphate as a replacement for tricresyl phosphate. The larger alkyl groups decrease the volatility of the phosphate ester and also make the formation of the *ortho* isomer more difficult.

### 4.1. Mechanism for the modification of metal surfaces by phosphate esters

The knowledge of the interaction of phosphate esters with iron-based surfaces begins with the work on vapor phase lubrication by Klaus [60]. A wide range of techniques have been used to

Figure 6. Reaction of phosphate esters with oxidized (a) and reduced (b) metal surfaces.

the reactions and the structure of the films formed on the surface, including Fourier transform infrared spectroscopy (FT-IR) [61], nuclear magnetic resonance(NMR) [62], and surface methods including x-ray photoelectron spectroscopy (XPS) [63], Auger electron spectroscopy (AES) [64] and x-ray absorption near edge spectroscopy(XANES) [65]. These techniques have demonstrated that tricresyl phosphate forms a multilayer film on steel surfaces which acts as a lubricious polymer. Later work by Forster [66] demonstrated that the diffusion of iron through the phosphate film was the rate-determining step in film formation and caused a lubricious coating to be maintained under wear. Iron is estimated to diffuse at a rate of 1–3×10^{-16} cm^2/sec through the phosphate glass [67].

Phosphate esters are known to react more rapidly with iron oxides than with metallic iron on steel surfaces. In the presence of an oxidized metal surface, a surface oxide or hydroxide initially adds to the phosphate, breaking a P-O bond and resulting in a surface bound dialkyl phosphate and releasing the substituted phenol. Continued reaction releases the remaining substituted phenols leaving an iron polyphosphate. If there is limited oxide or hydroxide at the surface, the C-O bond of the phosphate can be cleaved releasing the aryl group which then adds to an aryl group bound to another phosphate resulting in the same bound diaryl phosphate and a higher molecular weight soluble phosphate ester [68] as is shown in **Figure 6**.
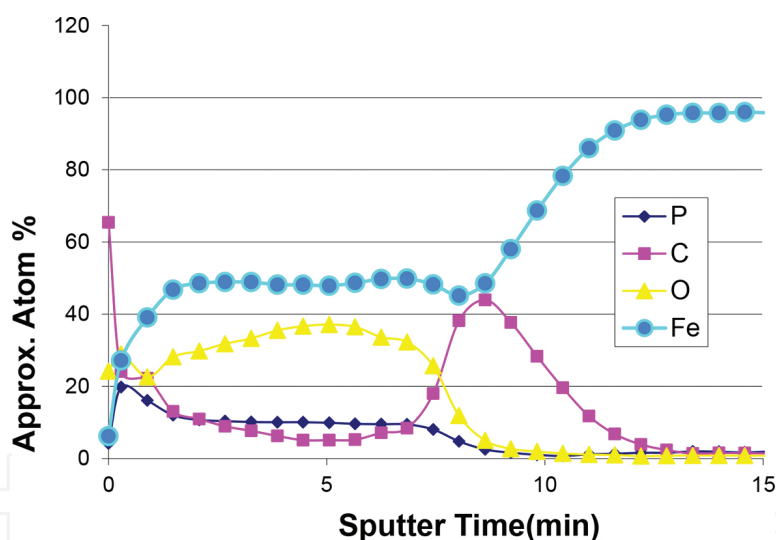
Figure 7. Auger depth profile of a film formed by the deposition of BTPP onto an iron foil at 425°C under nitrogen (sputter rate 1.5 nm/min).

An Auger depth profile showing the composition of the film formed is shown in **Figure 7**. Immediately adjacent to the iron surface, a carbon layer that has been characterized as either amorphous carbon or low-order graphite is observed under both thermal and tribological conditions. A layer of iron polyphosphate then extends to very near the surface of the coating. At the surface of the bearing, a layer containing bound alkyl groups is found as is seen in **Figure 8**. The bound alkyl groups help the surface retain some liquid lubricant upon standing resulting in additional reduction in wear on engine startup before adequate lubricant flow is achieved.
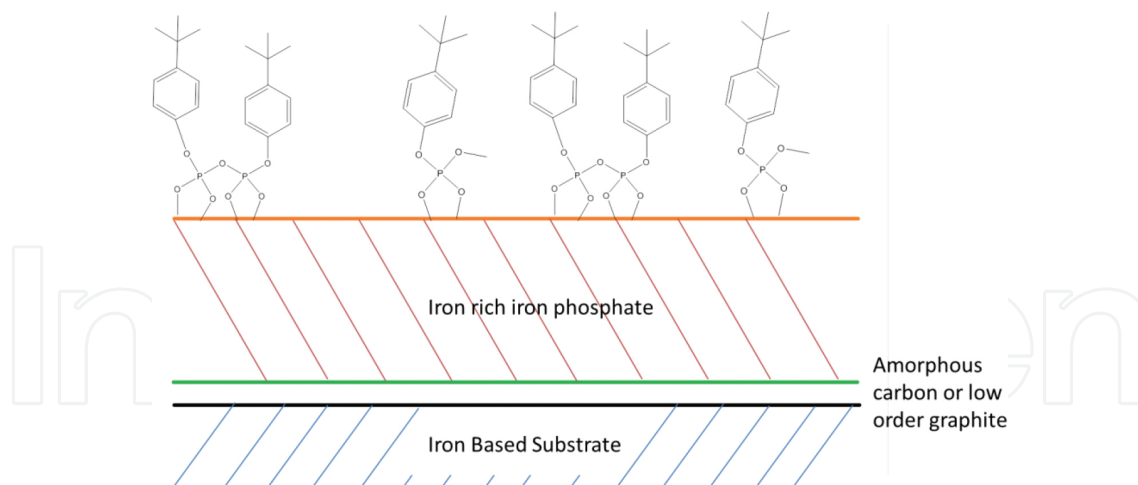
Figure 8. The layered structure of the film formed based on x-ray photoelectron spectroscopy and Auger depth profiling.

4.2. Safety of phosphate esters

One of the major perceived advantages of the phosphate esters in addition to their effectiveness is their relative safety. They are nonflammable [69], break down in the environment to phenols and phosphate and they exhibit only low-order toxicity with LD_{50}s in the range of 10–20 g/kg [70]. There are still concerns about delayed neuropathy that has been associated with certain isomers of the triaryl phosphates, as well as products that might be derived from the decomposition of the triaryl phosphates at high temperatures. There is evidence that a paralytic condition known as organophosphate-induced delayed neuropathy (OIDN) can develop [71].

A recent concern is that triaryl phosphates can enter the cabin as a part of the bleed air, especially given the air force shift from liquid oxygen carried on the plane to oxygen generated on board the aircraft [72]. Tricresyl phosphate has been reported in cabin air on aircraft at levels below toxicity thresholds [73]. Methods have been developed to detect and confirm human exposure to tri (o-cresyl) phosphate [74]. In a limited study of healthy pilots, none had evidence of tri (o-cresyl) phosphate exposure [75]. The contradictory reports indicate there are significant gaps in our knowledge of aerotoxic syndrome. These observations have accelerated the search for safer phosphate ester additives.

The general mechanism for the toxicity of organophosphates is through the inhibition of acetylcholinesterase [76]. This is the same mechanism that is associated with chemical warfare agents and organophosphorus insecticides. Considering the high LD_{50} associated with phosphate ester lubricant additives, it is unlikely that they operate by this mechanism. Organophosphate induced delayed neuropathy (OIDN) is an alternate type of toxicity that results in cramping, loss of coordination and may result in paralysis within 1–2 weeks after exposure. Victims recover only very slowly and the recovery is seldom complete [77].

Of the compounds used as lubricant additives, tricresyl phosphate containing the *ortho* (*o*-TCP) isomer is of particular concern for the development of OIDN. Exposures to *o*-TCP have

occurred in the cases of adulterated Jamaica ginger [78] and cooking oil adulterated with turbine engine oil [79]. Aerotoxic syndrome and OIDN have recently focused on *o*-TCP present as one of the isomers present in the additive even though less than 2% of the TCP is permitted to be the *ortho* isomer [80].
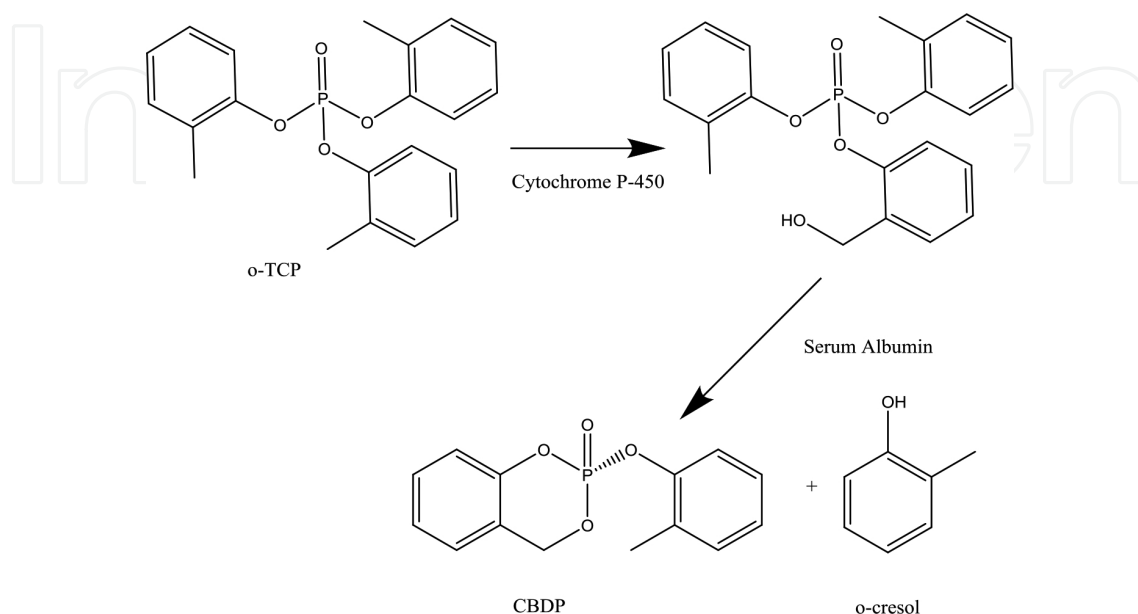
Figure 9. Conversion of *o*-TCP to CBDP, and irreversible inhibitor of human butyrylcholinesterase and human acetyl-cholinesterase.

The mechanism of OIDN by *o*-TCP is thought to begin with the benzylic oxidation of the *ortho* methyl group to give a benzyl alcohol by cytochrome P-450. The alcohol then cyclizes in a reaction catalyzed by serum albumin with the release of cresol as is shown in **Figure 9**. The cyclization product 2-(*o*-cresyl)-4H-1,3,2-dibenzodioxaphosphoranone (CBDP) is an irreversible inhibitor of human butyrylcholinesterase and human acetylcholinesterase [81].

In addition to the concern for the toxicity of the *ortho* isomers of TCP, there is concern about the products formulated lubricant components react with each other under extreme conditions. In particular, trimethylolpropane esters (a component of many neopentyl polyol ester-based basestocks) react with *o*-TCP to form neurotoxic compounds in fires [82, 83]. Currently available TCP contains only *meta* and *para* isomers, however there is evidence that isomerization to form *ortho* isomers is possible under engine conditions. Another approach is to remove the possibility of reaction at benzylic protons by the use of t-butyl groups as substituents on the aromatic rings.

5. Phosphorus-containing ionic liquids

In many lubricant applications, there is a need for increased durability, increased service intervals, reductions in friction and reductions in emissions. Phosphorus-containing ionic

liquids have demonstrated potential in solving some of these problems [84]. Ionic liquids have very low vapor pressures and tend to be soluble in a wide range of nonpolar liquids. They can be prepared with differing properties, depending on the nature of the anion and the cation, modification of which can involve a number of central atoms. Since the topic of this work is phosphorus containing species, only species containing phosphorus in either the anion or the cation will be considered.

In order to have an ionic compound that is liquid at room temperature, large irregularly shaped ions are required. Frequently, these compounds incorporate long organic substituent groups which also impart solubility in organic liquids. Many of these ionic liquids are miscible with hydrocarbon-based lubricants. Compounds can contain phosphorus in the cation, anion or both ions. Phosphorus-containing anions have been shown to be the most effective [85]. These compounds also have a tendency to interact strongly with metal surfaces to form a thin protective phosphorus-containing film under boundary lubrication conditions [86]. It has also been shown that phosphorus-based ionic liquids provide a decrease in friction and wear in used diesel engine lubricants where the additives had been depleted but an increase in wear was observed when the additives had not been depleted. This would indicate interference between phosphorus-containing ionic liquids and existing antiwear additives [87].

Ionic liquids can contain phosphorus either as part of the cation (a phosphonium ion) or the anion (a phosphate ion). Studies of alkyl imidazolium phosphate ionic liquids formed a phosphate containing layer on steel contacts that was thought to also incorporate the imidazolium ion which reduced friction [88]. Some initial investigations implied that only phosphate containing ionic liquids would form a lubricious film, and studies of phosphonium-based ionic liquids with nonphosphate anions have been shown to also form a phosphorus-containing film and ionic liquids with a nonphosphate anion performed better under high loads [89]. It appears that all phosphorus-containing ionic liquids operate by similar mechanisms where a tribo-boundary film is formed as a top layer and beneath that layer is a plastic deformation zone [90].

6. Advanced bearing materials

The desire for more energy efficient and more powerful turbine engines for military and aerospace applications has led a push for lighter bearing materials that can withstand higher temperatures and are more durable. Greater durability and temperature stability can be achieved by the development of either harder metal alloys or ceramic bearing materials. These more exotic materials however may not function properly with the current lubricant and additive packages.

6.1. Carburized metal alloys

One approach to achieve higher speeds and higher temperatures particularly for military aerospace applications has led to the development of a new series of metal alloys. These alloys have a bulk composition that is somewhat similar to existing bearing materials, however they

are either carburized or nitrided during the heat treating step. This added step forms a hard coating on the surface of the bearing that extends into the top 50–100 μM of the material. Carburization during heat treatment consists of heating the material in the presence of a reactive carbon species such as methane of carbon monoxide. The process converts the surface of the material from the normal oxides and hydroxides to a surface that contains mainly carbides. Similarly, the nitriding process converts the surface to nitrides by heating the material in an atmosphere of a reactive nitrogen species such as nitrous oxide.

The primary concern associated with carburized steels is due to the change in surface chemistry from oxides and hydroxides to carbides. Phosphorus-containing additives typically react with the oxide surface to displace one or more of the organic groups, forming a layer that contains an iron phosphate polymer that is durable and lubricous. In the absence of the oxides, it is unknown whether the phosphates will bind. An additional concern is the known reactivity of certain metal carbides with phosphate esters and lubricant esters [91]. Initial work has shown that phosphate esters react with the nonheat treated Pyrowear 675 rods under similar conditions as many other steel coupons [92]. The reactivity of the carburized steels with ester-based lubricants and phosphate esters are ongoing.

6.2. Ceramic bearings

Ceramic bearings have been investigated for a number of high-temperature applications in turbine engines. In general, unlubricated use has resulted in poor performance, but with an appropriate lubricant good performance was achieved [93]. Phosphate esters were found not to react with either silicon nitride or silicon carbide under conditions similar to those seen in steel bearings. At higher temperatures, a film is formed but it is ineffective in extending the life of the bearing [94]. In order to form an effective coating, a pretreatment which introduces iron onto the surface is required [95].

7. Conclusion

Phosphate esters and related compounds with sulfur and metals added have found wide application because of their ability to form thermal and tribological films on a wide range of materials. The mechanisms of film formation differ for different members of this series, but they all result in the formation of a tribofilm that is both lubricious and durable. The ability to make changes in the organic groups and the atoms forming the connections to the phosphorus atom allow compounds with a range of physical properties and reactivities to be prepared. A greater understanding of additive reactivity, as it pertains to the formation of durable films on metal surfaces, will allow the development of more effective phosphorus-containing additives. Although environmental and toxicity concerns are present, additives based on the chemistry of phosphorus-containing additives are likely to find application well into the future and the development of new materials has the promise to reduce those concerns.

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