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Spatial distribution of the chemical species generated under rubbing from ZDDP and dispersed potassium triborate

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The partial replacement of ZDDP by dispersed potassium triborate in engine oil was studied. X-ray Absorption Spectroscopy at the phosphorus, sulphur and boron edges was used to identify the chemical species in tribochemical films on the macro-scale. PhotoElecton Emission Microscopy (PEEM) was performed to study the distribution of the chemical species on the micron level. It was found that tribofilms are homogeneous at the 1-micron scale. It was established that zinc is associated only with sulphides and not with phosphates, and phosphates and borate have the same distribution. The cation associated with phosphates is most likely to be potassium from the borate additive. The wear scar width measured on the tribofilms and XANES analysis indicated that dispersed potassium triborate associated with ZDDP has a positive effect on wear prevention.

KEY WORDS: boundary lubrication, wear, ZDDP, borate, XANES, spectromicroscopy, AFM

1. Introduction

In "boundary lubrication", protection against wear is due to the formation of tribochemical films on the surfaces in contact. The films are generated by the reactions of lubricant additives with the contact surface or surfaces. Yet, the presence of tribochemical films is not sufficient, *per se*, to protect against wear: efficacy is highly dependent on the chemical and mechanical properties of the film. In engine oils, zinc dialkyldithiophosphates (ZDDPs) have been widely used as antioxidant and antiwear additives since the 1940s. The demand for reduction of phosphorus/sulphur content in engine oils has forced the oil suppliers to modify the formulation of lubricant additives. Thus, other additives might replace the ZDDP content of oil partially or totally. Organic boron compounds are possible candidates to replace ZDDP: alkali borates have been shown to possess good antioxidation and EP properties [1]. Their action can be related to the formation of a borate glass as a tribochemical film [2]. Yet, boron additives do not seem to be well suited to replace totally ZDDP in oil. When one type is used in combination with ZDDP, nearly half of the phosphorus could be replaced by approximately one-tenth the amount (on a weight basis) of boron [3]. However, the effect of the boron-containing additive on the antiwear properties of ZDDP could not be firmly established. A synergistic effect was later demonstrated between ZDDP and a multifunctional micellar additive through the formation of a borophosphate glass [4]. Thus, ZDDP and a simple boron-containing additive, namely dispersed potassium triborate, may also lead to the formation of a borophosphate glass.

X-ray absorption spectroscopy using synchrotron radiation is a powerful technique that can characterise the protective layers formed by lubricant additives. X-ray Absorption Near-Edge Spectroscopy (XANES) is the study of electronic transitions from atomic core levels to unoccupied molecular states (antibonding orbitals) below and above the vacuum level in the absorbing atom. XANES spectroscopy has been used at the P and S edges for chemical characterisation of antiwear and thermal films generated from ZDDPs [5,6]. XANES is well adapted to study the films generated from boron-containing compounds since the cross-section of the boron K-edge is very high, allowing the detection of small boron concentrations [7]. However, the analysed area is of the order of several mm^2, and the spatial distribution of the chemical species cannot be determined.

PhotoElectron Emission Microscopy (PEEM) is extremely useful for studying the spatial distribution of most chemical species on antiwear films at the micron

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level. These microscopes image secondary electrons, emitted after resonance excitation of a core electron to an antibonding level. The latest version of the technique is called MEPHISTO (Microscope à Emission de Photoélectrons par Illumination Synchrotonique de Type Onduleur, i.e., photoelectron emission microscope by synchrotron undulator illumination). It allows secondary electron microimages to be obtained, as well as high-resolution X-ray absorption spectra from selected areas. Lateral resolution better than 20 nm has been obtained with this instrument [8]. Canning *et al.*, in a detailed study, presented the potential applications of the MEPHISTO microscope for the study of antiwear films. They could, for example, map the chemical distribution of long-chain and short-chain polyphosphates in a film generated from ZDDPs [9].

In this paper, we present many XANES spectra acquired on the tribofilms generated from dispersed potassium triborate used in combination with neutral di-isobutyl ZDDP. MEPHISTO experiments at the micron level will then be presented to confirm the chemical composition of the film and to identify the precise nature of the phosphate cation.

2. Experimental conditions

Neutral di-isobutyl (primary) ZDDP, hereafter referred to as ZDDP, was synthesised according to a procedure described before [10]. The concentration in base oil (Chevron 100N) was 5 mmol/kg. The potassium triborate dispersion was synthesised by neutralising potassium hydroxide with an excess of boric acid to produce a potassium borate/boric acid solution. The solution was then dispersed in an oil/dispersant/sulphonate (Ca salt) mixture to form a water-in-oil emulsion [11]. Upon heating, a dehydration reaction forms an extended non-crystalline (amorphous) boron-oxygen molecular structure with the empirical formula KB_3O_5 [12]. The concentrations of boron and potassium in oil were 0.2 and 0.25 wt%, respectively. When associated with dispersed potassium triborate, the concentration of ZDDP in oil was set to 1 mmol/kg.

A pin-on-flat Plint High Frequency wear tester was used to prepare the antiwear films. The circular coupons (19 mm diameter) and cylindrical pins (6.2 mm diameter, 11 mm height) used in this study are 52100 steel and they were hardened to Rockwell C 60-64. The coupons were polished by 3 μ diamond paste to a mirror finish. Steel coupons and pins were cleaned using light hydrocarbon solvent prior to the experiment. The oil was placed in the Plint High Frequency wear tester along with a steel coupon and pin, and the bath temperature was set to 100 °C. The cylindrical pin was then loaded against the coupon in the oil bath ($F = 220$ N). The rubbing frequency was increased to 25.0 Hz and maintained for 1 h. The stroke length was 7 mm. After the test, excess oil was gently blotted from the surface with a tissue paper. The wear scar widths (WSW) were measured on the cylindrical pin using a calibrated optical microscope. The reported values correspond to at least ten measurements, made along the axis of the pin. All the tribofilms were made in triplicate.

The spectra of the tribofilms were compared to spectra of reference compounds. The reference compounds were commercially available products of high purity and were used without any further purification. During the XANES analysis, the reference compounds were maintained on the specimen holder by a double-sided conducting carbon tape.

Phosphorus and sulphur K- and L-edge, and boron K-edge X-ray absorption spectra (analysed area $\sim 5\,\text{mm}^2$) were obtained at the Canadian Synchrotron Radiation Facility (CSRF) situated at the 1 GeV Aladdin storage ring, University of Wisconsin, Madison. The coupons were not cleaned prior to XANES experiments, since the spectra obtained with and without cleaning with *n*-hexane yielded similar results [13,14]. The P and S K-edge spectra were obtained on the Double Crystal Monochromator (DCM) beamline, covering the region of 1500–4000 eV. The Grasshopper beamline was used to obtain the P and S L-edge spectra together with the B K-edge spectra. The X-ray beam was monochromatised by an 1800 g/mm grating and covers the photon region of 70–900 eV. The photon resolution at the P L-edge and P K-edge was less than 0.2 and 0.8 eV, respectively. Three scans were digitally combined and normalised by the incident photon intensity I_0. The edge of interest was then obtained by subtraction of a linear background.

The photoabsorption spectra were recorded in the Total Electron Yield (TEY) and Fluorescence Yield (FY) modes. The maximum analysis depth is about 5 nm for TEY, and about 50–100 nm for the FY at the P and S L-edges, and the B K-edge [15]. It is also about 50 nm for TEY at the P and S K-edges, and is calculated to be larger than 5 μm for the corresponding FY detection mode.

Atomic force microscope (AFM) topography images were recorded with a Nanoscope IIIa equipped with a MultiMode™ head (Digital Instruments, Santa Barbara, California). They were recorded in tapping mode with commercial V-shaped silicon cantilevers. The samples were rinsed in *n*-hexane prior to analysis.

The analysis of the films produced under rubbing was also performed at the Synchrotron Radiation Center–University of Madison using the MEPHISTO system connected to the 6-m TGM (Toroidal Grating Monochromator) beamline. The samples were rinsed in *n*-hexane prior to entry into the vacuum chamber to remove any excess oil.

The MEPHISTO analysis [16] consisted of acquiring microscopic images of secondary electron intensity from various areas on the sample. These show the emitted electron intensity over the observed sample area and are obtained by capturing an image of the emitted electrons on a phosphor screen at a specific photon energy. The electron intensity images can provide detailed chemical maps showing the spatial distribution of a given element or even a given element in a specific oxidation state. This is accomplished by taking microimages at different photon energies in the spectral region of an X-ray absorption edge of the relevant element. The comparison of images taken at photon energies above and below the edge reveals the distribution. The images presented were created through digital subtraction of an image captured at the peak energy of the species of interest and an image obtained at an energy below the peak. This procedure removes contrast created by surface roughness.

X-ray absorption spectra of selected areas inside the images were also obtained. Unlike the conventional X-ray absorption technique where the area being sampled is 5 mm^2 and the spectra is an average of the entire surface of the sample, MEPHISTO permits spectra to be obtained from a few hundred μm^2 quickly, or a few tens of μm^2 after multi-scanning. The spectra are obtained by taking the electron-emission intensity near the P and S L-edge and the Zn M-edge as a function of photon energy. The spectra provide precise chemical information of areas within the sample, including elemental composition and oxidation state. The spectra presented have been normalised for I_0.

3. Results and discussion

3.1. Wear scar measurements

The average Wear Scar Widths (WSW) for films generated from base oil, ZDDP, dispersed potassium triborate and the combination of ZDDP and dispersed potassium triborate are displayed in table 1. The performance of the antiwear additive can directly be related to the WSW. The most effective antiwear additive gives the smallest WSW.

ZDDP alone gives a very small WSW. The WSW for 5 mmol/kg ZDDP is almost half the WSW of the base oil ($125 \pm 7\,\mu m$ versus $235 \pm 12\,\mu m$). A relatively large WSW is obtained with dispersed potassium triborate alone ($169 \pm 6\,\mu m$). This additive is not well adapted for the total replacement of ZDDP. However, when it is used in combination with 1 mmol/kg ZDDP, dispersed potassium triborate shows no harm, since the WSW is equivalent to that of 1 mmol/kg ZDDP and slightly smaller than that of 5 mmol/kg ZDDP alone. The data suggest that ZDDP can be partially replaced with dispersed potassium triborate, thereby reducing the level of ZDDP used (see next section for discussion on XANES spectra and what this means for polyphosphate formation). Our conclusions are in agreement with the results found in the literature on other boron-containing additives, although the wear test used with our experimental conditions is far less severe than a standard four-ball test [3].

In the following, we will show that ZDDP and dispersed potassium triborate efficiently prevent wear, and we will analyse the chemical species present in the tribochemical film formed under friction.

3.2. Chemical analysis on a ~5 mm^2 area

The phosphorus L-edge XANES spectra of the tribofilm generated from ZDDP and dispersed potassium triborate, of the tribofilm generated from ZDDP alone and of several model compounds are displayed in figure 1. Several peaks can be distinguished on the spectrum of the tribofilm ([A]). Peak a_1, occurring at 134.0 eV, does not exist on the spectrum of the tribofilm generated from ZDDP alone ([B]). It originates from undecomposed ZDDP (spectrum [J]), or rearranged ZDDP, so-called linkage-isomer ZDDP, (Li-ZDDP), spectrum [I]. It has been suggested that in Li-ZDDP alkyl groups migrate from O atoms to S atoms [6]. This compound was proposed as an important precursor for thermal film formation from ZDDP. Peaks *a*, *c*, and *f*, at 135.2, 138.3, and 146.1 eV, respectively, correspond to phosphates and are also present in the spectrum of the tribofilm generated from ZDDP alone (spectra [B] to [H]). Peak *a* also partially originates from ZDDP ([J]) and Li-ZDDP ([I]). In spectrum [A], peak *b* is not

Table 1
Wear scar width (WSW) measurements for the tribochemical films. The WSW of ZDDP alone and ZDDP in combination with dispersed potassium triborate are similar.

Oil	Average wear scar width (μm)	Standard error of the mean (μm)
base oil	235	12
5 mmol/kg neutral di-isobutyl ZDDP	125	7
1 mmol/kg neutral di-isobutyl ZDDP	130	5
dispersed potassium triborate	169	6
1 mmol/kg neutral di-isobutyl ZDDP + dispersed potassium triborate	124	5

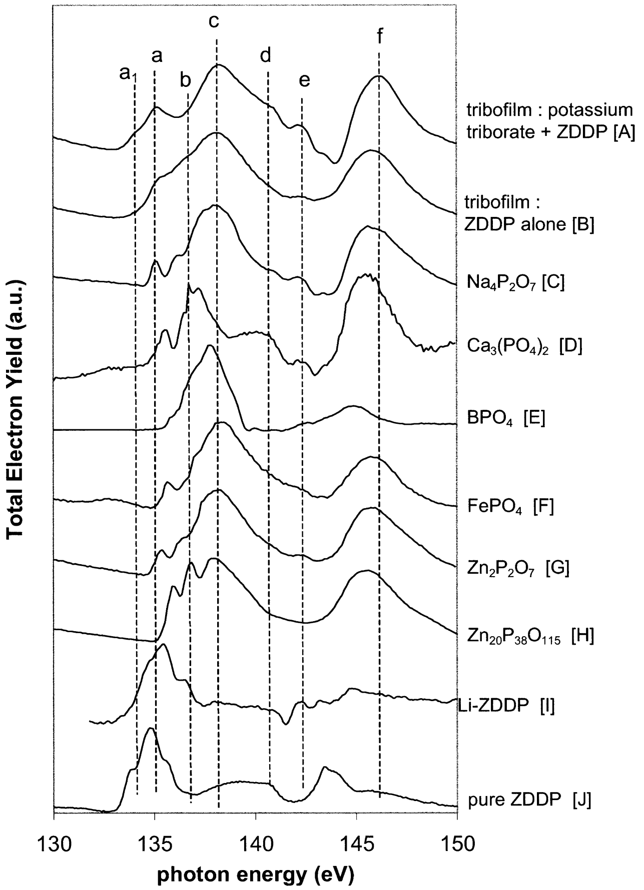


Figure 1. P L-edge XANES spectra of model compounds and tribochemical films using the Total Electron Yield (TEY).

resolved. This indicates that the tribofilm ([A]) lacks long-chain zinc polyphosphates (spectrum [H]). The observation of polyphosphates has been related to effective antiwear protection [5]. Shoulder *d* occurring at 140.8 eV gives more information about the cation associated with phosphate [17]. It is very noticeable for the spectrum of the tribofilm generated from ZDDP and potassium triborate ([A]), but not discernible on the spectrum of the tribofilm generated from ZDDP alone ([B]). Shoulder *d* is also very noticeable for $Ca_3(PO_4)_2$ ([D]) and it is weak for $Na_4P_2O_7$ ([C]) and zinc phosphates ([G] and [H]), but not seen on BPO_4 ([E]). Unfortunately, it was not possible to acquire a good spectrum of potassium pyrophosphate $K_4P_2O_7$ because it was not stable enough under the synchrotron beam. It will be assumed that its spectrum is similar to that of sodium pyrophosphate $Na_4P_2O_7$. The cation for phosphates in the tribofilm could most likely be Ca^{2+} originating from the detergent (calcium sulphonate), and/or K^+ from dispersed potassium triborate, and/or Zn^{2+}, but not B^{3+}. Shoulder *e* is due to C 1s from the 2nd order radiation from carbon on the film and carbon contaminations in the beamline (285/2 eV).

From the macro-scale analysis, it is not possible to state whether (i) there is a chemical interaction between ZDDP and dispersed potassium triborate to form potassium phosphate, or (ii) if ZDDP alone reacted to form zinc phosphate. Spectromicroscopic analysis (see below) will allow us to conclude that phosphate is most likely associated with potassium.

The sulphur XANES L-edge spectra of the tribofilms generated from ZDDP alone, dispersed potassium triborate alone, dispersed potassium triborate in combination with ZDDP, and several model compounds are presented in figure 2. The spectrum of the tribofilm generated from ZDDP and dispersed potassium triborate (spectrum [A]) is dominated by eight well-defined peaks, labelled *a* to *h*. This spectrum is clearly different from the spectrum of the tribofilm generated from ZDDP alone (spectrum [B]), which exhibits only the first three peaks. Peaks *a*, *b* and *c*, at 163.1, 164.4, and 165.7 eV, respectively, are characteristic of reduced forms of sulphur (sulphides) originating from undecomposed ZDDP and Li-ZDDP. This is in agreement with the P L-edge spectra (see figure 1). Zinc sulphide (spectrum [G]) exhibits a broad spectrum in the 163 eV region and it can also contribute to the reduced form of sulphur. Peaks *d*, *e*, *f* and *h*, occurring at 168.5, 170.5, 171.7, and 180.5 eV, respectively, can be assigned to sulphonate species ([F]). Since potassium triborate is dispersed in oil using a

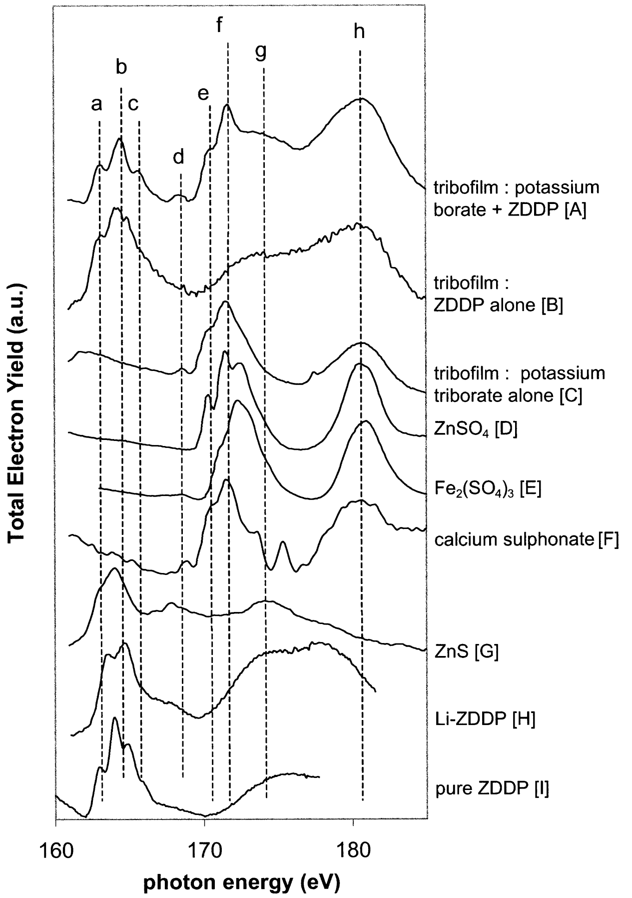


Figure 2. S L-edge XANES spectra of model compounds and tribochemical films using the Total Electron Yield (TEY).

dispersant and a detergent, calcium sulphonate, spectra [A] and [B] both show those peaks. Note that the small features present in the spectrum of calcium sulphonate ([F]) at 173.6 and 175.4 eV are Ca 2p from second order peaks. The sulphonate additive used in this work did contain calcium; however the spectra of the tribofilms do not exhibit such features.

The boron XANES K-edge spectra of the tribofilms generated from dispersed potassium triborate alone, dispersed potassium triborate in combination with ZDDP, and several model compounds are presented in figure 3. The spectra exhibit three peaks, *a*, *b*, and *c*. In general, peaks *a* and *c* are associated with boron in trigonal co-ordination (see spectrum [E]) and peak *b* to tetrahedral co-ordination (see spectrum [F]). The spectra of the two tribofilms (spectra [A] and [B]) are quite similar. This indicates that ZDDP has very little effect on the chemistry of boron. However, peak *b* at 198.8 eV seems to be stronger for the tribofilm generated from dispersed potassium triborate and ZDDP (spectrum [A]). Spectrum [A] and spectrum [B] indicate that there are substantial amounts of both trigonally- and tetrahedrally-coordinated boron, as indicated in spectra [E] (B_2O_3, trigonal) and [F] (BPO_4, tetrahedral).

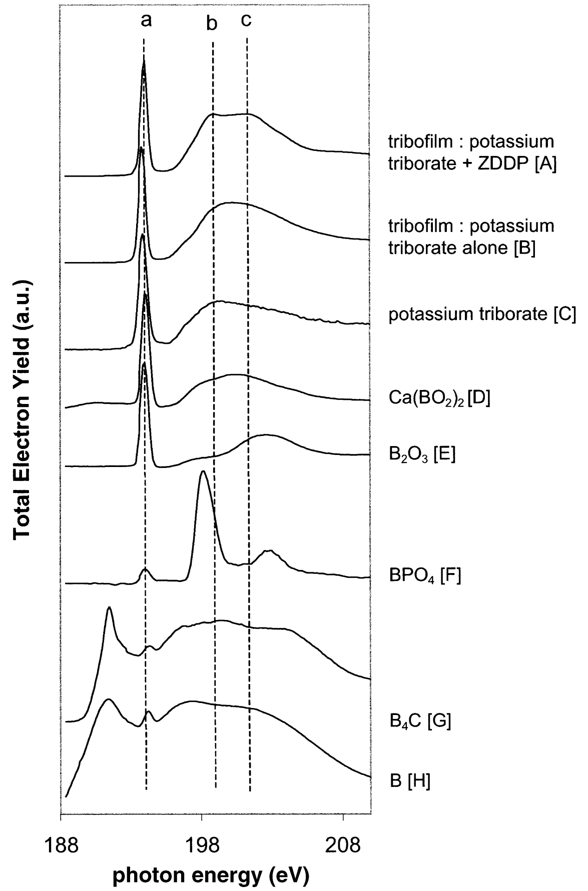


Figure 3. B K-edge XANES spectra of model compounds and tribochemical films using the Total Electron Yield (TEY).

As mentioned above, the spectra of the two tribofilms (spectra [A] and [B]) are quite similar. However, peak *b* is noticeably stronger when ZDDP is used in combination with dispersed potassium triborate, which shows that the tribofilm generated from ZDDP and dispersed potassium triborate contains more tetrahedrally-coordinated boron.

All the spectra discussed above were acquired in the Total Electron Yield (TEY) mode. The sampling depth of the TEY for P and S L-edge, and B K-edge is 5–10 nm [15] and thus refers to the surface of the tribofilms. Spectra in the Fluorescence Yield (FY) mode were recorded simultaneously, which refer to the bulk of the tribofilms (~50 nm at the P and S L-edge, and ~100 nm at the B K-edge). The FY spectra at the P and S L-edges (not displayed) are very noisy. That indicates that the films are relatively thin. It can, however, be deduced from the FY spectra that, at ~50 nm depth, phosphorus is only present as phosphate and sulphur only as the reduced form. No more precise information about the chemical species can be obtained.

The B K-edge spectra recorded in the FY mode are less noisy than the P and S L-edge spectra, because the boron cross-section is very high. The FY spectra of the tribofilms (not displayed) are remarkably similar to the spectra recorded in the TEY mode. The chemical species containing boron can thus be found both on the surface and in the bulk.

More information about the types of phosphates and reduced forms of sulphur can be obtained from the P and S K-edge spectra recorded in the TEY mode. At X-ray energies around P and S K edges, the TEY signal is expected to originate from the bulk of the tribofilm (50 nm) [15]. The phosphorus K-edge spectra (TEY mode) of the tribofilm generated from ZDDP alone, from ZDDP and dispersed potassium triborate, and of several model compounds are displayed in figure 4. The overall shape of the spectrum of the tribofilm generated from dispersed potassium triborate and ZDDP ([A]) is similar to that of the spectrum of the tribofilm generated from ZDDP alone ([B]). It is characteristic of phosphates, but in contrast to the spectrum of the tribofilm generated from ZDDP alone ([B]), long-chain polyphosphates are absent (cf. spectrum [D]). This agrees with the data found for the P L-edge. Peak *b* occurs at 2152.1 eV. It is at the same photon energy as the peak *b* in zinc phosphates (spectra [C] and [D]) and sodium pyrophosphate $Na_4P_2O_7$ (spectrum [F]), but not $FePO_4$ ([E]) and BPO_4 ([G]). The shoulder labelled *c*, at 2156.6 eV, on the spectrum of the tribofilm can also be attributed to sodium phosphate. Another shoulder, *a*, before peak *b*, at 2149.1 eV could reveal the presence of $FePO_4$ ([E]) and/or Li-ZDDP ([H]) and/or ZDDP ([I]). The presence of $FePO_4$ in the film is unlikely, since the main peak of iron phosphate is shifted by ~1.0 eV to the high energy with respect to that of the tribofilm. Thus the shoulder is due to the presence of undecomposed

ZDDP and Li-ZDDP, as found from the L-edge (see figure 1 and figure 2).

As far as the sulphur species are concerned, the S K-edge TEY spectra are displayed in figure 5. As expected, the spectra of the tribofilm generated from ZDDP and dispersed potassium triborate (spectrum [A]) is dominated by features characteristic of reduced forms of sulphur. The tribofilm generated from ZDDP alone (spectrum [B]) is also composed of reduced forms of sulphur, although peaks *a* and *d* are not present in its spectrum. Broad peak *b*, at 2473.0 eV, aligns relatively well with the main peak of zinc sulphide ([H]) and that of ZDDP ([I]). This is in agreement with the sulphur L-edge TEY spectra. A shoulder *a* is located before peak *b*, at 2469.5 eV. It can unambiguously be assigned to iron sulphide FeS (see spectrum [J]). Iron sulphide was not detected in the S L-edge TEY spectra (surface of the film). This means that iron sulphide is located close to the metal surface and is probably created early in the development of protective films. Two other peaks, labelled *c* and *d*, are located at 2476.5 and 2479.5 eV, respectively. Broad peak *c* can be assigned to SO_3^{2-} species (spectrum [F]) as has been reported before [17].

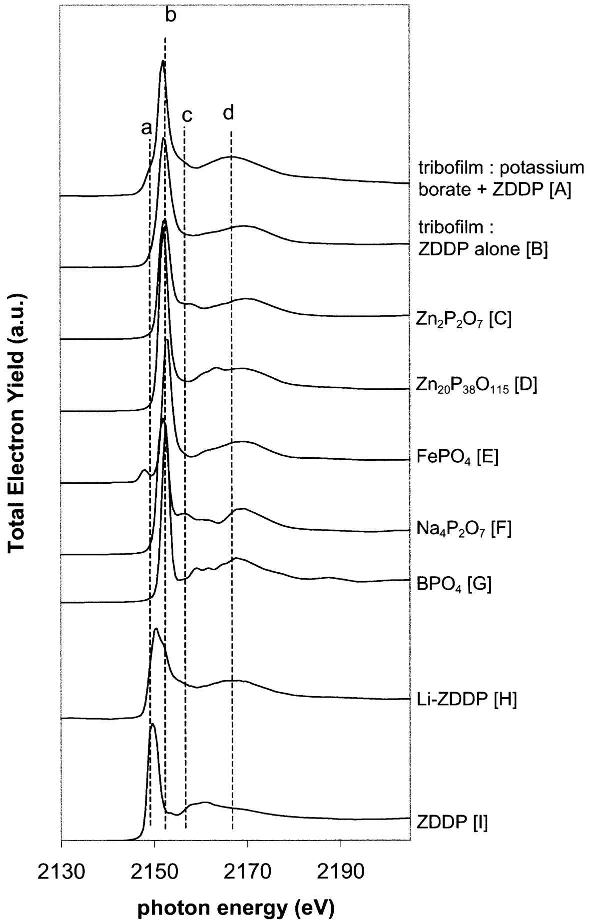


Figure 4. P K-edge XANES spectra of model compounds and tribochemical films using the Total Electron Yield (TEY).

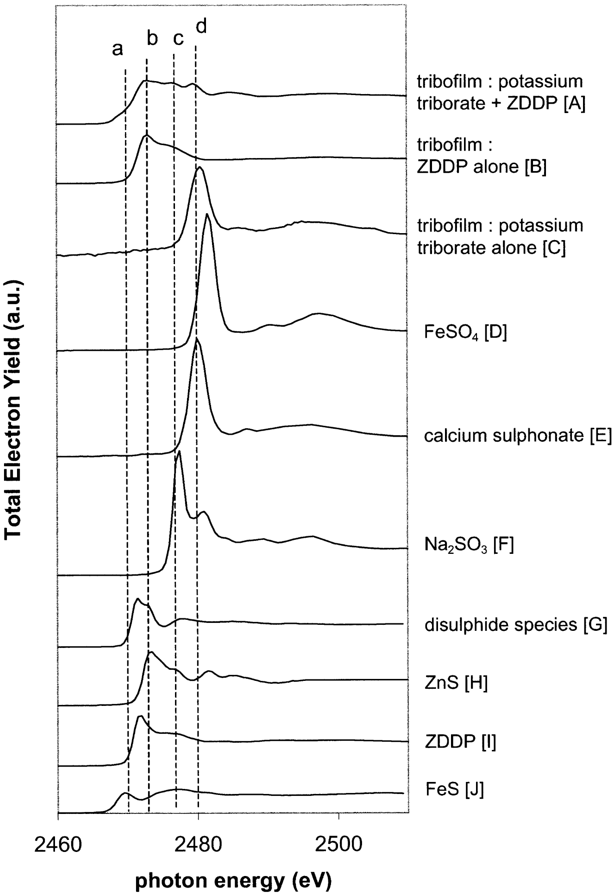


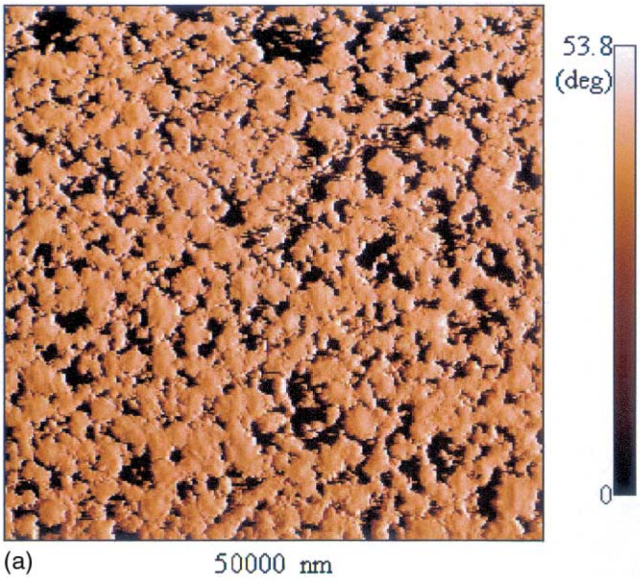
Figure 5. S K-edge XANES spectra of model compounds and tribochemical films using the Total Electron Yield (TEY).

Peak *d* can be assigned to sulphonate species (spectrum [E]), which originate from the boron additive. This was also detected on the surface of the tribofilm (see figure 2). In the absence of ZDDP, sulphonate species is oxidised to sulphate [17]. This is indeed visible on the spectrum of the tribofilm generated from dispersed potassium triborate alone (spectrum [C]).

The macro-scale analysis reveals that ZDDP reacts to form zinc and iron sulphides, created under rubbing on iron surfaces free of iron oxide, and phosphates. Potassium triborate additive reacts to form borate species with three coordinate and four coordinate boron. As far as phosphates are concerned, the associated cation could not be determined precisely, although in the triborate-ZDDP film, $Ca_3(PO_4)_2$ is present. The latter has recently been associated with reduced wear control [17]. Moreover, the spatial distribution of borates relative to phosphates needs to be investigated, in particular concerning the presence of borophosphates.

3.3. Heterogeneity of the sample

An AFM 50 × 50 μm image of the tribofilm generated from dispersed potassium triborate and ZDDP is displayed in figure 6(a). The surface of the tribofilm is quite heterogeneous. It is composed of small pads, whose diameters lie between 2 to 3 μm apart. The pads are not elongated along the sliding direction, but exhibit a rounded shape. Line cuts (elevation versus position along a continuous line) across the image clearly show that the pads are of equivalent heights. The presence of small and large pads was found to be characteristic of tribofilms generated from alkyl ZDDP [18]. It was concluded in that study that unlike the small pads, the large pads possess a very high indentation modulus and a significant resistance to plastic flow, and carry the load during wear testing. Previous MEPHISTO experiments determined that the large pads were composed of longer chain length polyphosphates compared to the smaller pads [9].



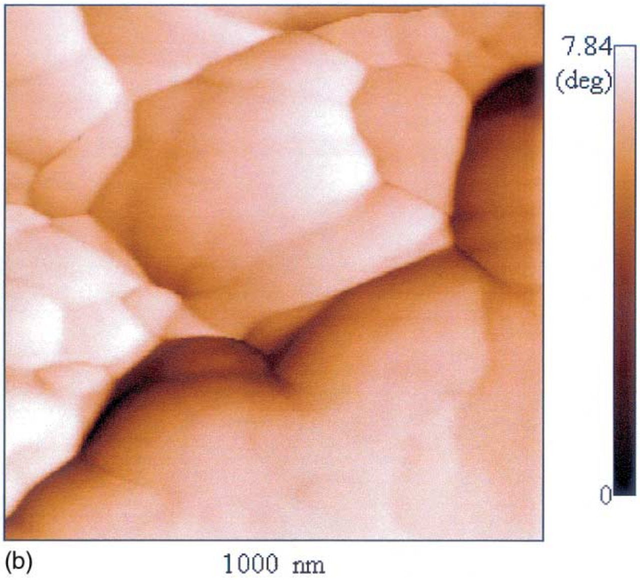


Figure 6. (a) 50 μm and (b) 1 μm wide AFM images of the tribofilm generated from ZDDP and dispersed potassium triborate (phase contrast). The images show a contrast due to differences in the thickness of the film. The film seems to be homogeneous in composition.

As far as the tribofilm generated in this study from dispersed potassium triborate and ZDDP, the pads are considered as “small pads,” but they ensure a good wear protection. Their composition is undoubtedly different from the composition of the pads generated from ZDDP alone (zinc polyphosphates).

Figure 6(b) displays an AFM 1 × 1 μm image of the same tribofilm. The surface of the pads is very smooth and clean, as demonstrated by the uniformity of intensity in the image. Dispersed potassium triborate in oil forms small spheres, with diameters of about 144 nm by light-scattering measurements [19]. No evidence of remaining 144 nm spheres could be found when imaging the tribofilm.

3.4. Distribution of the chemical species

Figure 7(a) shows the spatial distribution of borate in the tribofilm generated from dispersed potassium triborate and ZDDP. The image was taken at 193.8 eV with a background image at 192.5 eV subtracted. The bright areas on the image are where borate is present. The distribution map of phosphate is displayed in figure 7(b). It was obtained by subtracting the background image at 135.0 eV from the image at 139.0 eV. The main peak of phosphate is at 139.0 eV and that of undecomposed ZDDP at 134.8 eV. Thus ZDDP is not being imaged in figure 7(b). Phosphate and borate are present everywhere in the analysed area, except in the middle (black areas). At the micron scale, phosphate and borate are well mixed together. The existence of borophosphates, i.e., chains composed of phosphates and borates, cannot be excluded, although figure 1 shows that BPO_4 is not dominant. It is much more likely that the phosphate and boron oxide are present in a homogeneous or heterogeneous mixture. More work is needed to determine if borophosphates can be created from ZDDP and dispersed potassium triborate under rubbing.

Figure 7(c) shows the spatial distribution of sulphide species in the tribofilm. The image was taken at 164.7 eV with a background image at 162.0 eV subtracted. As was shown in figure 2, we cannot resolve peaks associated with ZnS and ZDDP, and thus sulphur in this region (white area) can originate from ZnS and ZDDP. Figure 7(d) shows the spatial distribution of zinc in the tribofilm. The image was taken at 90.1 eV with a background image at 87.8 eV subtracted. Obviously, sulphides and zinc are located in the same areas, where there is less borate and phosphate. This is in agreement with previous studies on ZDDP alone [9].

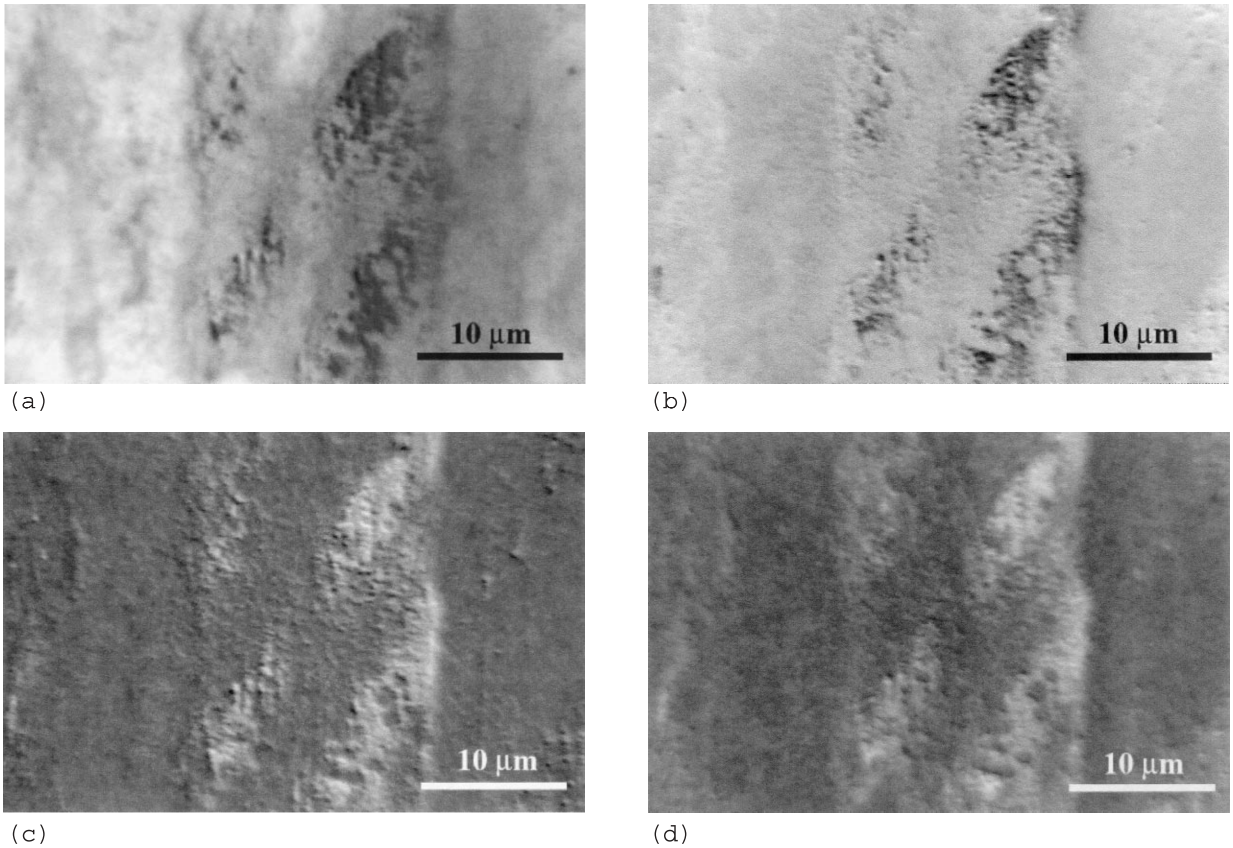


Figure 7. MEPHISTO images showing the distribution of (a) borate, (b) phosphate, (c) sulphide and (d) zinc. Sulphide and zinc are associated (ZnS or ZDDP). Borate and phosphate have the same distribution at the analysed scale.

We investigated whether zinc was exclusively present in the tribofilm as zinc sulphide/ZDDP or whether zinc could be associated with phosphates and borates. Three regions were defined in the tribofilm (see figure 8(a)). The image was recorded at the Zn M-edge (85.5 eV) in order to obtain a good contrast between the different areas in the tribofilm. From the previous analysis (see figure 7), region 1 is mainly zinc sulphide/ZDDP and region 2 is associated with phosphates and borates. Region 3 was defined to draw a comparison with the macro-scale analysis. Region 1 is $1.6 \times 7.5\,\mu\mathrm{m}^2$, region 2 is $5.6 \times 6.9\,\mu\mathrm{m}^2$, and region 3 is $40.6 \times 25.8\,\mu\mathrm{m}^2$.

The boron K-edge, phosphorus L-edge, sulphur L-edge and zinc M-edge spectra are shown in figure 8(b), (c), (d), and (e), respectively. The signal-to-noise ratio is dependent on the size of the region. All the spectra from region 1 exhibit a poor signal-to-noise ratio.

The spectra from region 3 are similar to the spectra acquired during the macro-scale analysis. The contributions of regions 1 and 2 are extremely different, revealing the different chemical compositions. As expected, region 1 exhibits significant peaks of sulphide species and zinc. Some phosphate could also be detected. Boron is also present, but due to the charging, the boron K-edge spectrum has been inverted. Charging phenomenon has been observed before [20]: when a localised area is less conductive than the surrounding specimen, the electrons emitted from nearby will be deflected and will be less likely to pass through the optics aperture. As the extent of the charging depends dynamically with the photon energy, spectra from nearby regions will contain energy-dependent intensity losses, which are greatest close to the charging feature. The fluctuations may even pull the intensity below the background level, creating negative dips in the TEY spectra. Region 2 exhibits a large amount of borate and phosphate, but no sulphide and no zinc could be detected. Region 1 is thus composed of zinc sulphide/ZDDP and some boron, in contrast to region 2, which contains a layer of phosphates. This is an interesting result: it can be concluded that zinc is exclusively present in the analysed area (region 1) as zinc sulphide/ZDDP and is not associated with phosphates. Although some $Ca_3(PO_4)_2$ is present in the film, charge balance probably requires that K^+ be present. It should be emphasised that in the MEPHISTO analysis we are using total electron yield mode of detection and thus probing a shallow depth of $\sim$5 nm. Any species hidden under this depth are not detected.

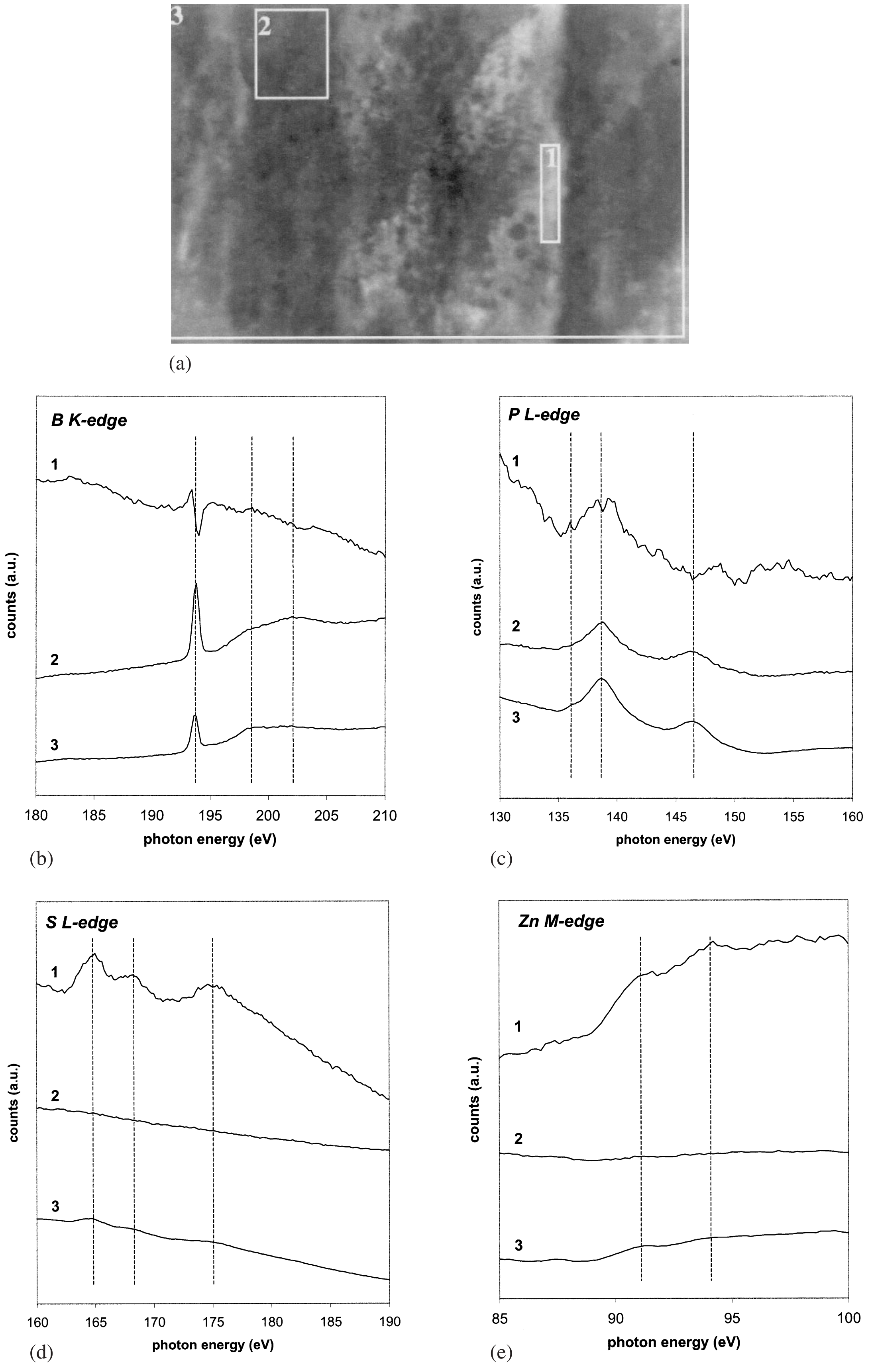


Figure 8. (a) MEPHISTO image of the film with the regions where the following spectra were recorded. (b) B K-edge, (c) P L-edge, (d) S L-edge, and (e) Zn M-edge spectra. Region 1 is almost exclusively composed of ZnS/ZDDP, although a little amount of phosphate could be detected. No zinc could be detected in region 2. The spectra acquired in the region 3 are equivalent to the spectra recorded on a macroscale.

4. Conclusions

The partial replacement of ZDDP using dispersed potassium triborate was investigated at a macro-scale using X-ray Absorption Spectroscopy at the phosphorus, sulphur and boron edges. The chemistry of the tribochemical film could be determined at the surface using the TEY and in the bulk using the FY detection modes. Spectromicroscopy experiments were carried out to determine the spatial distribution of the chemical species. The antiwear effectiveness was measured through the wear scar width (WSW). The following conclusions can be drawn from the results:

1. Combination of 1 mmol/kg ZDDP with dispersed potassium triborate exhibited excellent antiwear properties. The WSW was equivalent to the value obtained for 5 mmol/kg ZDDP. The possible partial replacement of ZDDP by potassium borate is in agreement with the results found in the literature on other boron-containing additives [3].
2. Macro-scale analysis of the tribofilm showed that both additives reacted under rubbing. ZDDP and dispersed potassium triborate generated phosphates and borates, respectively. From MEPHISTO experiments at the micron scale, phosphates and borates were found to have the same distribution map. AFM images revealed that the film was homogeneous at lower scales. However, we could not conclude whether phosphates and borates are located in separated regions (at a nanometer scale) or if they form borophosphate chains.
3. From MEPHISTO experiments it was found that zinc was exclusively associated with sulphur from ZnS or ZDDP, whereas it was associated with phosphates in the tribofilm generated from ZDDP alone. Sulphonate was also detected on the surface of the tribofilm originating from the boron additive.
4. By inference the cation associated with the phosphate (or borophosphate) chains is most likely to be potassium. Thus, the ZDDP and the dispersed potassium triborate react with each other under rubbing.
5. The observed WSW of the 1 mmol/kg ZDDP + potassium triborate combination is equivalent to that observed from the 5 mmol/kg ZDDP alone; the potassium triborate has a large effect, especially since no long-chain polyphosphate is observed, and $Ca_3(PO_4)_2$ is present in the combination film.

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