Tribofilms generated from ZDDP and DDP on steel surfaces: Part 2, chemistry

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The chemical constitution of tribofilms, generated from zinc dialkyldithiophosphate (ZDDP) and ashless dialkyldithiophosphate (DDP), has been examined by X-ray Absorption Near Edge Structure (XANES) spectroscopy. The identification of spectral features and interpretation of the results for P, O, Fe, and S species are given, allowing an overall mechanism to be deduced. The role of Fe in these films was investigated in some detail using P L-edge, O K-edge and Fe L-edge XANES spectra. From the P L-edge XANES spectra, the DDP films are uniformly very short chain iron polyphosphates. In contrast, the ZDDP films are formed initially as short chain polyphosphates; but after more rubbing, a bilayer phosphate film is formed with long chain Zn polyphosphates on the surface and shorter chain in the bulk of the film. The O K-edge XANES spectra show that there is, as expected, more Fe in the DDP phosphate films than in the ZDDP phosphate films. The S K-edge spectra of ZDDP films show the presence not only of ZnS as previously observed, but also the presence of FeS for the first time in the early stages of film formation. The predominant S species in the DDP films is FeS.

KEY WORDS: ZDDP, DDP, Chemistry of tribofilms, AFM, XPS, XANES

1. Introduction

Understanding the chemistry of tribofilms generated from lubricants is one of the most important keys to understand the mechanism of lubrication. Many advanced spectroscopic techniques have been applied to elucidate the chemical nature of tribofilms generated from antiwear agents. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) [1–5], reflectance infrared spectroscopy [5–9] and X-ray absorption near edge structure (XANES) spectroscopy [10–18] have played a major role to understand the mechanisms of formation of antiwear film on the rubbed surfaces. A good summary of the role of many of these techniques is given in a very recent paper [10]. The vast majority of this work has been done with zinc dialkyldithiophosphates (ZDDP's) along with dispersants and detergents; but a significant amount of research has been done recently on so-called ashless wear inhibitors [19], since the new GF-4 engine oil specification put a maximum limit (0.08 wt % P) on the allowed P in the engine oil. Even further reductions may occur in the future, thus bolstering the search for any new compounds with antiwear and antioxidant activity, since these functions may be lost as ZDDP levels are decreased in engine oils.

XANES measurements have been found to be ideally suited to the chemical studies of these films. First, most

of the important elements in these films (e.g., P and S) have suitable lines (e.g., P and S L- and K- edge), some of which give better chemical resolution than other techniques. Second, total electron yield (TEY) and fluorescence yield (FY) detection techniques allow for non-destructive study of the chemical nature of the surface, near surface and the bulk of the film. For example, for the P and S measurements, the maximum analysis depths are $\sim$5 nm for TEY at the L-edge, $\sim$50 nm for TEY at the K-edge and FY at the L-edge, and several μm for FY at the K-edge [20].

For ZDDP, it is now widely accepted that the tribofilms consist mainly of phosphates with some sulfides [21], and the average thickness of the films is less than 100 nm [22]. The infrared measurements suggested that there are polyphosphates in the films [6–9]. The XANES measurements have shown that the film has a bilayer structure with long chain Zn polyphosphates at the surface, and short chain polyphosphates in the bulk of the film [14–16, 18] with little or no Fe oxide between the Fe and the phosphate due to digestion of the Fe oxide layer during phosphate formation [10]. AES and XPS depth profiling showed that the amount of Fe increased from the surface to the bulk of the film [3,10], as suggested earlier in a mechanism to convert the long chain phosphate to short chain [15,17]. The sulphide is present as ZnS, with no evidence for FeS as suggested earlier [1]. More recently, the microscopic chemistry of these ZDDP films has been obtained with XPEEM measurements [23–25]; and these measurements have

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shown that the polyphosphate chain length varies even at the surface of these very inhomogeneous films.

Sarin *et al.* [26] showed that ashless thiophosphates gave comparable antiwear and antioxidant properties to those of ZDDP in bench tests. In contrast to the ZDDP film chemistry, XANES analysis showed that DDP gave short chain polyphosphates throughout the film and the sulphide formed was largely FeS [27]. It was assumed that the cation in the phosphate glass was Fe^{2+}.

The experimental work for this portion of the paper is described in Part 1 (preceding paper). The Results and Discussion pertain to the chemistry of tribofilms obtained from XANES spectroscopy and XPS are given in this paper (Part 2).

2. Results and discussion

2.1. Phosphorus characterization

P L-edge X-ray absorption near edge structure (XANES) spectra of tribofilms generated from ZDDP and DDP at different rubbing times and model compounds are given in figure 1. These spectra are characteristic of polyphosphate glasses observed in all of our previous studies of both ZDDP and DDP films [14–19, 27]. Comparing the ZDDP spectra in figure 1 (left), it can be seen that the peak positions in spectra A to F of the tribofilms generated at different rubbing times are extremely similar to the positions for the model compound, zinc polyphosphate. In particular, the position of peak *a* in the tribofilms is much closer to peak *a* for Zn polyphosphate than for Fe polyphosphate or a phosphate ester, Irgalube 349. This indicates that the major cation in the surface of these films is Zn^{2+} rather than Fe^{2+} or Fe^{3+}, consistent with all our pre-

vious results [14–17] on films formed from long rubbing times which showed long chain Zn polyphosphates at the surface of the ZDDP tribofilms and shorter chain zinc polyphosphates (with some Fe) formed in the bulk of tribofilms. XPS data presented in figure 5(a) (Part 1) also showed that there is no Fe in the surface of the film. The intensity of peak *a* or *b* relative to peak *c* has always been used to indicate the phosphate chain length: an *a/c* of about 0.3 is short chain length polyphosphate, and *a/c* of about 0.6 indicates a long chain polyphosphate [28]. The FY spectra on the ZDDP films show that the chain length is shorter (*a/c* of < 0.4) for the long term films, compared to the *a/c* of ∼0.6 from the TEY measurement (figure 1 E, F) as observed previously. These spectra show the bi-layer nature of the ZDDP films.

However, the present results on ZDDP antiwear films show, for the first time, that the polyphosphate chain length at the surface of these films increases with rubbing time. For spectrum A from the 10 second film, the ratio of intensity of peak *a/c* is 0.33. This indicates that zinc polyphosphate is short chain. With rubbing time increasing, the ratio of *a/c* in the spectra (A to F) increases. Thus, for the 10 h film (F), the ratio of *a/c* is 0.61. Because the Zn/P ratio of 1:2 in ZDDP is much smaller than the Zn/P ratio in a short chain polyphosphates (e.g., 1:1 in $Zn_2P_2O_7$), the initial formation of a short chain polyphosphate indicates that substantial Fe must be in these short term films. The availability of Fe (or Fe oxides) from the steel surface decreases as the film becomes thicker, and the chain length increases with relatively more Zn and less Fe in the surface of the films. The position of peak *a* is obviously not sensitive enough to the differences in the relative proportion of Fe and Zn in these films.
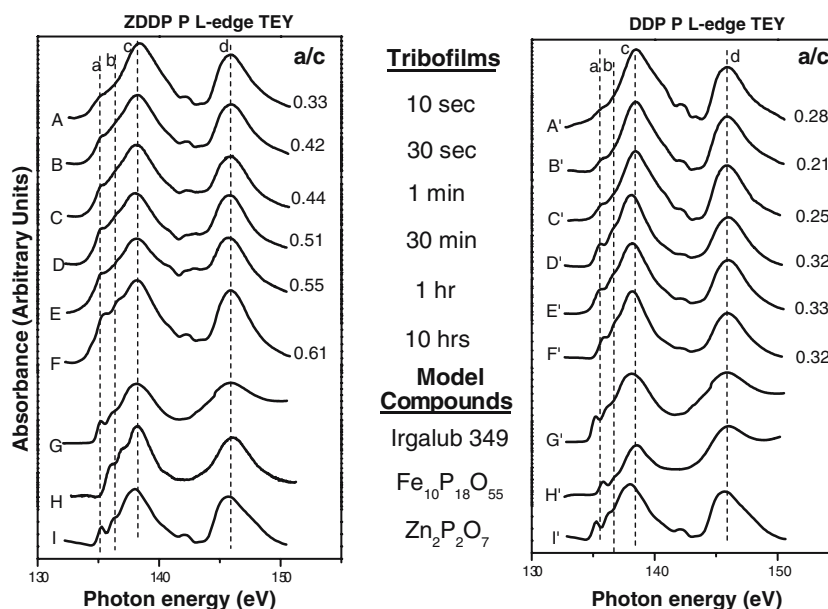

Figure 1. P L-edge XANES (in TEY mode) spectra of model compounds and tribofilms generated from 1 wt% ZDDP (left) and DDP (right) at different rubbing times.

The spectra of the DDP films (figure 1, right) are qualitatively similar to the ZDDP spectra – they are all characteristic of polyphosphates. However there are two obvious differences. First, the position of peak *a* in all spectra aligns very well with peak *a* for $FePO_4$ rather than $Zn_2P_2O_7$, suggesting that Fe is the predominant cation in these films as expected. Second, the ratio *a/c* in all spectra is close to 0.3: all films contain short chain polyphosphates as seen earlier by Najman et al. [27]. It is not easy to rationalize why DDP gives short chain polyphosphates, especially for the thick films, when the availability of cations for DDP has to be less than for ZDDP. However, careful examination of spectra shows that position of peak *c* in spectra D′ to F′ (30 min films to 10 hr film) shifts slightly (∼0.5 eV) to lower energy corresponding to zinc polyphosphate or Irgalube spectrum G′. This suggests that in the absence of Fe as a cation, contaminant zinc and/or alkyl group are balancing the charge in these films. The alkyl group would come from incomplete decomposition of DDP. Our recent studies on phosphate esters indicate that the P L-edge spectra of some of the organic phosphates have some similarity with those of metal phosphates [27].

Further support for this suggestion comes from the XPS analysis shown in figure 5 (Part 1). After a few seconds sputtering to remove the carbon contamination, the proportion of zinc in the ZDDP film is ∼4 times that of DDP film, whereas phosphorus proportions in both films are approximately the same. Also the proportion of carbon in the DDP film remains higher than that of the ZDDP film, throughout the sputtering, although quantitative assessment of carbon is not possible due to the carbon contamination in the instrument. Thus the presence of zinc cation and alkyl groups in the film may account for the lack of Fe in the thick polyphosphate film of DDP. As figure 1 (left) clearly indicates, the ZDDP films spectra correspond to zinc polyphosphate (see P K-edge section, Part 1, for more evidence).

P L-edge XANES spectra of model compounds and tribofilms generated after 1 h of rubbing from different concentrations of ZDDP are given in figure 2. These spectra are qualitatively similar to spectrum E in figure 1 for the 1 wt % (∼0.1% P) solution. Even with 0.1 wt % (∼0.01% P) ZDDP, an excellent spectrum is obtained showing that a well developed film has been produced, as indicated by the thick film shown in figure 3 (Part 1). It can be seen that peak positions in the spectra of the tribofilms are the same as the positions for $Zn_2P_2O_7$, showing that Zn is the predominant cation at the surface of these phosphate films. However, the ratio of *a/c* increases as the ZDDP concentration increases from *a/c* = 0.34 for the 0.1 wt % solution to *a/c* = 0.68 for the 2 and 5 wt % solutions. This ratio is affected by the presence of undecomposed or partially decomposed ZDDP in the low energy part of the spectrum which increases the *a/c* ratio (see shoulder *s* in figure 2 spectra D–E) [17]. However, even considering some ZDDP in
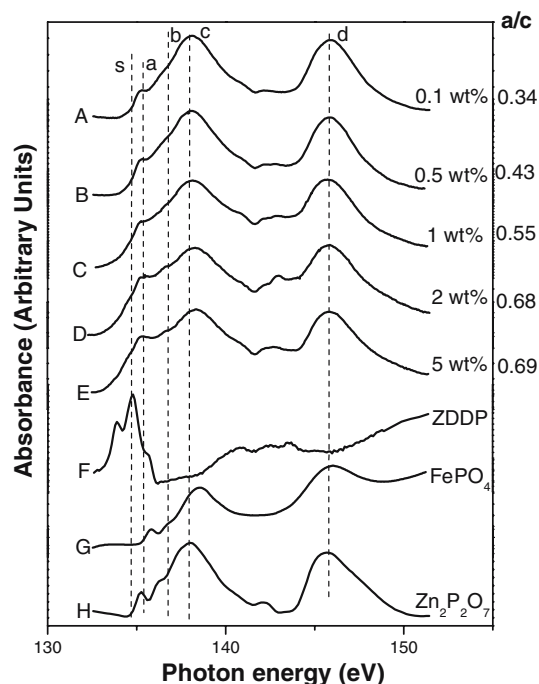

Figure 2. P L-edge XANES spectra of model compounds and tribofilms generated from different concentrations of ZDDP for 1 h rubbing.
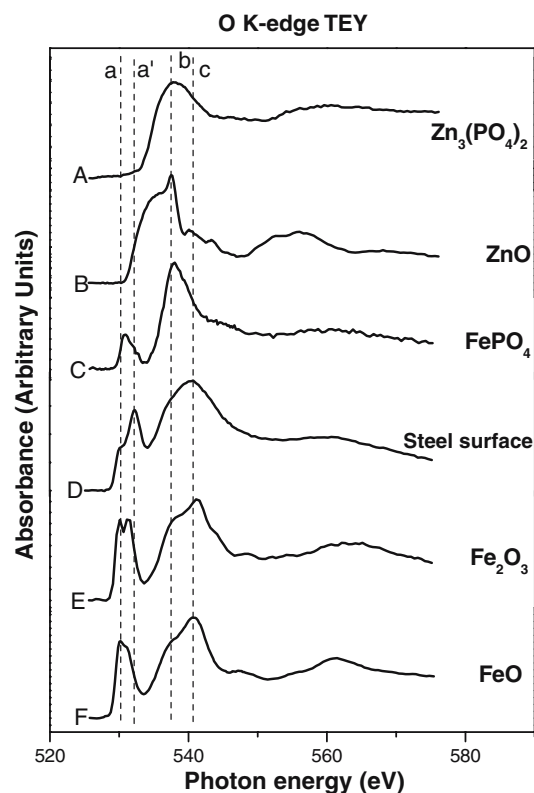

Figure 3. O K-edge XANES spectra of model compounds.

the films, it still appears that the *a/c* and *b/c* ratio increases as the ZDDP concentration increases. The FY spectra (not shown) for the bulk show a similar trend.

The a/c ratio increases from 0.17 to 0.5 for 0.1 to 2.0 wt % and drops to 0.25 for 5 wt % ZDDP. Once again, if we use the availability of cations argument, we would not expect this trend. Perhaps there is an optimum ZDDP concentration for antiwear film formation as has been shown before [29]. Although the adsorption experiments were conducted on iron and iron oxide powders, Plaza did show that the rate of ZDDP adsorption increases with increasing concentration [30]. He worked in the range of 1.6×10^{-3} moles/kg to 25×10^{-3} moles/kg, corresponding to roughly 0.088 wt % to 1.3 wt %, the range in which the XANES a/c ratio increases on rubbing. We hypothesize that an increased adsorption rate is an essential factor for a high a/c ratio to be observed, in this weight percent range. It may be that too high a concentration interferes with mature film formation.

2.2. Oxygen characterization and the role of Fe in the films

O K-edge XANES spectra (taken in TEY mode) of model compounds are shown in figure 3. These spectra are useful for distinguishing qualitatively the role of Fe and Zn in the phosphate glass tribofilms on the steel surface. Our spectra of Fe_2O_3 and FeO are in good agreement with those previously published from single crystals [31]. It can be seen that the general shape of the spectra of the Zn containing compounds (spectra A and B) is very different from the spectra of the Fe containing compounds (spectra C, D, E and F): the Zn compounds do not contain the low energy peak(s), a and a' at 530–531 eV characteristic of any Fe compound [31–33]. Peaks a and a' in the spectra of the Fe compounds are due to transitions from O 1s to O 2p states hybridized with the partially filled Fe 3d band that is highly localized around the metal–atom sites. Both Fe^{2+} and Fe^{3+} compounds give intense and overlapping peaks at about 530 eV, so it is not possible to distinguish between Fe^{2+} and Fe^{3+} from these spectra. The peaks at about 530 eV are not present in the Zn compounds because of the filled 3d orbital in Zn. Peaks b and c are generally attributed to O 1s to O 2p states hybridized with iron or Zn 4s and 4p states [31–33]. The splitting of peak a in spectra D, E and F has been interpreted as the Fe 3d e_g–t_{2g} symmetry bands separated by the oxygen octahedral (O_h) crystal field.

The spectrum of the steel surface (D) resembles the spectra of the two Fe oxides (E and F). All three spectra show peaks a and a' along with broad peaks b and c, showing that even this highly polished surface has been oxidized to give an appreciable iron oxide film. The spectrum of $FePO_4$ (C) is significantly different from the iron oxide spectra, making it possible to characterize Fe phosphates on an iron oxide film. The Fe phosphate spectrum has little or no peak a', peak b is narrower than for the oxides, and there is no obvious peak c.

The cation in the phosphate tribofilms generated from ZDDP and DDP is still an unresolved question: the above evidence from the P 2p spectra and the XPS results shows that the predominant cation in the surface of the ZDDP films is Zn^{2+}, while the predominant cation in the DDP films is Fe^{2+} and/or Fe^{3+}. Because of the stoichiometric shortage of Zn in ZDDP to form even long chain phosphates [14, 15, 17, 18], there must be some Fe in the bulk of the ZDDP films, and Fe cations must be dominant in the DDP films. However, there has been rather little spectroscopic evidence for Fe in these films. In the ZDDP films, Auger depth profiling [3,10] has given the best evidence for dominant Fe in the bulk of the ZDDP films. Our XPS results after depth profiling in this study are consistent with Martin's results.

Because of the promising results in figure 3, we synthesized six $(1-x)Zn-xFe_2O_3-P_2O_5$ glasses and investigated O K-edge XANES spectra of them, with the expectation that the relative amounts of Fe and Zn could be discerned from the O K-edge spectra. The spectra are shown in figure 4. Comparing spectra A ($FePO_4$) and F [$(Zn(PO_3)_2)$], the significant difference, as expected from figure 3 is that there is peak a in spectrum A, and no peak a in F. Comparing the spectra with increasing amounts of Zn (spectra A to F), it is apparent that the intensity of peak a decreases regularly as the amount of Zn increases. The ratio of peak heights a/b (right hand side of figure 4) decreases regularly from
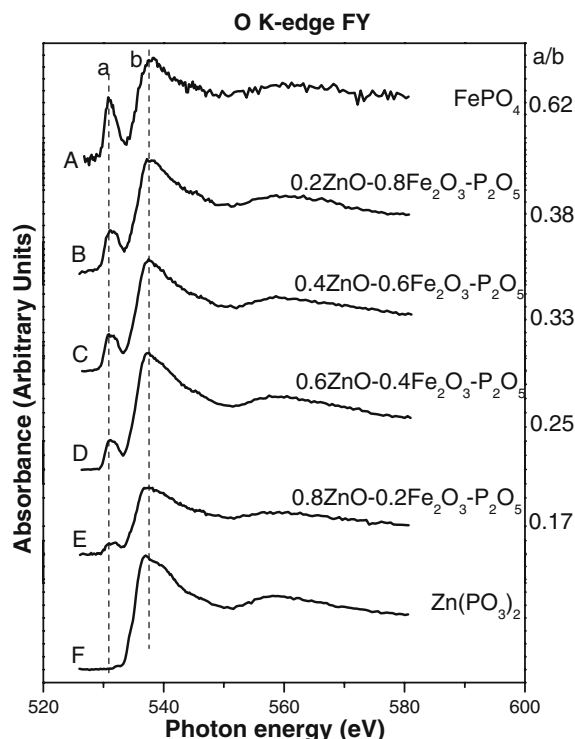
Figure 4. O K-edge XANES spectra of Zn/Fe polyphosphate glasses.

$FePO_4$ to $Zn(PO_3)_2$. We expected that these O K-edge spectra should be very useful in distinguishing the amounts of the two phosphates in the films.

O K-edge FY XANES spectra of tribofilms generated from ZDDP and DDP at different rubbing times, and model compounds are shown in figure 5(a) and (b), for FY measurement, respectively. The TEY spectra for all of these samples (not shown) are qualitatively similar. Spectra A (A′) to C (C′) are produced from tribofilms rubbed for 10 s, 1 min and 1 hr, respectively. Peaks *c* and *d* in some of these spectra originate from Cr L-edge XANES from a concentration of the 1% Cr in the 52100 steel surface oxide. This indicates that the analysis depth of greater than 500Å is large enough to detect the steel surface in these very thin films, although there could also be Cr incorporated into these phosphate films as also suggested in the XPS broad scans. Peak *a* is very weak in the ZDDP spectra (A and B) showing a rather small amount of Fe in these films. In contrast the spectra A′ and B′ from the DDP films show a very intense peak *a* without any noticeable *a′*. This certainly indicates that there is appreciable Fe phosphate in these films, although there is still a contribution to these spectra from the surface Fe oxide. However, after 1 h of rubbing (spectrum C′), peak *a* is very weak (although stronger than in the comparable ZDDP spectrum C), indicating rather little Fe in the films. If Fe is the only cation (or even the predominant cation due to some Zn incorporation) in these phosphate films, the intensity of peak *a* should be much larger in spectrum C′. However, it was shown in figure 1 for 30 min to 10 hr films that contaminant zinc cations and alkyl groups may balance the charge for these phosphates. We cannot explain this apparent discrepancy.

2.3. Fe L-edge results for Fe characterization

The Fe L-edge spectra of the films and model compounds taken with second order light are shown in figure 6 from the ZDDP films (left) and DDP films (right). As for the O K-edge spectra, the $FePO_4$ spectrum (D) is appreciably different from those of the oxides: peak *a* is very narrow and not split as for the other three Fe standards (spectra E, F and G). For ZDDP films, the 10 s film (A) shows mostly Fe oxides. However for the thicker 1 min and 1 h ZDDP films (B and C), the spectra are very weak showing that there is very little Fe in the surface of these films. For the very thin DDP films (A′ and B′), and thick film (C′) the spectra are very similar to the Fe oxide from the steel surface. This is not surprising. As was shown in figure 6 (Part 1), the DDP films were very inhomogeneous and are composed of small pads compared to the ZDDP films. The scratch marks are quite apparent in these films and obviously the Fe signals mostly originate from the substrate, although a small amount of iron phosphate can exist in the film.

2.4. Sulfur characterization

S K-edge XANES spectra of tribofilms generated from ZDDP and DDP at different rubbing time and model compounds are shown in figure 7. The spectra of the ZDDP films (spectra A, B and C) are extremely similar to the ZnS spectrum (with peak *c* dominating), as reported in our previous studies [12,13]. This indicates that the main chemical state of sulfur in the tribofilms generated from ZDDP at all rubbing times is ZnS. However, for the 10 s film (spectrum A), there are two shoulder peaks *a* and *d*. These two shoulder peaks
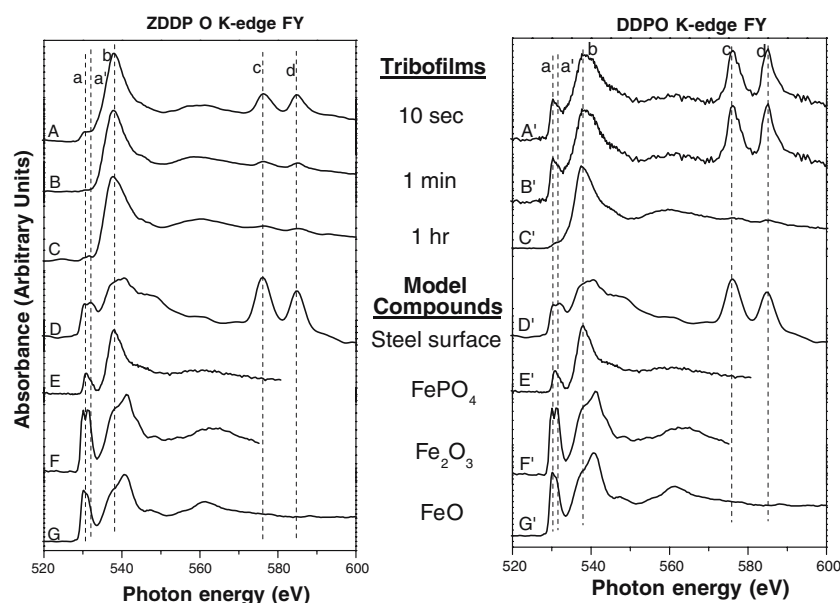

Figure 5. O K-edge XANES spectra of model compounds and tribofilms generated from 1 wt % ZDDP (left) and DDP (right) at different rubbing times.
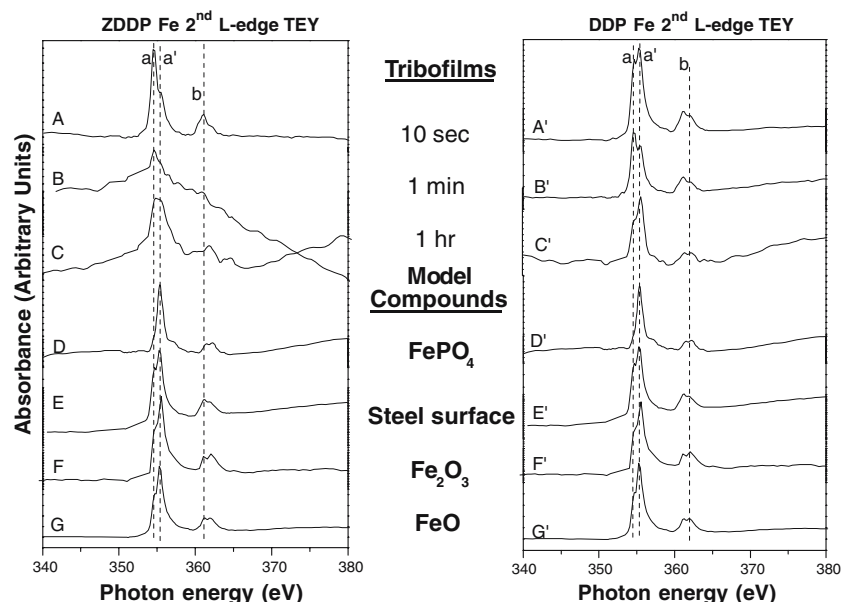
Figure 6. Fe L-edge XANES spectra (recorded with second order light) of model compounds and tribofilms generated from 1 wt % ZDDP (left) and DDP (right) at different rubbing times.
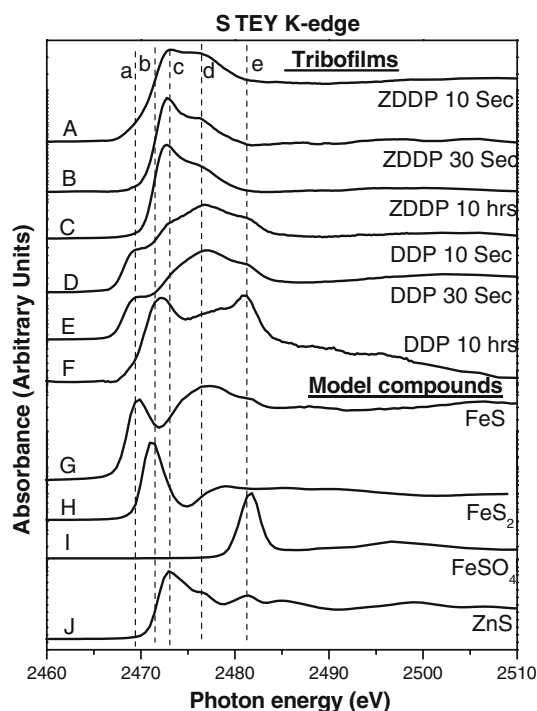

Figure 7. S K-edge XANES spectra of model compounds and tribo-films generated from 1 wt % ZDDP and DDP at different rubbing times.

correspond to the FeS spectrum (spectrum G). This result implies that there are two kinds of sulfides in the tribofilm generated from 10 seconds rubbing. Zinc sulfide is the main chemical state of sulfur, but there is also some iron sulfide in the film. Because the concentration of iron sulfide is lower, there are only two

shoulder peaks in spectrum A. This indicates that iron sulfide does exist in the tribofilm at the beginning; and more importantly, that Fe from the surface is available immediately for reaction with the S and/or P generated as the ZDDP decomposes. This is in agreement with previous findings [34].

As rubbing continues, peak *a* disappears and the intensity of peak *d* decreases. This indicates that the amount of FeS in the film decreases relative to the amount of ZnS. In the thick films, there is probably only FeS right at the interface between the tribofilm and the steel surface. This is not unexpected from the principle of hard acids and soft bases as outlined by Martin *et al.* [3,10]. The soft base S^{2-} prefers to react with the borderline soft acid Zn^{2+} over the harder acid Fe^{2+} or Fe^{3+}. This principle can also be expressed by thermodynamic predictions. For example, consider the reactions:

$$FeS + Zn^{2+} \longrightarrow ZnS + Fe^{2+} \qquad (1)$$

Or

$$FeS + ZnO \longrightarrow FeO + ZnS \qquad (2)$$

ΔG^0 is negative for these two reactions because of the very large negative ΔG_f^0 for ZnS (-201.3 kJ/mole) compared to FeS (-100.4 kJ/mole) [35]. In the presence of a Zn species, FeS is expected to convert to ZnS. However, the majority of the Zn ends up in Zn polyphosphates rather than ZnS. The very large ΔH_f^0 values (ΔG_f^0 values are not available [35]) for the Zn phosphates (e.g., -2892 kJ/mole for $Zn_3(PO_4)_2$ and -4479 kJ/mole for $Zn_3P_4O_{13}$) indicate that the Zn phosphates are the thermodynamically stable Zn prod-

uct in this complex system. For example, the ΔG value is -145 kJ for reaction 3

$$3ZnS + 2H_3PO_4 \longrightarrow Zn_3(PO_4)_2 + 3H_2S \qquad (3)$$
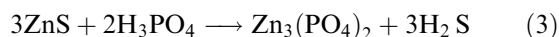
Indeed, the presence of Zn in the DDP films from a very minor Zn contamination shows that Zn phosphates are incredibly stable compounds. The XPS data shown in figure 5 (Part 1) support the above discussion. In DDP films in the absence of Zn (or very small amount due to contamination), the sulfur proportion ($\sim$1%) is very low compared to that of ZDDP films ($\sim$8%).

For the DDP films, Najman et al. [19] already reported that substantial FeS was present in these films after rubbing for greater than 5 min. The formation of FeS is much clearer in the 10 s and 30 s films shown in figure 7 D and E: indeed, FeS is the dominant S species in these two spectra. The presence of peak *c* in these spectra could be due to a small amount of ZnS from the contaminant Zn. The 10 h film shows the presence of sulfate (peak *e*) plus a some FeS and FeS$_2$ with perhaps a small amount of ZnS.

S K-edge XANES spectra of tribofilms generated from different concentrations of ZDDP were also investigated (not shown). The spectra of sulfur in the different concentration tribofilms are the same and align with zinc sulfide. This indicates that the concentration of ZDDP does not affect the formation of zinc sulfide in the tribofilm.

2.5. The overall mechanism

Taken together, the P L-edge, Fe L-edge and O K-edge spectra show that there is appreciable Fe in both ZDDP films and DDP films at the interface, with more Fe in the DDP films as expected. The XPS depth profiling results (figure 5, Part 1), along with the previous Auger depth profiles [3], also show appreciable Fe in the bulk of the ZDDP films, although these depth profiles may well expose substrate Fe or Fe oxide because of the very non-uniform films. However, the Fe and O spectra do not indicate the amounts of Fe that are expected from our model compounds and model glasses, although the Fe and O spectra certainly indicate some Fe in the films.

From the above observations, the mechanism of tribofilm formation, generated from ZDDP and DDP, in the rubbing contact can be described as follows:

1. Before rubbing, ZDDP and DDP adsorb on the steel surface.
2. When the rubbing begins, ZDDP and DDP decompose and react in the rubbing contact due to the high local temperatures at the rubbing surface. However, a recent publication by Fujita and Spikes [36] suggests that the thermal processes alone cannot be responsible for ZDDP decomposition. Catalytic and triboelectronic processes may play an important role. At first, sulfur and phosphorus from the ZDDP react with the steel surface to form iron sulfide and phosphate. Simultaneously, some decomposed ZDDP products, such as zinc sulfide and phosphate, deposit on the rubbing surface. As the rubbing time continues, the rubbing surface is covered by a mixture of iron sulfide/phosphate and zinc sulfide/phosphate. The rapid formation of the ZDDP tribofilm compared to the DDP tribofilm must be due to the rapid formation of ZnS and/or Zn phosphate. Both species are thermodynamically much more stable than their Fe analogues.
3. After the rubbed steel surface is covered by the tribofilm, the decomposed products of ZDDP (zinc sulfide and phosphate) continue to react on the rubbing contact, and the Fe diffuses from the steel surface to react with the long chain Zn phosphate to give shorter chain phosphates [15, 37, 38]. With DDP, short chain phosphates are always formed, despite the fact that the Fe should not be as available as the Zn from the ZDDP.
4. Zinc sulfide formation has used some of zinc from ZDDP. There is not enough zinc cation to form the constant ratio Zn/P phosphate observed. Zinc phosphate will polymerize with more phosphate from decomposed ZDDP to form longer chain length zinc polyphosphate. As the rubbing time continues, the chain length of zinc polyphosphate will be increased. This result can be used to explain the reason that long chain zinc polyphosphate is formed at the top of tribofilms and short chain zinc polyphosphate is formed in the bulk of tribofilms. In the case of DDP, no cation is available for a thick film (No Fe from the surface). At this stage, the additive decomposes, and alkyl groups do not leave the surface and form a phosphate ester type of compound with no metal cation present. This process is less likely with ZDDP, as long as sufficient Zn is available to form the long chain polyphosphate structures.
5. From above discussion, it can be concluded that the tribofilm generated from ZDDP is a multi-layer film. The mechanism of tribofilm formation for both ZDDP and DDP is given in more detail below:
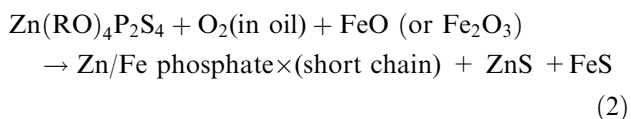
3. a. ZDDP

(Products entering solution are ignored)

Stage 1: Physical/chemical adsorption

$$Zn[(RO)_2PS_2]_2(\text{solution}) \rightarrow Zn[(RO)_2PS_2]_2 \qquad (1)$$
$$(\text{ZDDP adsorbed})$$
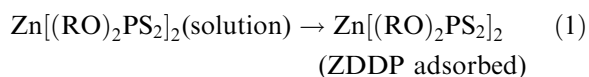
Stage 2: Initial film formation ($\sim$ 10 nm) on the surface when cations are plentiful.

$$Zn(RO)_4P_2S_4 + O_2(\text{in oil}) + FeO \text{ (or Fe}_2O_3)$$
$$\rightarrow Zn/Fe \text{ phosphate} \times (\text{short chain}) + ZnS + FeS$$
$$(2)$$

Stage 3: Surface is covered with a thin film and Fe is not accessible from the substrate:

$$Zn(RO)_4P_2S_4 + O_2(\text{in oil})$$
$$\rightarrow Zn \text{ phosphate (long chain)} + ZnS \quad (3)$$
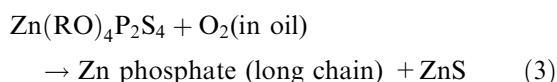
In stage 2 based on ΔH_f^0 values given above, the proportion of FeS will be very small. In stage 3, Zn phosphate formation is preferred over ZnS formation.

Stage 4: Conversion of long chain polyphosphate to short chain.

$$Zn \text{ phosphate (long chain)} + 6H_2O$$
$$\rightarrow Zn \text{ phosphate (short chain)} + 4H_3PO_4 \quad (4)$$
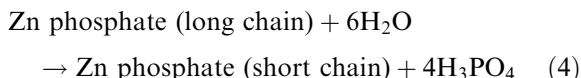
In stage 4, any water in the system can hydrolyze long chain polyphosphate to short chain [17,39]. As a result, the film becomes thicker, composed of short chain Zn phosphate (with little Fe). We can think of a tri-layer film, with the top layer consisting of longer chain phosphates, a middle layer of predominantly short chain phosphates, and an inorganic layer of ZnS and/or FeS.
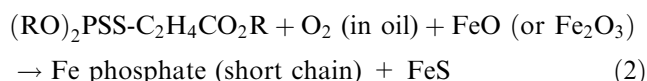
4. b. DDP

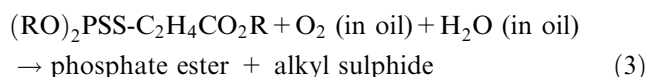(Products entering solution are ignored)

Stage 1: Physical/chemical adsorption

$$(RO)_2PSS - C_2H_4CO_2R(\text{solution})$$
$$\rightarrow (RO)_2PSS - C_2H_4COOR \text{ (DDP adsorbed)} \quad (1)$$
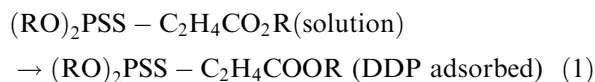
Stage 2: Initial film formation ($\sim$10 nm) on the surface when Fe are plentiful

$$(RO)_2PSS\text{-}C_2H_4CO_2R + O_2 \text{ (in oil)} + FeO \text{ (or } Fe_2O_3)$$
$$\rightarrow Fe \text{ phosphate (short chain)} + FeS \quad (2)$$

Stage 3: Surface is covered with a thin film of Fe phosphate and no cation is accessible from the substrate

$$(RO)_2PSS\text{-}C_2H_4CO_2R + O_2 \text{ (in oil)} + H_2O \text{ (in oil)}$$
$$\rightarrow \text{phosphate ester} + \text{alkyl sulphide} \quad (3)$$

In stage 3 the alkyl sulphide will be dissolved in oil. However, it is difficult to see how the phosphate ester can remain on the surface. It has been shown in the case of ZDDP that the ester hydrolyzes in part to a dithiophosphoric acid which can remain on the surface via a weak bonding [34,40].

5. Conclusion

The XANES spectra yield much information about the film chemistry. The P 2p spectra (along with the O K-edge spectra and Fe L-edge spectra for the first time) have been used to give information on the role of Fe in the films. For ZDDP, a bilayer phosphate film develops very quickly. Initially, the film is predominantly short chain polyphosphate with Zn as the predominant cation; but the film develops to give predominantly long chain Zn polyphosphate at the surface, and a shorter chain polyphosphate with some Fe in the bulk. The average polyphosphate chain length increases with an increase in ZDDP concentration up to a certain point. For DDP, the polyphosphate film is of short chain character throughout the test, with the major cation being Fe, although our spectra do not indicate as much Fe as would be expected for an Fe phosphate glass. The Fe from the oxide and from solution must become available at the high local temperatures for the phosphate film formation – even for the relatively thick films. Some S from the ZDDP reacts to form ZnS; but, in addition, the presence of FeS has been identified for the first time in the early films from both ZDDP and DDP.

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