

Resolving the Chemical Variation of Phosphates in Thin ZDDP Tribofilms by X-ray Photoelectron Spectroscopy Using Synchrotron Radiation: Evidence for Ultraphosphates and Organic Phosphates

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Abstract X-ray photoelectron spectroscopy using a synchrotron source (SR-XPS) with variable photon energy has been used to non-destructively elucidate the variations in surface chemistry from ~5 nm to ~10 nm into the tribofilm derived from zinc dialkyldithiophosphate (ZDDP) in a mineral oil under boundary lubrication conditions. The elemental ratio of P/Zn and “bridging” oxygen (BO)/“non-bridging” oxygen (NBO) decrease as a function of distance from the top surface of the film, suggesting a decrease of the polyphosphate chain-length into the film, as shown in many recent XPS and XANES studies. More importantly, the measured P/Zn ratio of ~3, the BO/NBO ratios of >0.5, the P 2*p* spectra, and the absence of other balancing cations such as iron, show the first strong evidence for an ultrapolyphosphate (such as ZnP₄O₁₁), organophosphates along with other Zn polyphosphates. The existence of ultraphosphates and/or organophosphates in this film appears to be the long-awaited answer to the apparent deficiency of cations in these antiwear films.

Keywords ZDDP · Chemical variation · SR-XPS · Ultraphosphate

1 Introduction

Zinc dialkyldithiophosphate (ZDDP) has been the most successful antiwear additive used in commercial automobile engine oils since its introduction to the industry over 50 years ago [1, 2]. Unrivaled in its cost versus performance and its impact on decreasing engine wear, ZDDP has two significant weaknesses that have been well documented. First, ZDDP is known to poison catalytic converters within automobiles exhaust systems and second, the decomposition products produced in a combustion engine have potential environmental impacts. These negative attributes have driven additive developers toward a need to develop cost-effective alternatives and thereby require a better understanding of the antiwear chemistry of ZDDP [1–11].

X-ray photoelectron spectroscopy (XPS) [3, 6–10], X-ray absorption spectroscopy [4, 5], and Auger electron spectroscopy [11] have all been employed to study the chemistry of ZDDP tribofilms. It is generally agreed that ZDDP undergoes very complicated tribochemistry processes in forming, very rapidly [12] (within 10 s of rubbing), a tribofilm on steel to curtail the direct metal–metal asperity contact under boundary lubrication conditions. Kasrai and Bancroft have applied X-ray absorption spectroscopy to show that a tribofilm produced by ZDDP has a multi-layer structure, consisting of a long-chain polyphosphate layer (~5 nm in thickness) on top of a short-chain polyphosphate layer [4, 5]. Further insight into the structure of the antiwear film was reported by Heuberger et al. [8], using angle-varied X-ray photoelectron spectroscopy and examining the top 3 nm, to show that the polyphosphate chain length increased towards the surface of the tribofilm.

Despite these detailed surface studies, the exact chemical nature within the top 5 nm surface layer is still open for debate; the apparent lack of cations to form the films,

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especially if part of the Zn forms ZnS. For example, ZDDP (P/Zn ratio of 2.0) decomposes to give orthophosphates (eg. $\text{Zn}_3(\text{PO}_4)_2$, P/Zn ratio of 0.6), short-chain polyphosphates (eg. $\text{Zn}_2\text{P}_2\text{O}_7$, P/Zn of 1.0), and polyphosphates (eg. $\text{Zn}(\text{PO}_3)_2$, P/Zn of 2.0). Since the bulk of the film is short-chain polyphosphates, there is not enough Zn in ZDDP to enable these to form. Martin and co-workers [13, 14] have proposed that there is enough Fe in the film (coming from the steel substrate) to solve this problem. Zhang et al. [12] have proposed that organophosphates may solve the cation shortage, especially using an ashless dialkyldithiophosphate (DDP) additive with no metal counter ion. In his review, Spikes [2] has suggested that a highly cross-linked ultraphosphates (general formula $[\text{P}_{(n+2)}\text{O}_{(3n+5)}]^{n-}$) could be a component of the film, and a number of recent papers in the literature [15–17] have described the preparation of many metal ultraphosphates, including the Zn ultraphosphate, $\text{ZnP}_4\text{O}_{11}$, P/Zn of 4 [16].

In order to shed further light on our understanding of the structure of polyphosphate antiwear films, X-ray photoelectron spectroscopy using synchrotron light will be employed. In conventional XPS, the incident photon energy is generally fixed (e.g. 1486 eV, Al $K\alpha$ radiation) therefore limiting the sampling depth to the top ~ 10 nm of a material. (The sampling depth equals 3 times the inelastic mean free path [18] in which 67% of the signal is obtained). In contrast, synchrotron-based XPS permits selection of photon energies and therefore the kinetic energy of photoelectrons associated with a particular photoelectron peak and therefore the sampling depth within the surface. It is well known that the mean free path length of photoelectrons in solids increases with photoelectrons kinetic energy with a minimum escape depth of ~ 0.5 nm at kinetic energy of 70 eV [18] (sampling depth of < 2 nm). Thus, using XPS and a synchrotron source (SR-XPS), one has the ability to vary the mean free path (or sampling depth) of the photoelectrons by tuning the X-ray source. Contarini et al. [6] applied SR-XPS to the study the ZDDP tribofilms, but the unique capability of probing depth variation was not examined.

The present paper describes the SR-XPS analysis of the P $2p$, Zn $3s$, and O $1s$ lines, collected from both tribofilm in the wear track and off the wear track, on a steel surface, using photon energies ranging from 500 to 1486 eV. This paper will show the first evidence for appreciable amounts of a Zinc ultraphosphate and/or an organophosphate species on the surface of antiwear film.

2 Experimental

2.1 Sample Preparation

The tribofilm was generated on a hardened AISI 52100 steel disk (surface roughness $R_a < 20$ nm and Rockwell

hardness of 60) using a Plint tribometer in a cylinder-on-disk configuration with applied load of 220 N. The load was applied through an AISI 52100 steel cylinder (surface roughness $R_a < 100$ nm and Rockwell hardness of 60). The cylinder is 6 mm in diameter and 9 mm in length. A C4/C6 secondary ZDDP was mixed to a mineral base lube to reach a phosphorous concentration of 500 ppm as the lubricant. The film preparation was carried out in this lubricant at 100 °C, 25 Hz with a stroke length of 7 mm for 1 h. The wear track was 9 mm \times 7 mm with a steel surface roughness of $\sim R_a$ 30 nm. The wear scar width on the cylinder is ~ 150 μm , therefore the applied pressure during the tribofilm making was higher than 0.2 GPa. The sample was rinsed in *n*-hexane and *n*-propanol to remove the oil residue and other contaminants prior to SR-XPS analysis.

2.2 Synchrotron Radiation-X-ray Photoelectron Spectroscopy (SR-XPS)

The SR-XPS experiments were performed at the spherical grating monochromator (SGM) undulator beamline at the 2.9 GeV third generation Canadian Light Source (CLS). The energy resolution ($\Delta E/E$) of the beamline is 10^{-4} with a flux of $> 10^{11}$ photons/s at the photon energy of 250–1500 eV. The entrance and exit slits of the beamline were set at 250 and 50 μm , respectively. The incident photons were incident at 30° to the sample. The analyzed area is about 1 mm by 0.2 mm. The Scienta 100 electron energy analyser (with a pass energy set at 100 eV) was oriented at 15° from the antiwear film normal. The analyser resolution was determined to be 100 meV at the pass energy of 100 eV used for this experiment. The photon energy resolution ($E/\Delta E$) is better than 5000, therefore the photon resolution is 100, 140, 200, and 300 meV for photon energy at 500, 700, 1100, and 1500 eV, respectively (the energy range used in this work). Thus, the experimental width (photon plus electron) is less than 0.5 eV. Thus, none of the peaks widths in the spectra presented in this paper are resolution-limited. The binding energy was calibrated by aligning the ubiquitous C $1s$ contaminant peak to 285.0 eV. XPS profiles were curve-fit with a Gaussian/Lorentzian (70%/30%) peak shape and a Shirley background subtraction. Peak widths were constrained to approximately 1.5 eV for O $1s$ spectra. However, using a 100% Gaussian peak shape made very little difference in the final results.

Quantitative XPS atomic ratios can be derived [19] at a given kinetic energy beginning with the Eq. 1

$$N_i(h\nu) = I_i(h\nu) / \sigma_i(h\nu) \lambda_i(h\nu) K \quad (1)$$

where $N_i(h\nu)$ is the atom density of element *i* being derived from SR-XPS obtained at a photon energy of $h\nu$, $I_i(h\nu)$ is the measured XPS area (collected at specific photon energy

of $h\nu$) under the peak of the element of i , $\sigma_i(h\nu)$ is the photoionization cross-section [19] of the corresponding element at specific photon energy of $h\nu$, and $\lambda_i(h\nu)$ is the inelastic mean free path of the photoelectrons from element of i [18]. It should be noted that the atom density is averaged over the total sampling depth. The sampling depth varies with the photon energy. K is all other factors related to quantitative detection of a signal, such as transmission function of the energy analyzer (assumed to remain constant at a given kinetic energy (KE)).

Element ratios of N_P/N_{Zn} along the tribofilm depth can thus be determined by Eq. 2

$$\frac{N_P(h\nu)/N_{Zn}(h\nu)}{[I_P(h\nu)/\sigma_P(h\nu)\lambda_P(h\nu)]/[I_{Zn}(h\nu)/\sigma_{Zn}(h\nu)\lambda_{Zn}(h\nu)]} \quad (2)$$

As the kinetic energies of P 2*p* and Zn 3*s* photoelectrons are very close, Eq. 2 can be simplified to Eq. 3

$$\frac{N_P(h\nu)/N_{Zn}(h\nu)}{[I_P(h\nu)/\sigma_P(h\nu)]/[I_{Zn}(h\nu)/\sigma_{Zn}(h\nu)]} \quad (3)$$

3 Results and Discussion

Figure 1 shows the SR-XPS broad scan of the tribofilm recorded photons at 1486 eV. The spectra show all the elements expected in a typical tribofilm: Zn, P, S, and O. The P 2*p* and P 2*s* peaks are much larger than the corresponding S 2*p* and S 2*s* peaks, respectively, showing that the S:P ratio is about 0.3, in contrast to the S:P ratio of 2.0 in the ZDDP starting compound. The S exists mainly as a sulfide as revealed by XANES (not shown) [5]. Of particular note, there is little noticeable Fe present in the film which is indicated in Fig. 1 by the lack of obvious Fe 2*p* peak near 710 eV binding energy. From the very large Zn 2*p* intensity, the Fe 2*p* peak at ~ 710 eV has to be less than 1% of the Zn 2*p* intensity: any Fe present in the ~ 10 nm film has to be extremely small, and cannot be a major component of the cations required for charge balance. N 1*s* (a peak centered at ~ 400 eV) and Ca 2*p* (a peak centered at ~ 350 eV) could be surface contamination and their concentration relative to Zn would be very low (less than 2%). The broadscan spectrum off the wear track was also recorded (not shown). In contrast, apart from ZDDP elements, Fe from the substrate is clearly detected and the S/P ratio from either the 2*s* or 2*p* peaks is close to 2, as expected from the stoichiometry of undecomposed ZDDP and/or thermally decomposed ZDDP.

Figure 2 shows the SR-XPS analysis (for 500 eV photon energy) of Zn and P content within the wear track and as well as off the wear track of the film are compared. Two observations are immediately apparent. First, the P 2*p* peak energy increases by about 0.9 eV from the predominantly

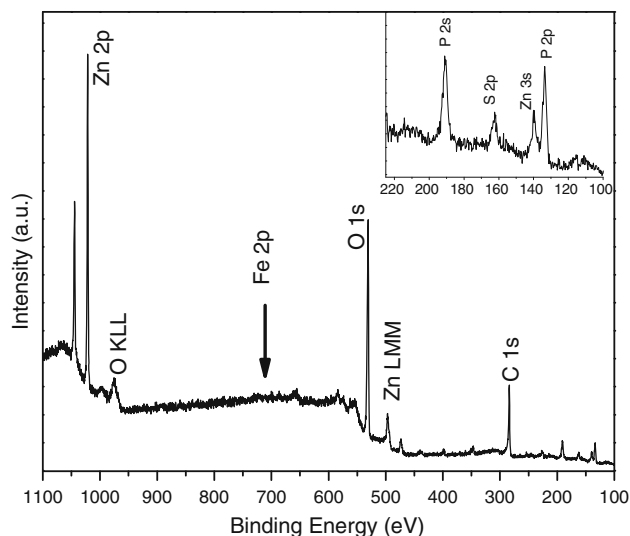


Fig. 1 X-ray photoelectron survey scan at the photon energy of 1486 eV within the wear track of the antiwear film produced by ZDDP. Note the absence of a peak at approximately 700 eV which would indicate the presence of iron in the film

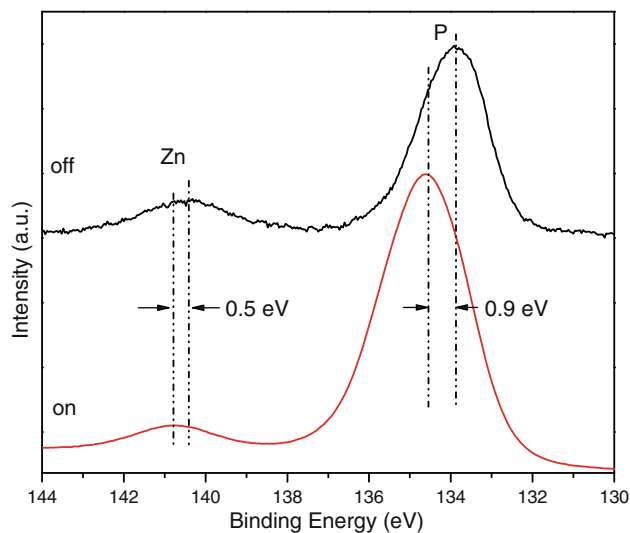


Fig. 2 The X-ray photoelectron narrow scans of the Zn 3*s* and P 2*p* regions collected at a photon energy of 500 eV both inside and outside of the wear track of the antiwear film produced by ZDDP

ZDDP off-track film to the polyphosphate on-track film indicating the presence of undecomposed ZDDP [7, 8]. Second, it is obvious that the P/Zn ratio of 2.6 within track (Table 1) is much larger than off the track (P/Zn ratio of 1.4). For undecomposed ZDDP, the ratio of P/Zn is expected to be 2.0. However, it is well known that above 100 °C, thermal decomposition of ZDDP occurs giving short- and long-chain polyphosphates [4] that will result in a P/Zn ratio of < 2 (Table 2).

Table 1 The atomic ratio of P/Zn at the surface (5–10 nm) of the tribofilm

Photon energy (eV)	1486	1100	700	500
Kinetic energy (eV)	1346	960	560	360
Sampling depth (nm) ^a	10.2	8.6	6.6	5.3
σ_P/σ_{Zn}	0.016/0.014 = 1.14	0.042/0.024 = 1.75	0.160/0.053 = 3.01	0.408/0.088 = 4.64
I_P/I_{Zn}	69.7/30.3 = 2.3 (0.1)	77.6/22.4 = 3.5 (0.2)	91.1/8.9 = 10.2 (1.0)	92.4/7.6 = 12.1 (1.0)
N_P/N_{Zn}	2.0 (0.1)	2.0 (0.1)	3.4 (0.3)	2.6 (0.3)

Errors are in *brackets*

^a The inelastic mean free path λ_n was calculated using Eq. 6 in Ref. [18] using the B value of 0.096 for inorganic compounds. The total sampling depth (99% of the photoelectrons detected) is given by $3\lambda_n \cos(15)$

Table 2 Atomic ratios of P/Zn and ratios of bridging to non-bridging oxygens (BO:NBO) for a number of standards and tribofilms

Compound	N_P/N_{Zn}	BO:NBO
ZDDP	2:1 = 2	N/A
$Zn_3(PO_4)_2$	2:3 = 0.6	0
$Zn_2P_2O_7$	1:1 = 1	1:6 = 0.16
$Zn_6P_{10}O_{31}$	1.67:1 = 1.67	1:2.1 = 0.47
$Zn(PO_3)_2$ (very long chain linear polyphosphate)	2:1 = 2	1:2 = 0.5
ZnP_4O_{11} (ultraphosphate)	4:1 = 4	1.2
R_3PO_4	–	0
Film (560 eV KE), 6.6 nm	3.4	0.73
Film (960 eV KE), 8.6 nm	2	0.49

Figure 3 shows the narrow Zn 3s and P 2p SR-XPS spectra of the tribofilm collected using different photon energies. The individual spectra were normalized to the P 2p peak (~ 135 eV) intensity maximum. It is very interesting to observe that the intensity of the Zn 3s peak, relative to that of P 2p peak, increases dramatically from low-photon energy (500 eV) to high-photon energy (1486 eV). These relative peak intensity variations are due in part to the change in photoionization cross sections of the Zn 3s and P 2p orbitals (Table 1), and partially due to the increase in atomic P/Zn ratio as a function of depth in the film. Quantitative values of N_P/N_{Zn} as a function of depth in the tribofilm (Table 1) have been calculated using Eq. 3. The sampling depth of SR-XPS has been determined from the universal inelastic mean free path curve and the emission angle of the photoelectrons [18]. The results of these calculations are summarized in Table 1. It is obvious that the relative concentration of P to Zn of ~ 3 in the topmost surface (~ 5 nm) of the film is significantly larger than in the first ~ 10 nm of the film of ~ 2 .

In general, there are three categories of polyphosphates: linear polyphosphates with general formula of $O(PO_3)_n O^{(n+2)-}$ (eg. $P_2O_7^{4-}$), a three-dimensional polyphosphate with a general formula of $[P_{(n+2)}O_{(3n+5)}]^{n-}$ called

ultraphosphate (eg. $P_4O_{11}^{2-}$), and organophosphates, such as R_3PO_4 . In the case of linear polyphosphates, P–O–P links (bridging oxygen, BO) replace some of the $(P-O)^-$ anions (non-bridging oxygen, NBO). As a result, this latter category contains fewer cations per P, and a ratio P/Zn of much greater than 2.0 can easily be obtained. In recent years, several ultraphosphates of Zn, Cd, and Fe (such as MP_4O_{11} ($M = Zn, Cd, Fe$)) have been synthesized and well characterized [16]. Using the general formula for polyphosphates, we can calculate the N_P/N_{Zn} ratios for different phosphates (Table 2). It is observed that for an $n = 2$ linear polyphosphate (eg. $Zn_2P_2O_7$), P/Zn is 1.0, and for a large n (say >100) polyphosphate, we can approximate the chemical formula to $Zn(PO_3)_2$, (so called metaphosphate) in which P/Zn is 2.0. In contrast, for an ultraphosphate such as ZnP_4O_{11} ($P/Zn = 4$) [16], P/Zn is greater than 2. Another possible contributor to the antiwear film is organophosphates of the type R_3PO_4 [20] ($R = \text{aryl, or alkyl}$ in this case) (containing no Zn) and could yield a very large P/Zn ratio.

Our observed P/Zn ratio of ~ 3.0 is strong evidence for a multi-component film containing an appreciable amount of an ultraphosphate or organophosphate in the top ~ 5 nm of the film along with the previously identified linear metal polyphosphates.

Figure 4 shows the O 1s photoelectron spectra within the wear track of the antiwear film and provides more evidence for the existence of ultraphosphates and/or organophosphates. The spectra at kinetic energies of ~ 560 eV (1100 eV photon energy) and ~ 950 eV (1486 eV photon energy) are at the same kinetic energies (within 10 eV) as the P 2p and Zn 3s spectra (Fig. 3) taken at 700 and 1100 eV, respectively, and therefore examine the same depth within the sample (~ 6 and 8 nm, respectively). The individual spectra in Fig. 4 were normalized to the O 1s peak intensity maximum at ~ 532 eV. The two most intense peaks at 532 and 533.4 eV (Table 3) have been assigned for Zn phosphate glasses [21] and ZDDP tribofilms [8] to NBO and BO, respectively, within the polyphosphate structure and our peak positions for these two peaks are in excellent agreement with previously reported

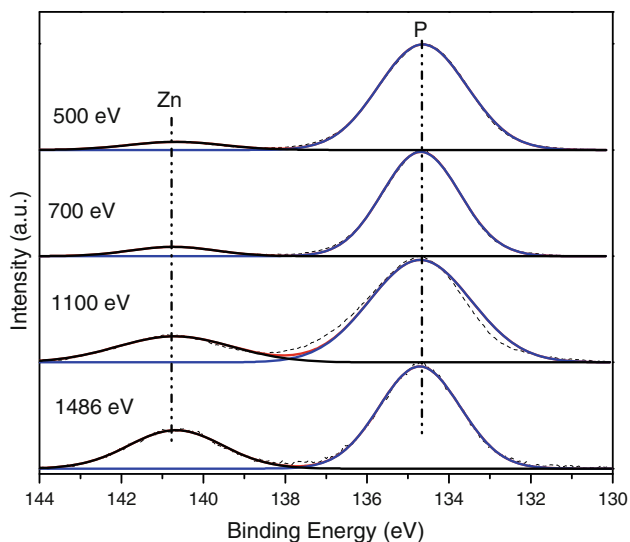


Fig. 3 The X-ray photoelectron narrow scans of the Zn 3s and P 2p regions collected at photon energies of 500, 700, 1100, and 1486 eV, respectively, within the wear track of the antiwear film produced by ZDDP

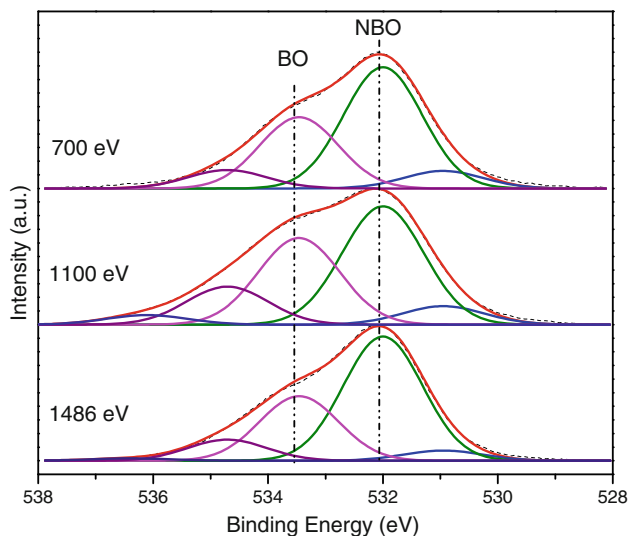


Fig. 4 The X-ray photoelectron narrow scans of the O 1s region collected at photon energies of 700, 1100, and 1486 eV, respectively, within the wear track of the antiwear film produced by ZDDP

positions for a similar tribofilm [8]. The very small peak at lower BE peak at about 531 eV arises from the surface metal oxide, as seen in the previous XPS study [8]. This peak is just above detection limits and could be due to a very small amount of FeO or ZnO. This peak cannot be due to iron oxide because of the lack of an Fe 2p peak in the broad scan. The assignment to ZnO is very difficult because the large Zn peaks in Fig. 1 are mainly associated with Zn phosphates. The peak at 534.7 eV (also seen in ref.

Table 3 O 1s binding energies for the tribofilms (Errors are 0.1 eV)

Photon energy (eV)	Kinetic energy (eV)	Binding energy O 1s	% (total O)	Assignment
700	168	531.0 (530.3) ^a	5.0	Oxides
		532.0 (531.9) ^a	56.2	NBO
		533.4 (533.4) ^a	31.6	BO
		534.7	7.2	See text
1100	568	531.0 (530.2) ^a	5.8	Oxides
		532.0 (531.8) ^a	44.8	NBO
		533.4 (533.4) ^a	32.6	BO
		534.7 (535) ^a	15.7	See text
		536.1	1.7	H ₂ O
1486	954	531.0(530.2) ^a	2.3	Oxides
		532.0(531.8) ^a	59.4	NBO
		533.4(533.4) ^a	29.0	BO
		534.7(535) ^a	8.0	See text
		536.1	1.2	H ₂ O

Peaks are curve-fitted with Gaussian (70%) and Lorentzian (30%) and peak width of 1.6 eV

^a Ref. [8]

[8]) could be due to the BO in ultraphosphate. To our knowledge, no XPS spectra of ultraphosphates have been published, and such spectra are necessary now to confirm this assignment. The very small peak at 536 eV probably arises from partially adsorbed water as previously observed on pyrite samples [22].

The ratios of BO/NBO in both phosphates [21] and silicates [23] are very sensitive to the composition and polymerization of the glass. It is apparent immediately from Fig. 4 that the O 1s peak from BO at 533.4 eV in the middle spectrum at 1100 eV (analyzing the first 5 nm) is much larger than in the bottom spectrum at 1486 eV which analyzes deeper into the sample. The BO:NBO ratios for these two spectra are 0.73 and 0.5, respectively (Table 2, bottom). For linear polyphosphates, the ratio of BO to NBO range from 0.16 for Zn₂P₂O₇ (Table 2) to 0.5 for Zn(PO₃)₂ whereas for ultraphosphate the BO/NBO ratio is >1 depending on the structure (1.2 for our model ultraphosphate, ZnP₄O₁₁). Our observed BO/NBO of 0.5 at a kinetic energy of 960 eV indicates the presence mostly of long-chain linear polyphosphate with small amounts of short chain and ultraphosphate, and the BO/NBO ratio of 0.73 at a kinetic energy of 560 eV indicates that there is substantial Zn ultraphosphate in the top 5 nm of the film in agreement with the large P/Zn of >3 at the same kinetic energy. As for the organophosphate, the O 1s binding energy for an organophosphate (R₃PO₄), with only NBO oxygens, is very similar (532.1 eV) [20] to the above NBO for metal polyphosphates and therefore if any significant amount of organophosphates are present will be reflected

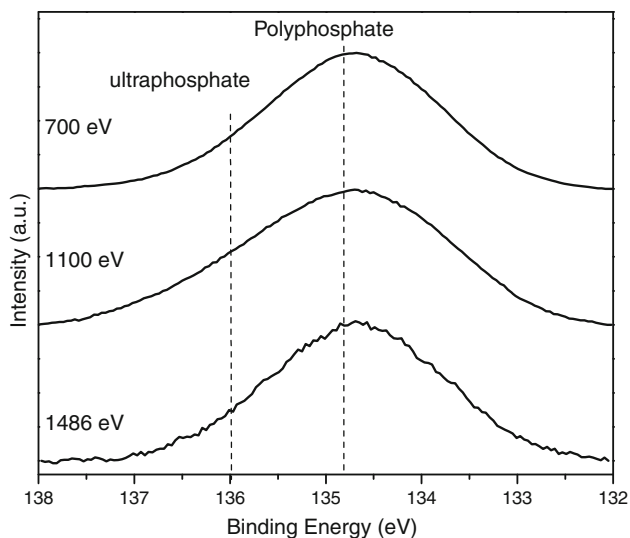


Fig. 5 The X-ray photoelectron narrow scans of the P $2p$ region collected at photon energies of 700, 1100, and 1486 eV, respectively, within the wear track of the antiwear film produced by ZDDP

by a decrease in the BO/NBO ratio. Such a species is probably the cause of the lower BO/NBO ratio at 700 eV, where the analysis depth is ~ 2 nm.

Figure 5 shows the P $2p$ spectra of the within the wear track at photon energies of 1486, 1100, and 700 eV. The P $2p$ peak is broad and shows no significant structure, making any fitting very difficult and unreliable. The most intense P $2p$ at 134.8 can be assigned to the P $2p_{3/2}$ of polyphosphate [8]. A smaller P $2p_{3/2}$ binding energy of 133.8 eV could be assigned to either a orthophosphate, a small chain polyphosphate, or organophosphate [8]. A higher energy peak from ultraphosphate could be present at higher binding energy, since P_4O_{10} gives a binding energy of ~ 136 [24]. Thus, from P $2p$ data we cannot draw any reliable conclusion on the identities of the P species. We must rely on the O $1s$ spectra and P/Zn ratios for P characterization in the film as described above.

4 Conclusions

We report the first variable photon energy SR-XPS study on the chemistry variation of the ZDDP-derived tribofilm surface as a function of depth non-destructively. The structure variation in the tribofilm surface can be derived by the quantitative analysis of SR-XPS spectra at different excitation photon energies. It has been found that the ratio of P/Zn decreases along the tribofilm depth, suggesting the decrease of chain-length in the zinc polyphosphate tribofilm. High resolution O $1s$ SR-XPS results also resolve same chain-length variation in the tribofilm through comparing the ratio of BO/NBO. More interestingly, three-dimensional ultraphosphate structure is strongly suggested

in the top 5 nm tribofilm (probably in the top 2 nm which yields 67% of the intensity) according to P ($2p$), Zn ($3s$), and O ($1s$) SR-XPS, along with a possible contribution from an organic phosphate.

Strong evidence presented here, for the first time, for the formation of ultraphosphate solves the apparent lack of cations required to form metal phosphates in the tribofilms. It has been suggested in the past that, under AW condition, iron along with zinc are the counter ions for phosphates (short chain or long chain) in the film [13, 14]. In this study, it was shown that no substantial iron is detected in the film and thus not enough Zn is available for the formation of zinc phosphate. Formation of ultraphosphate is the answer to this dilemma.

Due to the high sensitivity, SR-XPS has also successfully recorded the adsorbed ZDDP thermally derived species on steel surface off the wear track. It should be mentioned that further study of antiwear films generated with fully formulated engine oil by the same SR-XPS method could be extremely useful to enriching our knowledge of the chemistry of antiwear film.

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