

***Is More Always Better?* Tribofilm Evolution and Tribological Behavior Impacted by the Concentration of ZDDP, Ionic Liquid, and ZDDP-Ionic Liquid Combination**

Yan Zhou^{1,}, Joel Weber¹, Michael B. Viola², Jun Qu^{1,*}*

1. Materials Science and Technology Division, Oak Ridge National Laboratory, USA

2. General Motors, USA

* Corresponding authors, e-mails: zhouyansdu@gmail.com; qujn@ornl.gov

Abstract

Anti-wear additives (AWs), like zinc dialkyldithiophosphates (ZDDPs), have been used in lubricants for more than a half-century, and more effective candidate AWs, like oil-soluble ionic liquids (ILs), are emerging. However, there is a lack of fundamental understanding of how the AW concentration impacts the tribochemical activities at the contact interface. This study systematically investigated the friction and wear behavior in correlation to the tribofilm morphology and composition as a function of the concentration of a ZDDP, a phosphonium-alkylphosphate IL, and an IL+ZDDP combination. The ZDDP concentration rising from 0.4 to 6.4 wt% caused a proportionally increased friction coefficient, which was well correlated to a thicker, rougher, and more brittle tribofilm. This was further understood by the decreasing phosphates but increasing sulfur compounds in the ZDDP tribofilm. In contrast, the IL and IL+ZDDP maintained a low and stable friction coefficient at 0.5 wt% or above. There was no sulfur in the IL tribofilm and the sulfur compounds were maintained at a very low level in the tribofilm for IL+ZDDP even at high concentrations. Results suggested minimizing the sulfur content in the tribofilm would be an effective way to control the friction. An interesting V-shape relationship between the AW concentration and the wear loss was observed for both the IL-containing AWs, with an optimum at 2 wt% for the IL alone and at 0.46–0.92 wt% for the IL+ZDDP, respectively. A unique heat map was created using the phosphorus binding energy distribution to reveal the phosphate polymerization at different depths of the tribofilms, which provided additional insight for the tribofilm evolution.

Keywords: lubricant, anti-wear additive concentration, ionic liquid, ZDDP, tribofilm

1. Introduction

Anti-wear additives (AWs) in lubricants are essential for protecting the contact surfaces from scuffing and wear. Conventional zinc dialkyldithiophosphates (ZDDPs) have been successfully used for over 70 years.¹ ZDDPs are capable of decomposing and then self-reacting to deposit a tribofilm primarily composed of metal phosphates and oxides.²⁻³ The concentrations of conventional AWs in practice are based on empirical experience, EPA restrictions, and costs, but there is lack of mechanistic insights of the effects of concentration on the functionality. Gao et al.⁴ performed a systematic study on the AW performance of secondary ZDDP at different temperatures. There seemed a weak trend, if any, with a higher concentration leading to lower wear. However, for a given oil temperature, wear varied by up to 200% between two adjacent concentrations; and for a given ZDDP concentration, wear showed little correlation to the temperature with change up to 300%.

Oil-soluble ionic liquids (ILs) have recently developed as next-generation AWs and gained significant interest from both the fundamental and application sides.⁴⁻¹³ Their unique physiochemical properties, such as ashless and inherent polarity for strong surface adsorption, make their tribological behavior and tribofilm formation mechanism¹⁴⁻¹⁸ different from the conventional ZDDPs.¹ While the literature on using ILs as lubricant additives involved various concentrations^{4-11, 13, 15-18, 23, 25-26}, there is no clear trend for the effects of the IL content on the lubricating behavior. Gusain et al. showed that increasing an ammonium bis(salicylato)borate IL from 1 to 2.5 wt.% resulted in little reduction in wear rate.¹⁹ In another study, friction and wear remained literally unchanged when the amounts of ammonium phosphite ILs were increased from 0.5 to 3 wt.%.²⁰ Furthermore, imidazolium-based ILs were reported to even worsen their AW performance at a higher content.²¹⁻²² In contrast, an effort exploring the impact of the concentration of a phosphonium-phosphate IL in oil lubrication using atomic force microscopy showed that the lateral (friction) force stayed the same from 0.01 to 0.1 mol % but reduced significantly at 0.5 and 1 mol %.¹² One specific group of ILs have recently shown synergistic effects with a ZDDP in wear protection²³ while another exhibited ultra-low friction when used together with an organic frictional modifier (FM).²⁶ The impact of the concentration of IL+ZDDP or IL+FM is not fully explored.

In this study, we investigated the impact of AW concentrations for a secondary ZDDP (0.1–6.4 wt.%), a phosphonium-alkylphosphate IL (0.13–8.32 wt.%) and IL+ZDDP

combinations ((0.065+0.05) – (4.16+3.20) wt.%) at equivalent phosphorus concentrations (100–6400 ppm). The friction and wear behavior was correlated with the worn surface morphology and tribofilm composition to gain fundamental insights. Surface characterization was carried out using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS).

2. Materials and Methods

The base oil used in this work was a poly-alpha-olefin (PAO) with a kinematic viscosity of 4 cSt at a temperature of 100 °C (supplied by ExxonMobil). Two AWs were elected to study: a secondary ZDDP that contains 5–10% mineral oil, and a tetraoctylphosphonium bis(2-ethylhexyl) phosphate IL ([P₈₈₈][DEHP]). This IL was selected because of its synergistic effect with ZDDP as reported previously.²⁷ ZDDP was supplied by GM and the IL was synthesized in house following the procedure previously described²⁸ and the IL purity was >98%. The IL is fully miscible in the base oil, and the ZDDP has oil solubility of 1–2 wt.% at room temperature.

For the IL+ZDDP, three molecular ratios between the IL and ZDDP: 2:1, 1:1, and 1:2 were tested. Our previous work has discovered a synergistic effect between this particular pair of IL and ZDDP at 1:1 molecular ratio and a ligand exchange between the IL and ZDDP was found to produce zinc alkylphosphate alkylidithiophosphate (ZOTP)²⁷. Since each ZDDP molecule contains two dithiophosphates, using a ratio of 2:1 for IL:ZDDP was thought to possibly exchange both dithiophosphates of the ZDDP with the alkylphosphates of the IL to presumably produce zinc alkylphosphate (ZOOP). For comparison, a ratio of 1:2 for IL:ZDDP was selected to produce a half amount of ZOTP. Results (Fig. 1) suggested that the optimal molecular ratio for IL:ZDDP is 1:1, which was then used in the later tests to study the impact of the phosphorus content.

AWs were added alone or in combinations to the PAO at a specific concentration with respect to phosphorus content in ppm. For example, 800 ppm P content requires 0.80 wt.% ZDDP, 1.04 wt.% [P₈₈₈][DEHP], or 0.40 wt.% ZDDP plus 0.52 wt.% [P₈₈₈][DEHP]. Table 1. correlates the P content and AW concentration. Each lubricant was sonicated using a Symphony Ultrasonic Cleaner for 15 mins before testing to improve the AW distribution in the oil, particularly for the concentrations above the solubility.

Table 1. Correlations between the AW concentration and phosphorus content in oil

P content (ppm)	ZDDP concentration (wt.%)	IL concentration (wt.%)	IL+ZDDP (1:1) concentration (wt.%)	IL+ZDDP (1:2) concentration (wt.%)	IL+ZDDP (2:1) concentration (wt.%)
100	0.10	0.13	0.065 + 0.05		
200	0.20	0.26	0.13 + 0.10		
400	0.40	0.52	0.26 + 0.20		
800	0.80	1.04	0.52 + 0.40	0.35 + 0.53	0.69 + 0.27
1600	1.60	2.08	1.04 + 0.80		
3200	3.20	4.16	2.08 + 1.60		
6400	6.40	8.32	4.16 + 3.20		

All lubricants were tested using a ball-on-flat reciprocating sliding configuration, where a 10-mm diameter hardened AISI E52100 steel ball was used to slide against a CL35 grey cast iron flat on a reciprocating tribometer (Plint TE77). The steel ball met the specifications of ASTM A295 with hardness of Rockwell C60 and the cast iron flat was polished using P1200 SiC abrasive paper. Both the ball and flat were cleaned with isopropanol alcohol before each test. Each testing condition was repeated for 2–3 times. Testing parameters include a normal load of 100 N, an oscillation frequency of 10 Hz with a 10-mm stroke, a sliding distance of 1000 m, and an oil temperature of 150 °C. The lubrication regime was determined to be boundary lubrication based on lambda ratio calculation.²⁶

Samples were sonicated in isopropanol alcohol for 2 min before surface characterization. Wear volume was quantified by using a white light interferometer (Wyko NT9100) and the wear rate was calculated by normalizing the wear volume by the load and sliding distance. Because of the much higher wear resistance of the steel ball than the cast iron flat, the material loss was dominantly from the cast iron flat (two orders of magnitude higher than that from the steel ball). Thus, wear results and worn surface characterization were focused on the cast iron flats in this study. Roughness (R_a) of the cast iron wear tracks was measured using a contact profiler (Mahr M2 perthometer). Worn surface morphology and chemical composition were examined by SEM (Hitachi S4800 field-emission SEM) and EDS, respectively. Further chemical analysis was conducted using X-ray photoelectron spectroscopy (XPS) on a Thermo Scientific K-Alpha XPS

system, with a signal acquisition at 400 μm diameter spot in the middle of a wear track. Composition-depth profiles were aided by argon-ion sputtering at 3.5 keV, and the acquisition time was up to 2500 sec. All XPS data were analyzed using Thermo Advantage software (version 4.61, Thermo Fisher Scientific). The position of carbon 1s peak was used to check the possible charging and no noticeable peak shift was observed.

3. Results

3.1. Optimal ratio between IL and ZDDP

[P₈₈₈][DEHP] and the secondary ZDDP showed a synergistic effect when used in combination at a 1:1 molecular ratio.²⁷ However, whether 1:1 is the optimal ratio is still being explored. Here, we added the IL and ZDDP together to the PAO at three molecular ratios, 1:2, 1:1, and 2:1, while maintaining a constant 800 ppm phosphorus content. The lubricants were then evaluated in the ball-on-flat reciprocating sliding test and Figure 1 compares the wear rates of the cast iron flats (the steel ball wear is two orders of magnitude smaller and it was therefore neglected). The IL or ZDDP alone already reduced the wear compared with the neat PAO. For IL+ZDDP, while all three combination ratios outperformed either the IL or ZDDP alone and the ratio of 1:1 seemed to be the best. The IL+ZDDP synergy was believed as a result of anion-exchange between the IL and ZDDP molecules to produce the critical new compound of ZOTP²⁷ and the 1:1 molecular ratio would max out the ZOTP concentration in the oil at a given P content. Thus, further investigation of the IL+ZDDP concentration was carried out on the ratio of 1:1. Moreover, scuffing occurred during tests with PAO but the addition of AW(s) eliminated such incidents, resulting in smaller variations in wear.

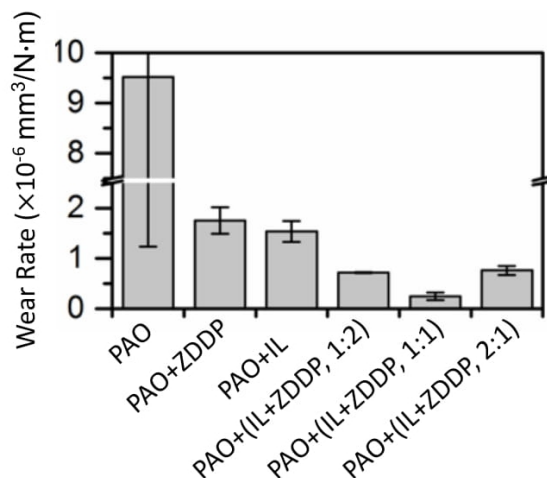


Figure 1. Wear rates of the cast iron flats tested in PAO, PAO+IL, PAO+ZDDP, and PAO+(IL+ZDDP) at 1:2, 1:1, and 2:1 molecular ratios between the IL and ZDDP. Additives were supplied at a total 800 ppm phosphorus content in each lubricant.

3.2. Optimal concentrations of IL, ZDDP, and IL+ZDDP

Figures 2a and 2b present the wear rates and the steady-state coefficient of friction (COF) for the PAO containing the ZDDP, IL, or IL+ZDDP at a variety of concentrations. The ZDDP alone showed little correlation between its concentration (100–6400 ppm of P) and the wear rate, which is similar to the literature report.²⁹ Using the IL alone showed that the wear rate was reduced when the P content was increased from 100 to 1600 ppm, where the wear protection reached the maximum; further increase in the concentration (up to 6400 ppm P content) had little effect. For IL+ZDDP, both the wear rate and COF resembled a large “V” trend with the optimal concentration around 400–800 ppm of P.

The friction behavior appeared to respond differently to the AW concentration. For using the ZDDP alone, the COF dropped when the P content increased from 100 to 400 ppm, but then increased along with the P content from 400 to 6400 ppm. The rising COF was associated with the increased roughness of the ZDDP tribofilm produced at a higher ZDDP concentration, as shown in Figure 2c. For the IL, the friction gradually decreases at a higher concentration in the entire range (100–6400 ppm of P). The IL+ZDDP exhibited a quick reduction in friction when the P content was increased from 100 to 400 ppm and stayed at the lower level for further increase in concentration.

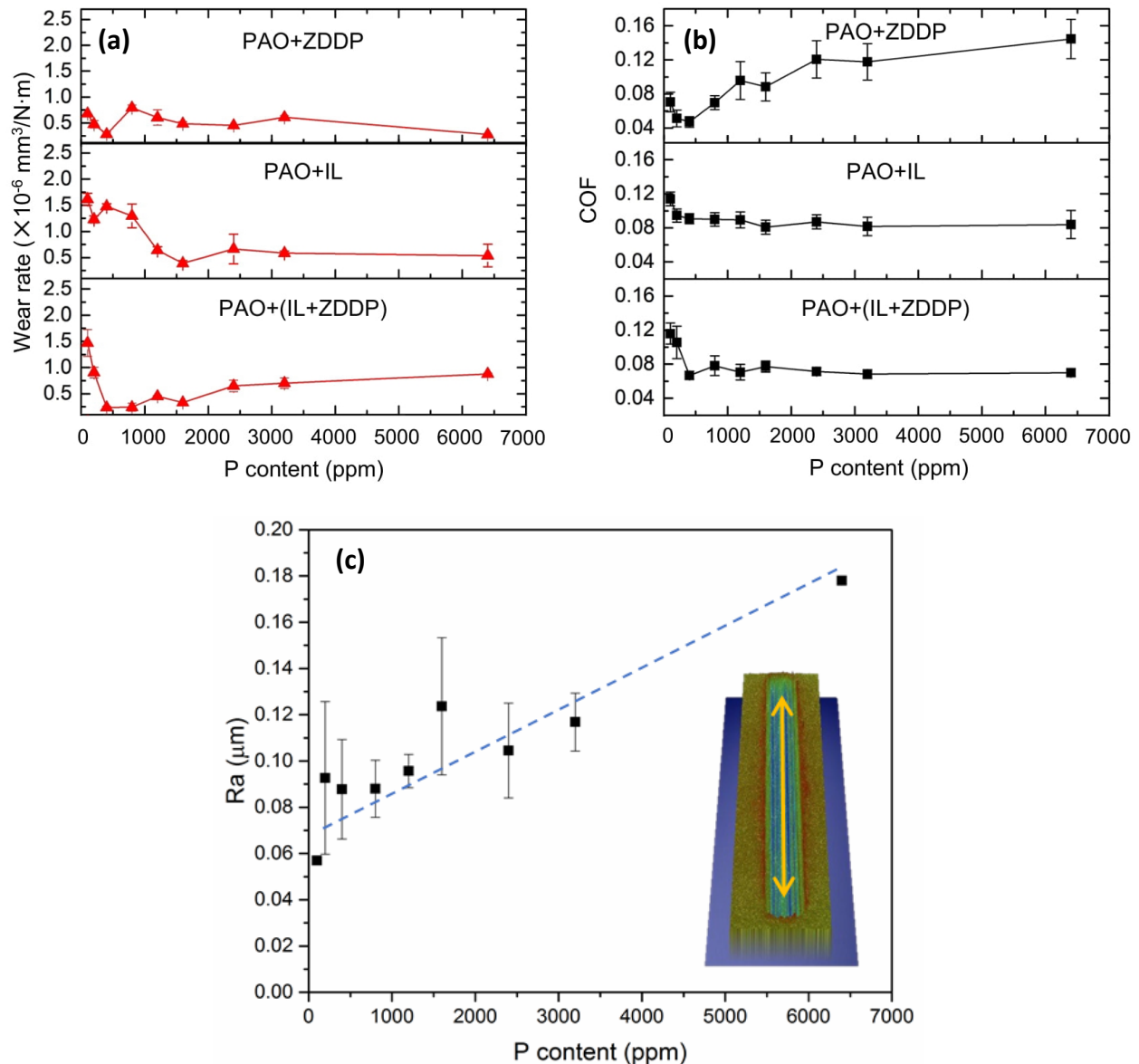


Figure 2. Impact of the AW concentration on tribological behavior. (a,b) Wear and friction results of various concentrations (represented by the phosphorus content) of ZDDP, IL, and IL+ZDDP combination in a PAO base oil. (c) Roughness of the worn surfaces produced by PAO+ZDDP at different phosphorus contents.

3.3. Surface morphology examination and compositional analysis using SEM/EDX

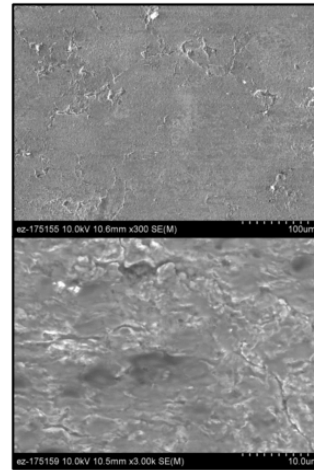
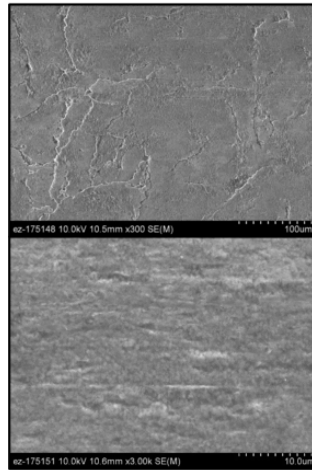
Surface morphology and compositional characterization of the wear tracks on the cast iron flats was achieved using SEM imaging accompanied by EDX analysis. (Note: the CL35 cast iron contains silicon of 1.8-2.3 wt.%, which resulted in the Si peak in the XPS spectra.) Figure 3

shows the worn surfaces that were lubricated by PAO+ZDDP with various ZDDP concentrations (presented in phosphorus contents of 100, 400, 800, 1200, 3200, and 6400 ppm). In the range of 100–800 ppm P in the oil, the worn surfaces appeared relatively smooth and the increased Zn, P, S contents on the worn surface suggested either a thicker tribofilm or a higher tribofilm coverage, or both. For the worn surface, it was also noticed that the P and O peaks were significantly higher than the S peak, which implied that the tribofilm was primarily composed of metal phosphates and oxides and contained only a small amount of metal sulfides. Starting at 1200 ppm P content in the oil, the worn surface appeared to be rougher, in agreement with the roughness measurement (Figure 2c), with darker patch-like material, a classic feature of ZDDP-induced tribofilms. When lubricated by the oil containing 3200 ppm P content, the tribofilm started cracking and fracturing. The tribofilm formed in the 6400 ppm P oil clearly showed signs of delamination. The EDX spectra revealed the compositional change when the oil's P contents increased from 800 to 1200 ppm and above: the tribofilm's S peak increased significantly but its P and O peaks dropped in the meantime. At 3200 or 6400 ppm P content in the oil, the tribofilm seemed to be dominated by metal sulfides (ZnS and FeS), which are likely more brittle than metal phosphates and responsible for the tribofilm fracture and delamination. It was noticed that the Zn content in the tribofilm had no clear trend at lower ZDDP concentrations in the oil (100–1200 ppm P content) but it started increasing along with the oil's ZDDP concentration from 1200 to 6400 ppm.

P= 100 ppm

400 ppm

800 ppm



P= 1200 ppm

3200 ppm

6400 ppm

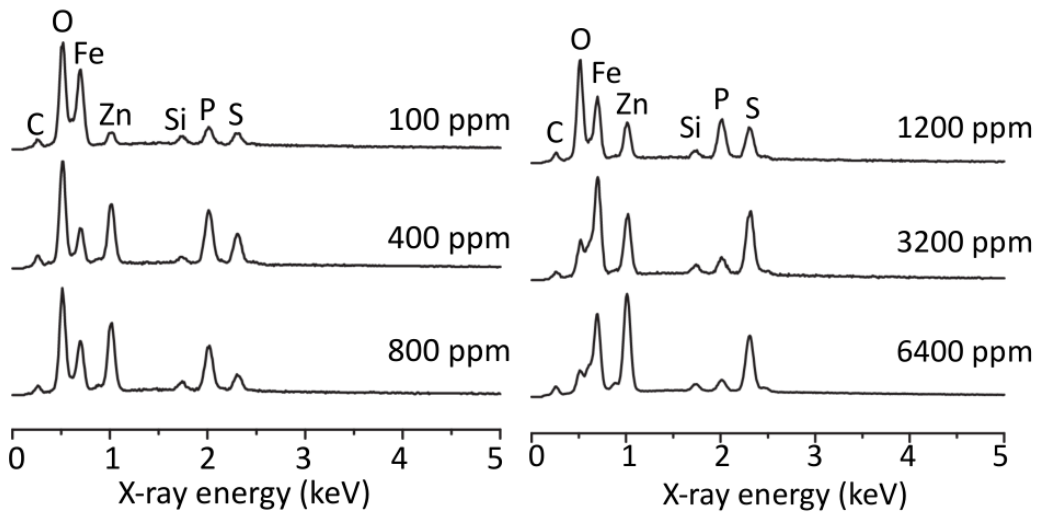
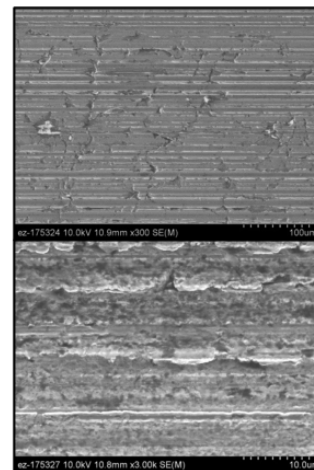
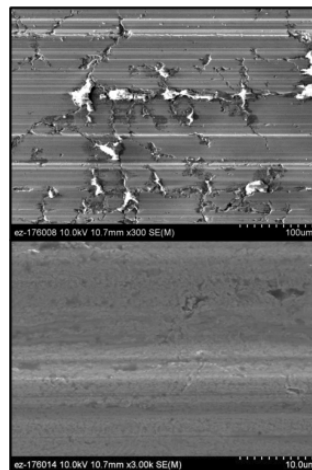
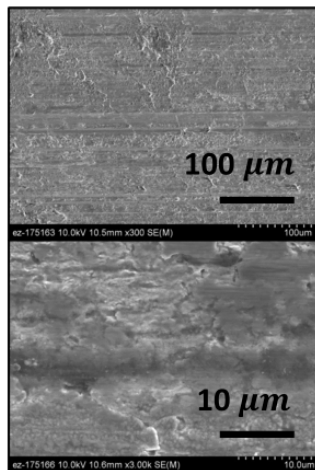


Figure 3. SEM images and EDX spectra of the cast iron worn surfaces generated in PAO+ZDDP lubricants with various ZDDP concentrations (presented in phosphorus contents).

The worn surface morphology and composition indicated a distinct tribofilm formation progress for the PAO oil containing the IL at various concentrations (presented in phosphorus contents), as shown in Figure 4. At 200 ppm P content in the oil, the worn surface showed little sign of tribofilm macroscopically, though small tribofilm patches were detected under higher magnification imaging. Accordingly, EDX barely detected a small amount of phosphorus. When the IL concentration in the oil was increased to 800 ppm P content, classic patch-like tribofilm appeared with fairly large surface coverage. Interestingly, the phosphorus peak in the EDX spectrum was still rather low, indicating that the tribofilm was relatively thin. In contrast, the P peak of the worn surface became much more significant, implying a thicker tribofilm, on the worn surface tested in the PAO+IL oil containing 1600 ppm phosphorus. This may help explain why the PAO+IL oil provided much better wear protection at the phosphorus content at 1200 ppm and above (see Figure 2).

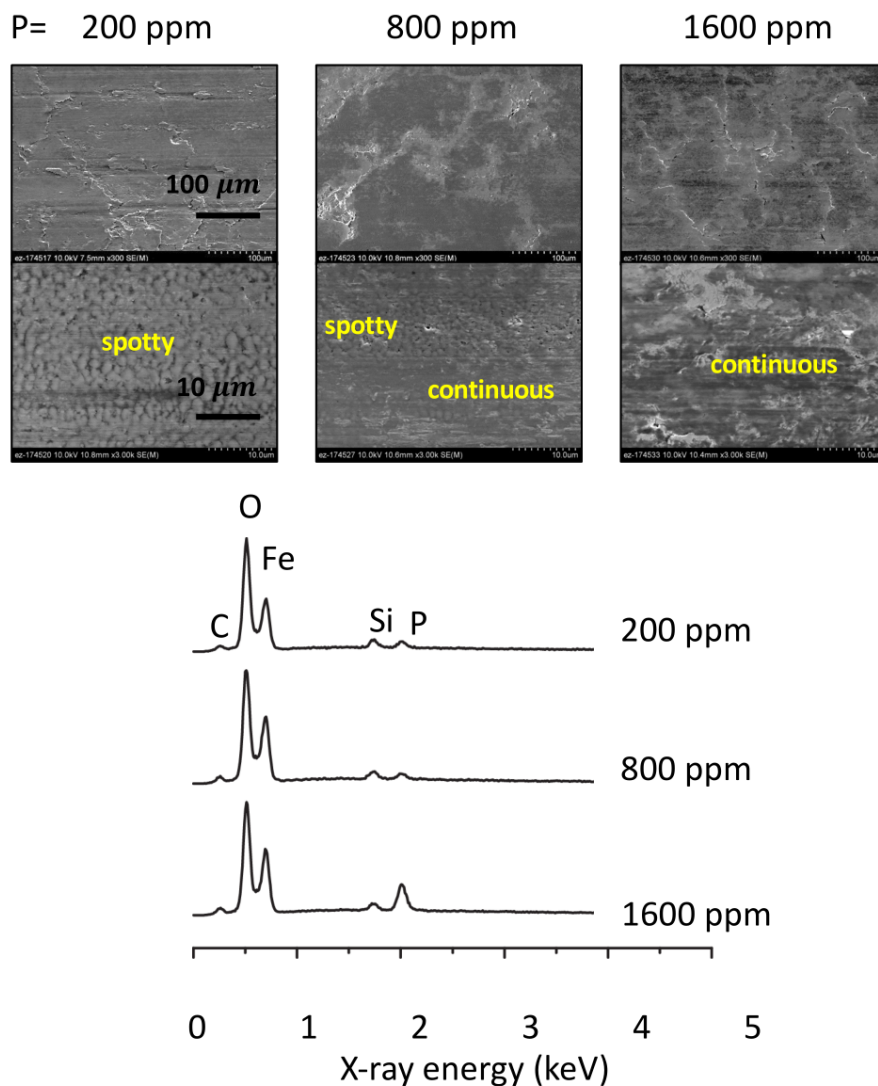
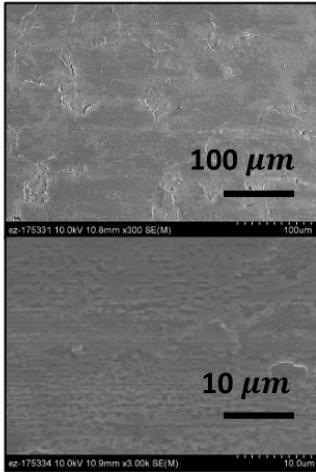


Figure 4. SEM images and EDX spectra of the cast iron worn surfaces generated in PAO+IL lubricants with various IL concentrations (presented in phosphorus contents).

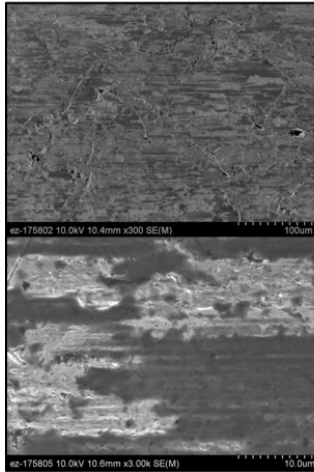
In lubrication of PAO+(IL+ZDDP), the effects of additive concentration on the tribofilm morphology and composition seemed quite different than those in either PAO+ZDDP or PAO+IL, as shown in Figure 5. As indicated by the EDX spectra, PAO+(IL+ZDDP) produced an interesting inverted V-shape trend for the Zn and P contents in the tribofilm: increasing along with the P content in the oil from 44+44 to 200+200/400+400 ppm, and then started decreasing at a further increased IL+ZDDP concentration. This is in a good agreement with the V-shape wear behavior with the optimal protection at the oil's P content of 400 and 800 ppm, as shown in

Figure 2. It seemed that a tribofilm containing more zinc phosphates provided better wear protection. Unlike PAO+ZDDP, where a transition in the tribofilm composition from metal phosphates and oxides to metal sulfides when the ZDDP concentration increased, PAO+(IL+ZDDP) had little S compounds at all concentrations. The mechanism of the IL+ZDDP synergy had been previously discussed.²⁷

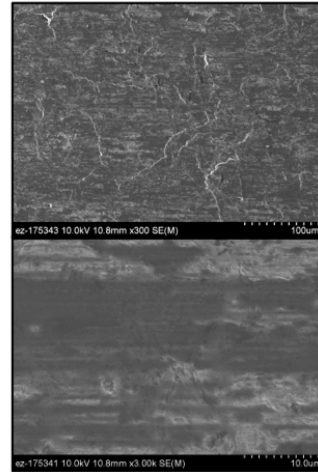
P= 44+44 ppm



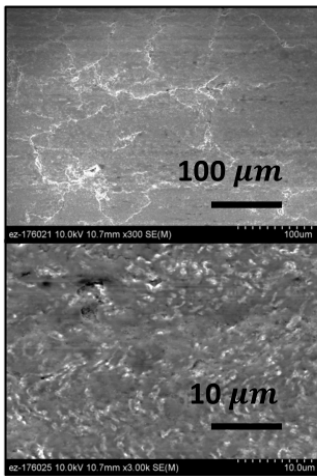
200+200 ppm



400+400 ppm



P= 1600+1600 ppm



3200+3200 ppm

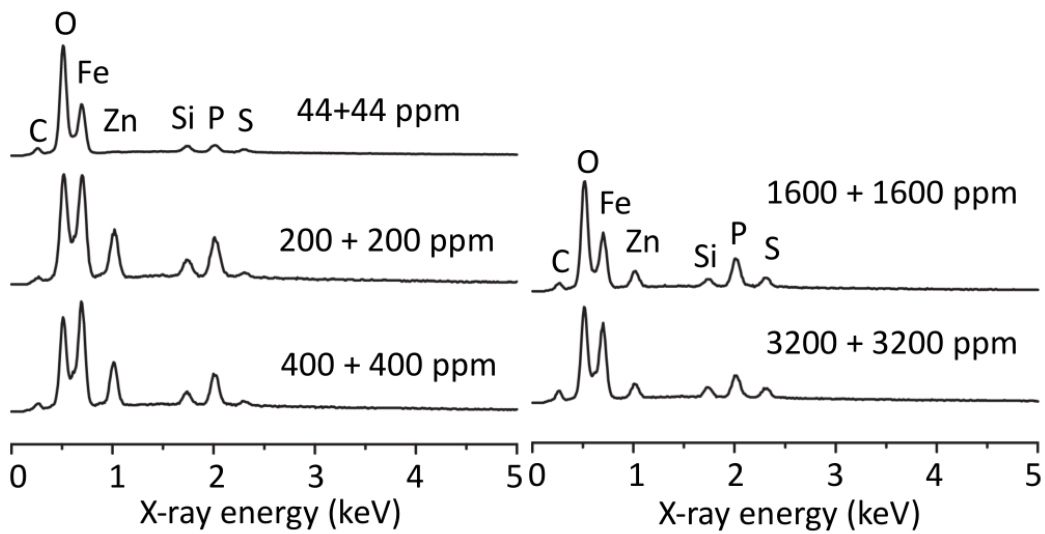
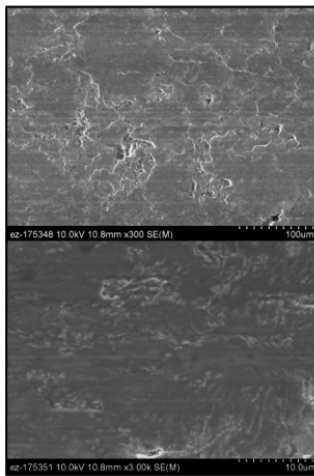


Figure 5. SEM images and EDX spectra of the worn surfaces generated in PAO+(IL+ZDDP) lubricants with various concentrations (presented in phosphorus contents).

3.4. Depth profile of tribofilm

XPS analysis was based on signal acquisition from an area of 400 μm diameter on the cast iron wear track to get averaged tribofilm thickness and composition. Figure 6(a) shows the composition-depth profiles of cast iron surfaces lubricated by PAO+ZDDP at 200, 800, and 3200 ppm P contents. Elemental compositions were plotted against etching time with the etching rate roughly at 10 nm/min. For the wear scar generated in the oil at 200 ppm P content, a tribofilm was detected but it was relatively thin that both P and S dropped significantly for less than 500 s of etching, which is evidenced by the elemental comparison in Figure 6(b). The swift reduction of ZDDP elements (P, S, and Zn) was accompanied by a sharp increase of metallic Fe, which was a sign of substrate exposure. When lubricated by the oil containing 800 ppm P, the tribofilm seemed to contain higher P, S, and Zn contents. Interestingly, when the ZDDP concentration in the oil was increased to 3200 ppm P, the P and Zn contents in the tribofilm actually dropped to a level similar to that of the oil containing 200 ppm P, but the S content in the tribofilm increased drastically. Results confirmed the compositional observation in the EDX spectra in Figure 3. Regarding the tribofilm thickness among the three oils, the film generated in the 200 ppm P oil was the thinnest (<500 s etching) as expected, and 800 ppm P oil seemed to form a thicker film (>2000 s etching) than the 3200 ppm P oil (~1000 s etching).

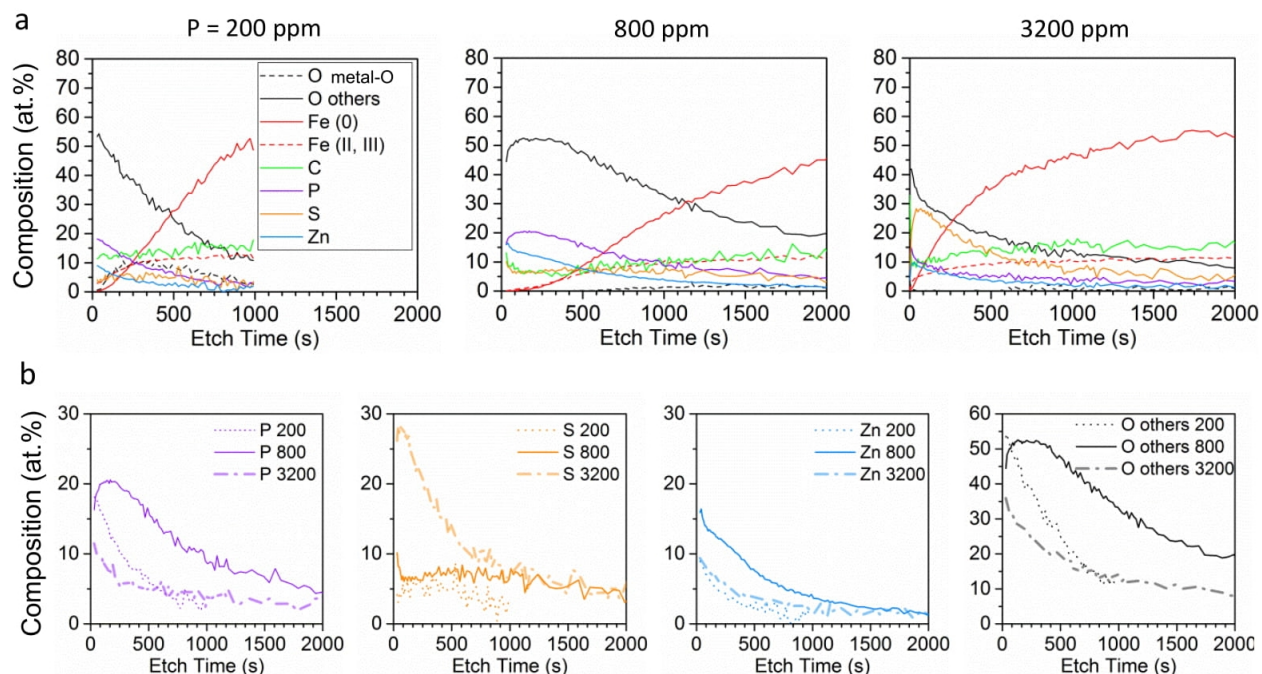


Figure 6. (a) XPS depth profiles of the cast iron surfaces lubricated by PAO+ZDDP at 200 ppm, 800 ppm, and 3200 ppm phosphorus contents; (b) individual profiles of P, S, Zn, and O (not bonded to metal).

The tribofilms formed by the phosphonium-alkylphosphate IL ($[P_{888}][DEHP]$) is of simpler chemistry, containing only P but not S or Zn. Figure 7(a) shows the composition-depth profiles of the cast iron worn surfaces lubricated by PAO+IL at 200, 800, and 3200 ppm P contents. The characteristic elements P and O are compared side-by-side in Figure 7(b). Along with the increased IL concentration from 200 ppm to 3200 ppm P in the oil, the P and O contents in the tribofilm were increasing as well. Again, the XPS results agreed well with the EDX data presented in Figure 4. In comparison, for the oils containing 200 ppm and 800 ppm P, the P contents in the PAO+IL tribofilms were much lower in comparison with the ZDDP tribofilms generated in the PAO+ZDDP oils containing the same amount of P. One explanation is that half P in $[P_{888}][DEHP]$ is in the inactive phosphonium cations while all P in ZDDP is in the active phosphate anions. The IL tribofilm thickness appeared to be proportional to the IL concentration in the oil.

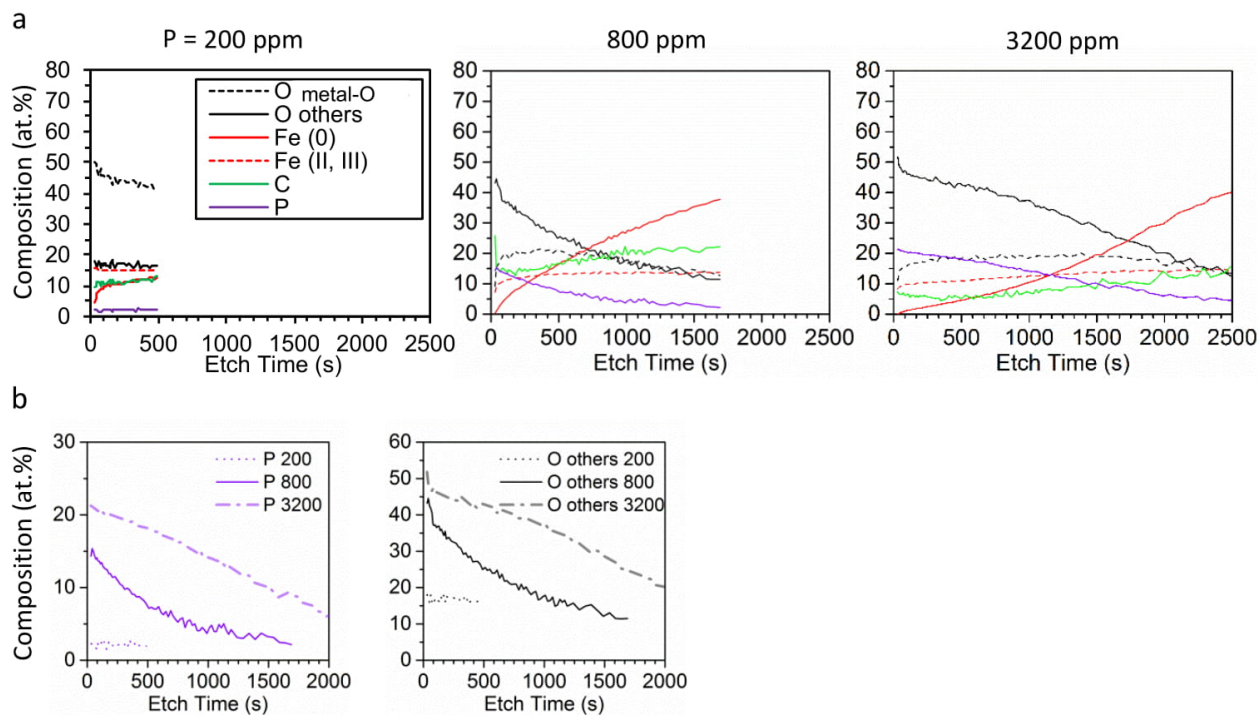


Figure 7. (a) XPS depth profiles of the cast iron surfaces lubricated by PAO+IL at 200, 800, and 3200 ppm phosphorus; (b) individual profiles of P and O (not bonded to metal).

Figure 8 presents depth profiles of the cast iron surfaces lubricated by PAO+(IL+ZDDP) at 100+100, 400+400, and 1600+1600 ppm P contents. The characteristic elements (P, S, and Zn) are compared side-by-side in Figure 8(b). It is interesting to observe that the 400+400 ppm of P oil generated a tribofilm with higher Zn, P and O contents than other two oils containing 100+100 or 1600+1600 ppm of P. S was very low at 3% for all three tribofilms, again confirming the EDX observation. This indicates that phosphates dominate the tribofilms formed by the IL+ZDDP combinations. The Zn content in the tribofilm by PAO+(IL+ZDDP) was about a half of that by PAO+ZDDP, because of the half amount of Zn supply in the oil. To balance the change of polymerization, the reduction in Zn was complemented by the increase of Fe (II, III), resulting in more participation of Fe compounds in the tribofilm. The IL+ZDDP tribofilm thickness seemed to be the highest for 400+400 ppm, agreeing with the trend of wear behavior, which implies that wear protection has a positive correlation with the film thickness.

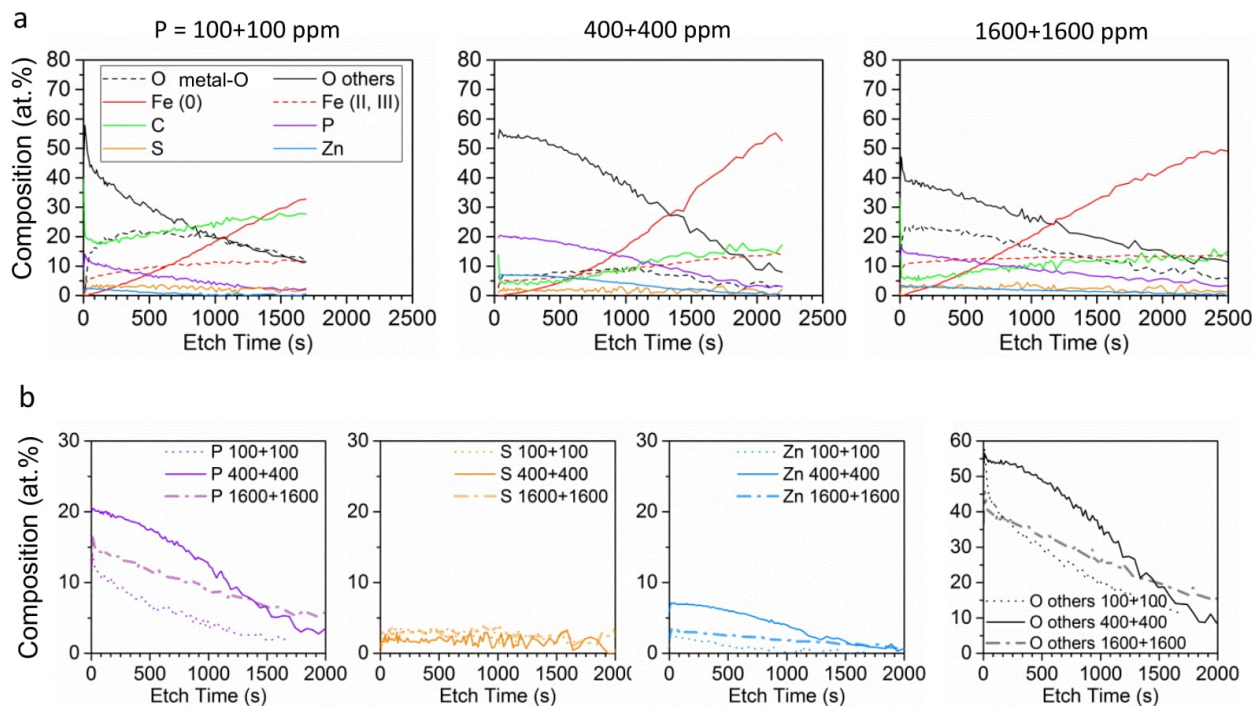


Figure 8. (a) XPS depth profiles of the cast iron surfaces lubricated by PAO+(IL+ZDDP) at 100+100 ppm, 400+400 ppm, and 1600+1600 ppm phosphorus; (b) individual profiles of P, S, Zn, and O (not bonded to metal).

4. Discussion

4.1. Phosphate polymerization gradients of tribofilms

Phosphate polymerization is essential in tribofilm formation. Phosphorus $2p$ binding energy ranges from 127.5 to 137.7 eV.³⁰ The phosphate groups involved in the ZDDP tribofilms formation include orthophosphate PO_4^{3-} , pyrophosphate $\text{P}_2\text{O}_7^{4-}$, polyphosphate $\text{O}(\text{PO}_3)_n\text{O}^{(n+2)-}$, and metaphosphate (cyclic) $(\text{PO}_3)_n^{n-}$, etc. A higher P $2p$ binding energy has been correlated to a higher level of phosphate polymerization. Crobu et al. showed that the deconvoluted P $2p_{3/2}$ peak of ortho-, pyro-, poly-, and metaphosphate was 134.10, 134.35, 134.49, and 134.75 eV, respectively.³¹ Figure 9 shows a unique “heat map” representation of the polymerization of the tribofilms formed by ZDDP, IL, and IL+ZDDP at three P content levels, 200, 800, and 3200 ppm. The heat maps were created by plotting the P binding energy versus the depth from the top surface using ion-sputtering aided XPS analysis. Red represents the highest intensity (a.u.) in XPS plots. Green indicates a lower intensity and black means background noise. The friction and wear data of these concentrations were also listed in Table 2.

Table 2. Friction and wear of ZDDP, IL, and IL+ZDDP

Lubricant	Tribological performance	Phosphorus content in the lubricant (ppm)		
		200	800	3200
PAO + ZDDP	Friction coefficient	0.05 ± 0.01	0.07 ± 0.01	0.12 ± 0.02
	Wear rate (10 ⁻⁶ mm ³ /N · m)	0.48 ± 0.07	0.80 ± 0.05	0.61 ± 0.03
PAO + IL	Friction coefficient	0.09 ± 0.01	0.09 ± 0.01	0.08 ± 0.01
	Wear rate (10 ⁻⁶ mm ³ /N · m)	1.23 ± 0.07	1.30 ± 0.23	0.58 ± 0.04
PAO + IL+ZDDP	Friction coefficient	0.11 ± 0.02	0.08 ± 0.01	0.07 ± 0.01
	Wear rate (10 ⁻⁶ mm ³ /N · m)	0.90 ± 0.10	0.24 ± 0.08	0.70 ± 0.10

For the ZDDP tribofilms generated in the oils with 200 ppm and 800 ppm P contents, more polyphosphates were detected on the top of the tribofilms as the polymerization level decreased with the etching time. When lubricated by the oil with 3200 ppm P content, the polymerization level of the tribofilm seemed to be lower than that from the oils with 200 and 800 ppm P and had little change throughout the film thickness. The gradient of phosphate polymerization at 200 and 800 ppm in the z-direction is postulated due to the prolonged high contact pressure on the top surface of the tribofilm that energetically drove phosphate polymerization. In contrast, the tribofilm grown in the oil containing 3200 ppm P experienced cracking and fracturing, as seen in Figure 3, which reduced the contact pressure to some extent. As a result, the phosphate polymerization was less significant.

For the IL-additized oils, each tribofilm showed a relatively constant polymerization level throughout the film depth. As listed in Table 2, friction and wear were indifferent between 200 ppm and 800 ppm, but were reduced as the concentration increased to 3200 ppm, which seemed to be correlated to the tribofilm thickness (as presented in Figure 7).

For the IL+ZDDP tribofilms, there are three primary observations: 1) little polymerization gradient change along the z-direction, which is similar to the IL tribofilms but not to the ZDDP tribofilms; 2) highest polymerization in the 400+400 ppm tribofilm among the three concentrations and lowest polymerization in 1600+1600 ppm tribofilm, which is more

similar to the ZDDP tribofilm (800 ppm highest, 3200 ppm lowest) than that of the IL tribofilms; 3) the 400+400 ppm tribofilm having the highest polymerization and the best wear reduction. A schematic of the tribofilms is shown in Figure 10.

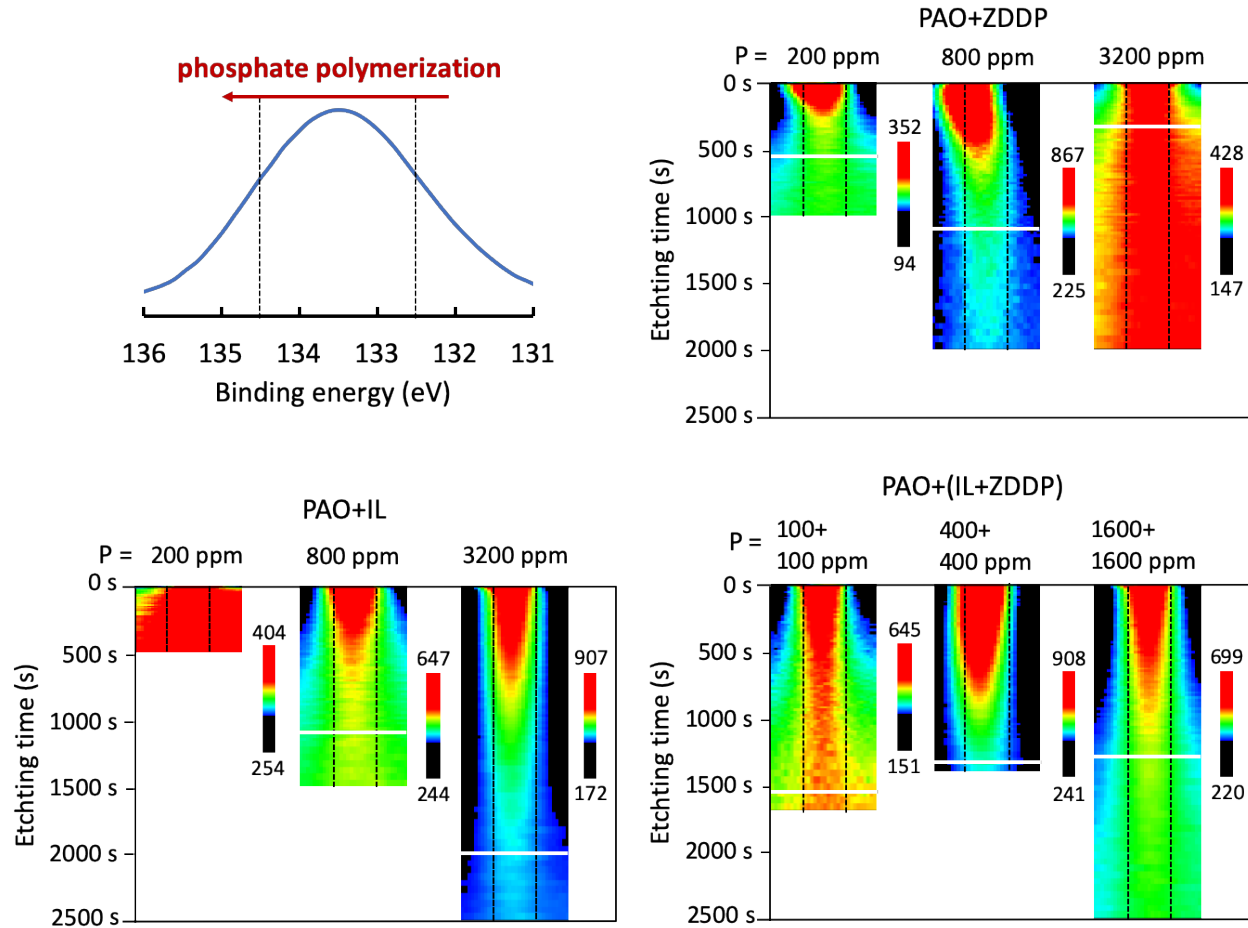


Figure 9. Polymerization gradient of phosphate in tribofilms formed by lubricants containing PAO+ZDDP, PAO+IL, and PAO+(IL+ZDDP), based on the peak position and intensity of XPS depth profiles. Each heat map spans 5 eV between 131 and 136 eV, with two dashed lines indicate the positions of 132.5 and 134.5 eV. The relative heat map contrast of each scan was adjusted individually. The white line represents the etching time where Fe⁰ reached 30%. For PAO+ZDDP, the etching time for 200, 800, 3200 ppm was 540, 1120, and 380 sec, respectively. For PAO+IL, the etching time for 200, 800, 3200 ppm was >500, 1160, and 2000 sec, respectively. For PAO+(IL+ZDDP), the etching time for 100+100, 400+400, 1600+1600 ppm was 1550, 1450, and 1400 sec, respectively.

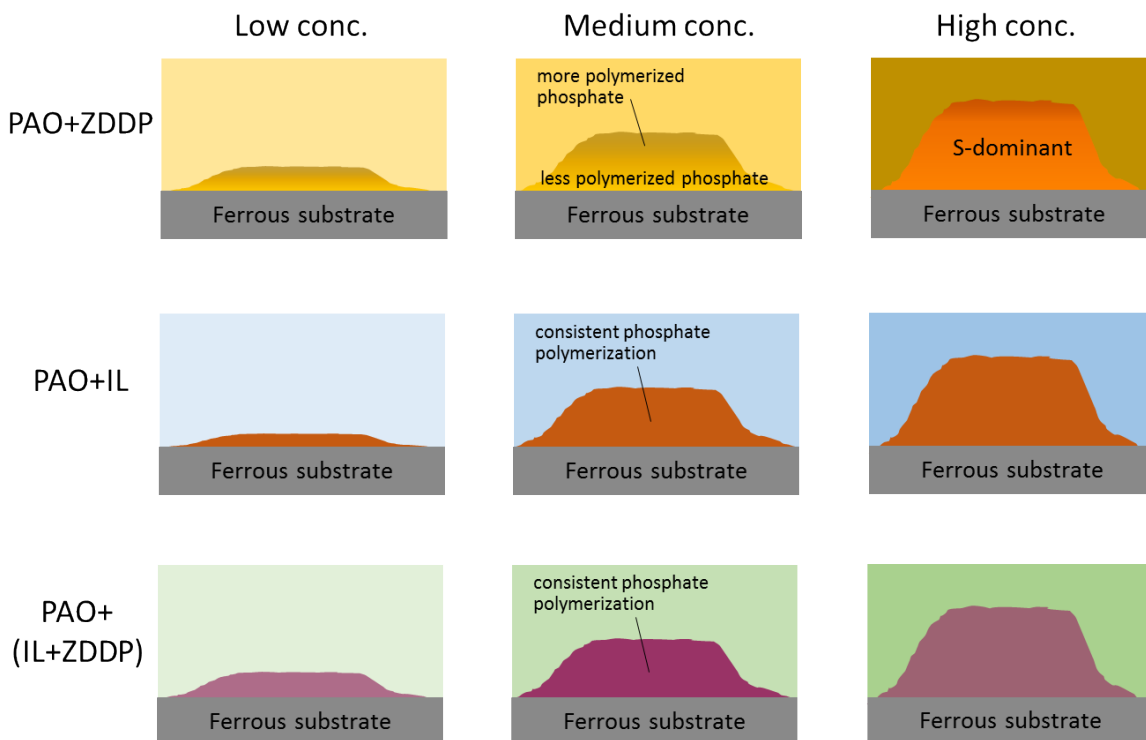
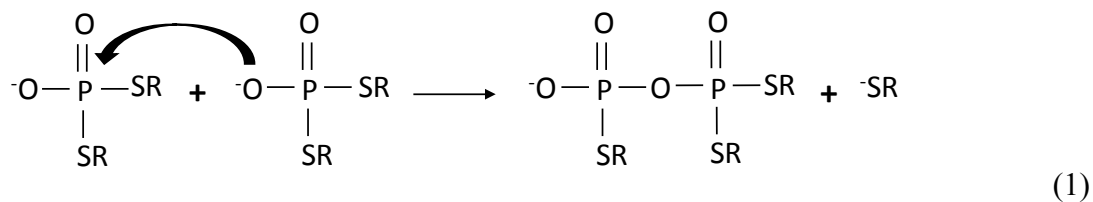


Figure 10. Schematic of tribofilms produced by ZDDP, IL, and IL+ZDDP.

The polymerization gradient inside ZDDP tribofilms has long been known¹. Figure 6(b) compared the P, S, Zn, and O (other than metal oxide) profiles of the ZDDP tribofilms formed in oils of three phosphorus levels. The tribofilm grown at 800 ppm P had the highest P, Zn, and O contents, while the tribofilm formed in the 3200 ppm P oil showed an enrichment of S in the top layer. ZDDP is supposed to decompose to Zn^{2+} and two dithiophosphates $(RO)_2PSS^-$. Dithiophosphates are strong alkylating agents that are intended for self-alkylation to generate $(RS)_2POO^-$.³² Two $(RS)_2POO^-$ could possibly react to form a polythiophosphate, leaving a sulfide radical, as illustrated in equation (1) below. The RS group in $(RS)_2POO^-$ is also vulnerable to the phosphoryl group (PO_3^{2-}) attack, possibly resulting polyphosphates and organic sulfides. Either way, S is likely reduced in phosphate polymerization and thus a higher S content in the tribofilm could indicate a lower level of phosphate polymerization. On the other hand, the low S content in the IL+ZDDP tribofilm suggest that the tribofilm formation might have skipped the step of S removal and directly utilized the readily available organophosphates in polymerization.



5. Conclusions

This study comprehensively analyzed the effects of the concentrations of a ZDDP, an IL, and the combination of IL+ZDDP, when used in a synthetic base oil, on the tribofilm evolution and tribological behavior. Boundary lubrication tests were conducted at 150 °C using a ball-on-flat sliding contact of 52100 steel against grey cast iron. Results clearly showed that the lubricating performance was not proportional to the AW concentrations. Based on the key learnings below, we can confidently conclude that a higher AW concentration is not always better.

- The ZDDP was basically trendless in wear protection, in agreement with the literature. On the other hand, a higher ZDDP concentration in the range of 400–6400 ppm P content clearly increased the friction along with a thicker, rougher, and more brittle tribofilm, as a result of decreasing phosphates but increasing sulfur compounds in the tribofilm.
- The IL showed a V-shaped wear rate curve with the best performance at 1600 ppm P content in the oil. The optimal molecular ratio between the ZDDP and IL was determined to be 1:1, and the combination seemed to have an optimal zone of 400–800 ppm P content in the oil. Both the IL alone and combined with ZDDP had a low and stable friction at 400 ppm P content or above in the oil. The tribofilm surface morphology is distinctive among those three groups. There was no sulfur in the IL tribofilm and the sulfur compounds were maintained at a very low level in the tribofilm for IL+ZDDP even at high concentrations. All data suggested strong correlations between the friction behavior and the sulfur content in the tribofilm.
- Unique XPS-generated heat maps of P 2p binding energy revealed the polymerization characteristics of the tribofilms in their z-direction. At low and medium concentrations, ZDDP tribofilms showed more polymerized phosphates in the outer layer that grading to less polymerized phosphate in the bulk, but at a high concentration, the phosphate

grading disappeared and a significant amount of sulfur emerged. In contrast, the IL and IL+ZDDP tribofilms showed little gradient in their phosphate polymerization. The distinct tribofilm morphologies and compositions among the three types of AWs are well correlated to their lubricating behavior.

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