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Understanding the effect of water on the transient decomposition of zinc dialkyldithiophosphate (ZDDP)

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Abstract: The effect of water on the transient kinetics of the decomposition reaction of zinc dialkyldithiophosphate (ZDDP) additive has been investigated using X-ray photoelectron spectroscopy (XPS). Water was found to have a long-lasting detrimental effect on ZDDP triboreactive film layers by changing their composition depending on their proximity to the metal surface. Particularly, water impeded the polymerisation reaction in the top layers, which results in the formation of short zinc (thio)phosphate chains. The most probable explanation for this was related to the formation of a single or multiple bridges between water molecules and PO_2^- groups of the decomposed ZDDP. This caging effect, which does not fade away as water evaporates, can suppress the chemical reactivity of these groups to a great extent, which in turn can hinder their polymerisation into long phosphate chains.

Keywords: ZDDP antiwear, tribofilm, decomposition reactions, XPS, water contamination

1 Introduction

The use of ZDDP is ubiquitous across different industries and applications such as engine oils and bearings lubrication. This ubiquitous use is related to the capability of ZDDP to be used as not only antiwear additive but also as antioxidant and anticorrosion [1–3]. However, despite its wide use, ZDDP contains zinc and phosphorus, which can degrade the catalyst performance of the catalytic converter in the vehicle's exhaust system and thus increases harmful emissions [4, 5]. Therefore, ever-growing strict environmental rules are currently imposed to reduce or zero the concentrations of Zn and P in the formulated oils [6]. However, one of the greatest difficulties in replacing the ZDDP with additives of similar superior antiwear properties is the lack of full understanding of all the reaction pathways and associated kinetics of ZDDP decomposition in base oils and on steel surfaces [7].

The wide body of literature concerning ZDDP has thus far focused on understanding the composition, wear and friction of ZDDP antiwear films under different levels of temperature, load and rubbing time [1, 6–8]. However, there are fewer studies [9–13], which examined the impact of contaminants such as water in the oil. Water, in particular, is expected to alter the pathways of the reactions associated with the decomposition of the ZDDP additive and its tribofilm generation. The different possible reaction pathways in the presence of water led to some conflicting findings in the literature. For instance, Rounds [9] showed that when free water is mixed with oil, it accelerates the formation of the ZDDP tribofilm.

However, numerous other studies [11, 12, 14, 15] found just the opposite, i.e. the mixed water with oil slows down the tribofilm formation rate. The effect of water extend beyond reducing just the thickness of the generated tribofilm as it can also change its chemical composition by shortening the phosphate chain length [11, 14] and mechanical properties by forming less tenacious films that can be easily washed out of the contact [14].

Despite the wider support for the finding that the ZDDP decomposition is hindered by water, which was basically inferred from the formation of short phosphate chains or thin tribofilms, the reason behind this is still not completely known. Furthermore, the mechanism of short chains formation and its rate remain undetermined. Fuller et al. [16] showed that this can be a result of the reaction occurring between water and the initially-formed long phosphate chains, which intensifies as the oil temperature increases. Similar conclusions were reported by other studies [11, 12, 14], which suggested that water can induce a depolymerisation reaction that shortens the long polyphosphate chains. Furthermore, Nedelcu et al. [11] suggested that the increase in surface distress in the presence of water, which was inferred from the high density of surface micropits, can be responsible for the formation of the short phosphate chains.

It should be noted that these conclusions still do not give clear answers about the rate at which the long phosphate chains depolymerise. In addition, the mechanism by which water possibly reacts with ZDDP to suppress the decomposition reaction remains unresolved. This study will assess the kinetics of ZDDP decomposition in the presence of water and the rate of polymerisation and possibly depolymerisation reactions of the phosphate chains. This will be achieved by following the ZDDP tribofilm formation over time, which

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Table 1
Experimental conditions during the MTM tribotests.

Operational variable	Value
Material	AISI 52100
Lubricant	PAO+ZDDP (0.08 wt.%P)
Temperature (°C)	80
Load (N)	60
Entrainment Speed (mm/s)	35
Water (wt.%)	0, 2
Time (minutes)	2.5, 5, 10, 20, 30, 60, 120

should enable the examination of the different changes in the tribofilm composition that can occur to not only the formed phosphate chains but also the other species in the tribofilm such as sulphur.

2 Experimental

2.1 Materials

Secondary ZDDP additive (P: 800 ppm) mixed in Poly- α -olefin (PAO-4) oil was the lubricant used in the tribological tests. The PAO-ZDDP oil was mixed with 2 wt.% of water. The mixture was shaken by hand for one minute then placed in ultra-sonication bath for 10 minutes. After mixing, a sample of 100 ml to be used for the tribological tests was kept for 10 minutes at room temperature until all the entrapped air bubbles were removed.

2.2 Tribological characterisation

The tribological tests were performed using the mini-traction machine (MTM). The tribofilm thickness was measured using the spacer layer imaging (SLIM) accessory of the MTM. The tribological surfaces consisted of a polished steel disc of 46 mm diameter and a polished ball of a 19 mm diameter both had < 13 nm root mean square roughness and were made of AISI 52100 alloy bearing steel with average hardness of 64 on Rockwell scale and elastic modulus of 210 GPa. The different experimental parameters are summarised in Table 1. The tests were performed at 80 ± 0.1 °C, as at higher temperatures evaporation of water from the oil [12] and the decomposition reaction itself occur at a much faster rate [3]. Different tests were performed after different rubbing times ranging from 2.5 to 120 minutes. Below 60 minutes, each test was repeated at least three times. The 120 minutes tests were repeated two times.

A 5% slide-to-roll ratio (SRR), 35 mm/s speed and 60 N load (contact pressure of 1.2 GPa) were maintained for all the tribological tests. These conditions corresponds to a nearly pure rolling condition with a minuscule sliding in order to slow down the decomposition reaction of ZDDP. The chosen high contact pressure and low entrainment speed result

in a λ ratio below 0.1, which indicates a boundary lubrication regime.

2.3 Surface analysis

2.3.1 XPS: Prior to the XPS surface analysis, the MTM discs were washed gently with heptane to remove the oil layer on the top of the surface. This was performed without rubbing the samples in order to avoid any unintended tribofilm removal in the process of cleaning. The XPS analysis measurements were conducted using a 5000 PHI spectrometer. Each XPS measurement was repeated three times in different locations. A detailed discussion of the settings during the XPS analysis can be found elsewhere [17]. Briefly, as the tribofilm is expected to have phosphorous, oxygen, sulfur, carbon, zinc and possibly iron, all these elements were scanned. The acquired signals were collected from P2p, O1s, S2p, C1s, Zn2p and Fe2p. These acquire signals were analysed using CasaXPS software. The detailed analysis procedure including data calibration and attenuation correction is discussed in great detail elsewhere [17].

2.3.2 White light interferometry: A diluted solution (0.05 M) was prepared of EthyleneDiamineTetraAcetic acid (EDTA). A local part of the tribofilm was removed using a drop of this solution. To assess the wear damage on the MTM disc surface, a white light interferometer (NPlex Bruker) was utilized to capture interference patterns, which were analysed using Vision64 software (Bruker, USA). At least three interferometric images were obtained from the disc countersurface after rinsing it with a solvent (heptane).

2.3.3 Titration: The water concentration in the oil was measured using Mettler KF V30 Karl Fisher titrator by measuring samples of about 3 ml of the test bath after different heating times.

3 Results

3.1 Tribological characterisation

Wear was barely noticeable, as shown in Fig. 1 for the different profiles across the wear scar after rubbing for 120 minutes, regardless whether water is present or not.

The progression of the friction coefficient, tribofilm thickness and water content are shown in Fig. 2. The mixed water appeared to have a considerable effect on friction (Fig. 2a) and tribofilm thickness (Fig. 2b), which was more prominent during the early stage of the tribotest than in the later stages in which the friction coefficient as well as the tribofilm thickness both reached steady state. The small effect of water on the steady state friction is in agreement with previous studies [12, 18], which related it to the evaporation of water. As the oil contains more water in the beginning of the tribotest than in the later stages (Fig. 2c), the friction and tribofilm thickness are expected to be more affected.

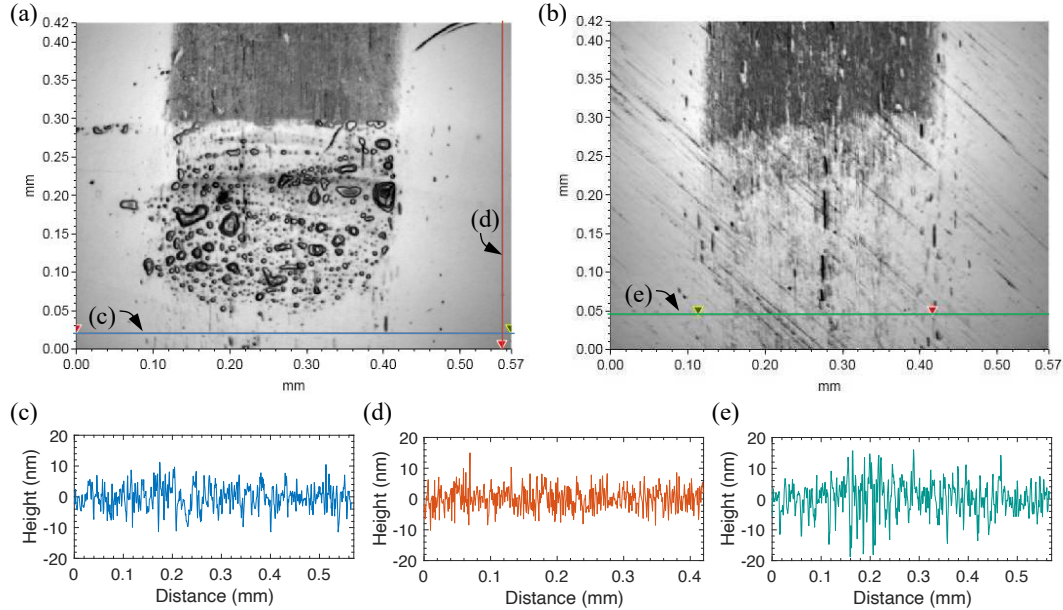


Figure 1. White light interferometry results showing optical images across the tribofilm formed in a) the absence and b) the presence of water from oil. c), d) and e) are roughness profiles as indicated in a) and b).

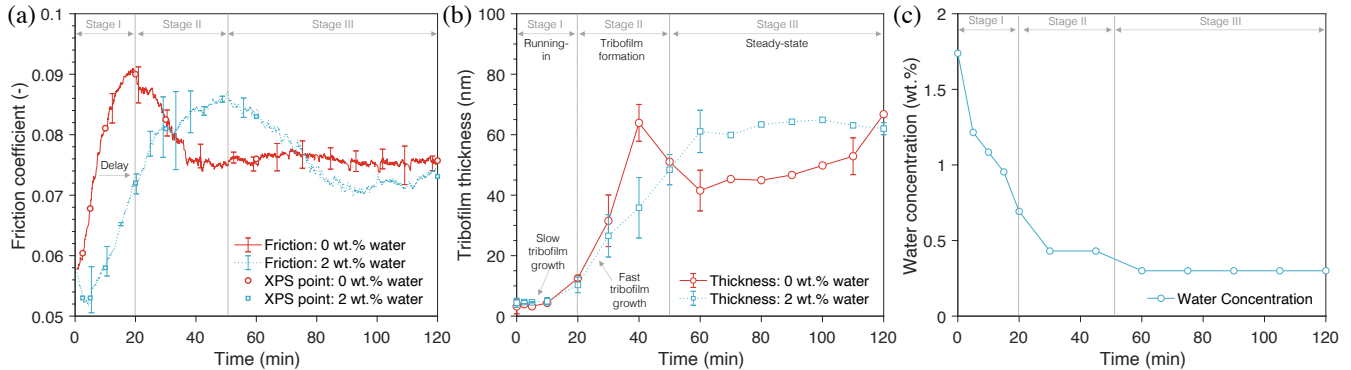


Figure 2. Evolution of a) the friction coefficient and b) the tribofilm thickness without and with water in the oil. Representative SLIM images are also shown in the case of no added water. c) the evolution of the water concentration in the oil, where 2 wt.% water was added, during the tribological test.

In general, the friction coefficient and tribofilm thickness followed three different stages, whether water was present in or absent from the oil. During the first 20 minutes, where the running-in occurs, the friction coefficient in the absence of water increased from 0.05 to 0.092, whereas in the presence of water it increased to a slightly lower value of 0.085, which was reached after a longer running-in period extending to 50 minutes instead of 20 minutes. Following this increase, the friction coefficient decreased until it reaches steady state around 0.077 and 0.072, in the absence and presence of water, respectively.

Contrary to the friction coefficient, the tribofilm thickness barely grew at $t < 20$ minutes, whether water was present in or absent from the oil. This was followed by a sharp growth up to $t < 50$ minutes, in which water had an adverse

effect, i.e. reduced the thickness of the tribofilm. Lastly, at $t > 50$ minutes after water largely evaporated from the oil, the tribofilm thickness where water was mixed becomes larger than that of no water. However, it is worth noting that the last phase ended with a tribofilm thickness that was similar whether water is absent or present in the oil.

3.2 Surface analysis

The peaks identification in O1s, P2p, Zn2p, S2p, C1s, and Fe2p signals was carried out by fitting each one with a specific number of peaks, as shown in Fig. 3. This analysis is summarised in Table 2, which lists the binding energies of these components over rubbing time.

The O1s signal appears to comprise three main peaks (Fig. 3a), corresponding to non-bridging oxygen (NBO),

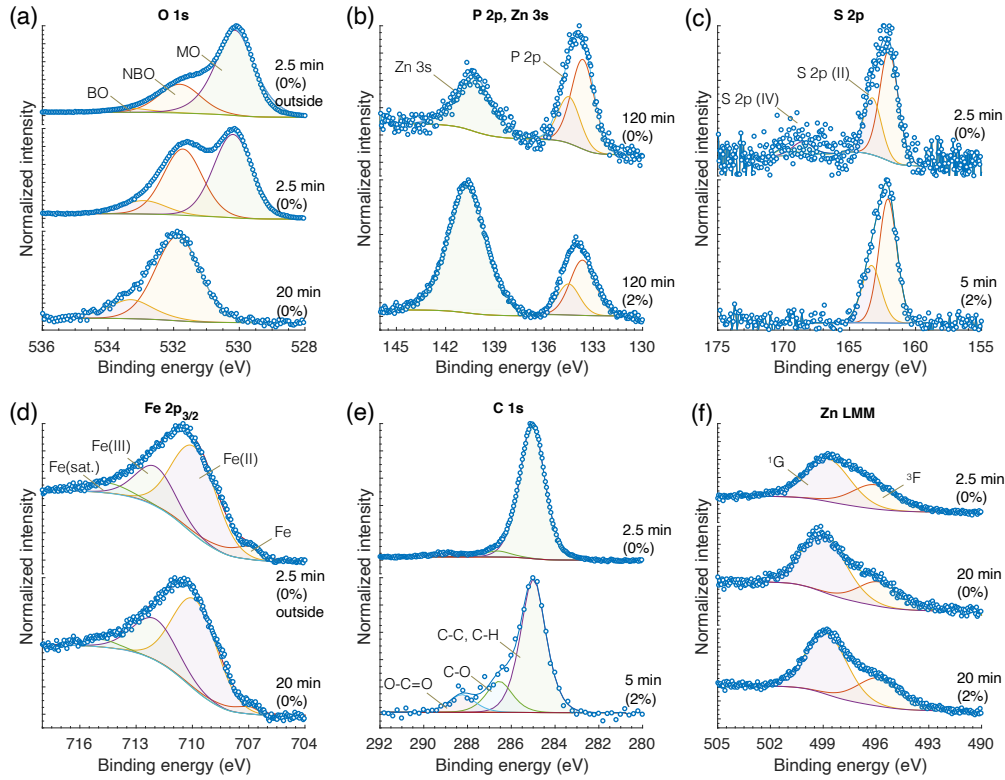


Figure 3. Fitting of high resolution XPS spectra (over rubbing time not the itched scans) of a) O1s, b) P2p and Zn3s, c) S2p, d) Fe2p, e) C1s and f) Zn LMM, after different rubbing times. The water content and whether the signal is captured inside or outside the wear track are noted in each figure.

Table 2

XPS component analysis of high resolution XPS spectra (over rubbing time not the itched scans) of tribofilms formed in case of 0% and 2% (shown in parenthesis) water is present in the oil.

Species	Water	Time (minutes)						
		2.5 [†]	5	10	20	30	60	120
O1s: BO (eV)	0%	533.05	532.25	533.09	532.76	533.06	533.13	533.15
	(2%)	-	(533.37)	(533.08)	(533.82)	(532.73)	(533.08)	(533.14)
O1s: NBO (eV)	0%	532.79	531.92	531.82	531.21	531.73	531.70	531.72
	(2%)	-	(531.65)	(531.68)	(531.68)	(531.57)	(531.65)	(531.77)
O1s: MO (eV)	0%	530.25	530.60	530.65	530.73	-	-	-
	(2%)	-	(530.00)	(530.21)	(530.58)	-	-	-
Zn3s (eV)	0%	140.36	140.47	140.42	140.42	140.42	140.40	140.31
	(2%)	-	(140.43)	(140.37)	(140.32)	(140.28)	(140.41)	(140.46)
P2p 3/2 (eV)	0%	133.55	133.57	133.64	133.64	133.53	133.64	133.66
	(2%)	-	(133.55)	(133.49)	(133.41)	(133.44)	(133.55)	(133.44)
S2p 3/2 (eV)	0%	162.13	162.22	162.33	162.27	162.23	162.37	162.31
	(2%)	-	(162.29)	(162.23)	(162.11)	(162.09)	(162.18)	(162.24)
(Zn3s-P2p) (eV)	0%	-	6.79	6.82	6.78	6.89	6.76	6.65
	(2%)	-	(6.88)	(6.88)	(6.91)	(6.84)	(6.86)	(7.01)
BO/NBO	0%	0.22	0.25	0.28	0.32	0.26	0.34	0.38
	(2%)	-	(0.26)	(0.23)	(0.25)	(0.26)	(0.26)	(0.15)
P/Zn	0%	1.06	0.99	0.96	1.06	1.26	1.25	1.35
	(2%)	-	(0.53)	(0.54)	(0.52)	(0.61)	(0.65)	(0.41)

[†] No XPS measurements were possible in the case of 2% water as the wear scar was not visible.

bridging oxygen (BO) and metal oxide (MO). In all the tribotests, the BO, NBO and MO were identified at 533.06 ± 0.2 eV [19–25], 531.76 ± 0.2 eV [19–21, 23, 26], and 530.36 ± 0.3 eV [21, 23, 26, 27], respectively. The presence of water does not appear to have a clear trend on these binding energies as the effect is small whether during the running-in period in which water concentration is highest or during the later stages where water evaporates.

Zn3s signal appeared at 140.36 ± 0.05 eV as shown in Fig. 3b, which can be attributed to zinc phosphate or ZnS [20, 21, 28]. Similarly, Zn2p signal appeared at 1022.5 ± 0.1 eV corresponding to either zinc phosphate [20, 21, 28, 29], which is more probable, or ZnS, $\text{Zn}(\text{SO}_4)$ or ZnO [30].

P2p appeared at 133.55 ± 0.1 eV as shown in Fig. 3b, which can be ascribed to zinc phosphate [19, 21, 22] or possibly $\text{Fe}(\text{PO}_4)$ [19, 30, 31]. The shift to higher binding energy indicates that the short phosphate chains are polymerised into longer ones [19–22, 28]. The presence of water appears to reduce this the binding energy with the continued rubbing, which implies that shorter chains were formed.

S2p main peak was located at 162.13 ± 0.1 eV (Fig. 3c), which was ascribed to sulphide [22, 30] or to thiophosphate or organosulphur [30]. Sulphate signal at 168.5 ± 0.1 eV was detected at < 2.5 minutes, which is related to either FeSO_4 [32] or $\text{Fe}_2(\text{SO}_4)_3$ [33]. In the case water is present in the oil, no measurements at 2.5 minutes were possible, therefore, the presence of sulphate cannot be confirmed in this case. Nevertheless, similar to P2p, in general water reduced the binding energy of the sulphide signal with rubbing.

Fe2p signal was only present in the beginning of the tribotest when the tribofilm thickness was minimal. The signal was not affected by the presence of water. This signal was broad as shown in Fig. 3d, suggesting the presence of both FeO and Fe_2O_3 [34]. Four peaks were fitted at 707.1 ± 0.2 eV, 709.0 ± 0.3 eV, 710.5 ± 0.2 eV and 714.0 ± 0.2 eV, corresponding to metallic iron [29, 30, 33], Fe(II) oxide [22], Fe(III) oxides [19], and Fe(II) satellite, respectively.

C1s signal at 285.0 eV was attributed to aliphatic carbon (Fig. 3e). After short rubbing time before the formation of a thick tribofilm, three more peaks were identified at 283.0 ± 0.1 (iron carbide), 286.5 ± 0.1 (COH) and 288.6 ± 0.1 eV (COOH) [35]. The presence of water appeared to enhance the intensity of these groups.

ZnLMM signal shown in Fig. 3f appeared to consist of two main peaks: ^1G at 498.4 ± 0.3 eV and ^3F at 495.7 ± 0.5 eV [21]. The evolution of the binding energy difference and ratio between these two peaks were followed and presented in Fig. 4. The presence of water in the oil lowers the binding energy difference and ratio significantly, which can be related to the phosphate formation of shorter chains [21].

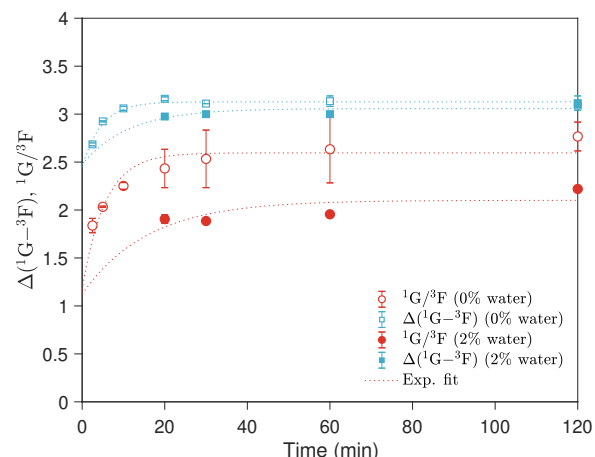


Figure 4. Effect of water on the evolution of the ratio and energy difference of the peaks of Zn LMM XPS signal over rubbing time. The dotted lines are for the guidance of eye.

3.3 XPS concentration evolution

The sputtering depth profiles formed after rubbing for 120 minutes are shown Fig. 5 whether water is present or absent from the oil. Water appears to lower the concentration of phosphorus, whereas it generally enhances the formation of more zinc and sulphur species. Furthermore, near the steel surface, the concentration of oxygen was high, which indicates the presence of metal oxide layer. On the top of this layer and throughout the tribofilm, zinc appears at high concentration particularly in the presence of water. This may indicate the formation of more zinc species such as short chain zinc phosphate or zinc sulphides and sulphates. This is in line with several previous studies [19, 31, 36, 37] suggesting the presence of Fe/Zn sulphides as well as Fe/Zn sulphate [17, 31, 38, 39].

Apart from sputtering, the XPS analysis was also performed after different rubbing times. The temporal changes in the P/Zn and P/O ratios are presented in Fig. 6. The results show that in the absence of water, the tribofilms formed at the beginning of the tribotest after 2.5 minutes of rubbing initially have very low P/Zn and P/O ratios. However, after 5 minutes of rubbing, these ratios increase to a value of 0.20 and about 1.0, respectively. The low ratios suggest the formation of short chains ZnPO_4 . In line with these results, BO/NBO (Table 2) were 0.22 in the first 2.5 minutes, suggesting that initially short chain phosphate are formed.

After 5 minutes of the tribotest, the ratios of P/Zn, P/O (Fig. 6), and BO/NOB (Table 2) generally increased over rubbing time. The increase of the P/Zn and P/O ratios was 31.3%, 31.4%, respectively. The trend of these ratios generally matches the one in the presence of water. However, in this case water appears to impede the growth of the ratios to levels much lower than those in the absence of water, which

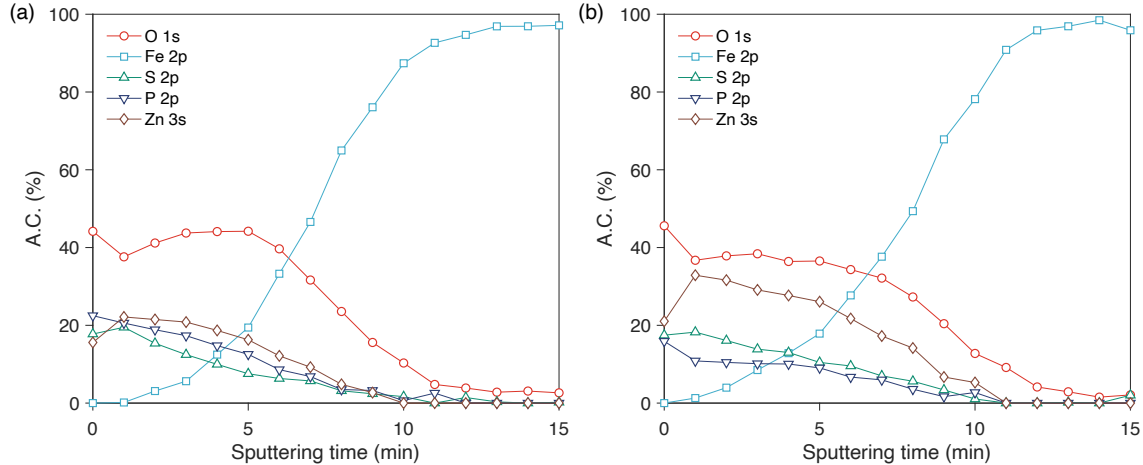


Figure 5. XPS depth profile after 120 minutes of rubbing a) in the absence of water and b) in the presence of water in the oil.

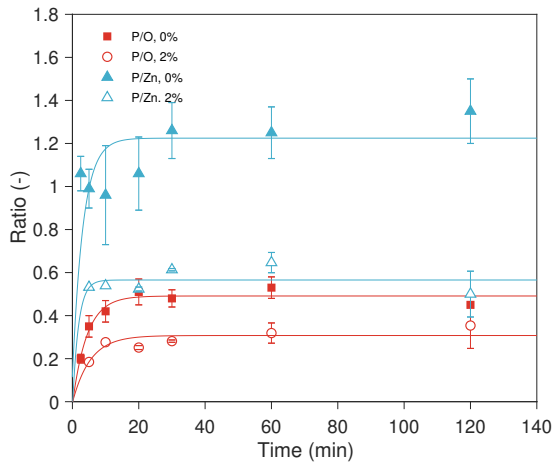


Figure 6. Effect of water on the temporal changes of the P/Zn and P/O ratios of ZDDP tribofilms.

suggests the formation of short chains ZnPO_4 even after long rubbing times.

4 Discussion

4.1 Effect of water on friction and tribofilm thickness

A number of previous studies suggested that the transient behaviour of friction can be linked to the tribofilm thickness, i.e. when the tribofilm thickness becomes large, the friction follows and gets higher [17, 40]. This relation can be examined by following the simultaneous temporal changes in the friction coefficient and tribofilm thickness (Fig. 2). The thickness evolution appears to resemble the one of the friction coefficient, which is clear from the general trend of the initial increase in thickness then decrease followed by steady state. The effect of water on this evolution does not appear to be uniform throughout the test, but instead it follows three

different phases. Interestingly, the last phase ends with a tribofilm thickness that is similar whether water is absent or present in the oil. In addition, although those three phases resemble the friction coefficient evolution, the timing is different. This indicates that the transient coefficient of friction might be linked to the composition of the tribofilm not just its thickness.

The initial steady increase in the coefficient of friction is probably related to the smearing of the asperities, which increases the contact area. In addition, it can also be related to the increasing interaction between the continuously increasing phosphate chains [17]. On the other hand, when water is present in the oil, shorter phosphate chains are formed [11], which have shorter relaxation time than that required for any significant interactions to occur between the extended chains across the contact. This can be one of the reasons of the slower growth in the friction coefficient and the reduced maxima reached after 60 minutes of rubbing as compared to the case after 20 minutes when water is absent from the oil. The results thus suggest that the increased friction in the beginning of the test can be partially attributed to the interactions between the phosphate chains on the rubbing surfaces rather than to solely the tribofilm thickness. The longer the chains, the larger the interactions and thus the larger the friction.

The decline in the friction coefficient after reaching a maximum can be related to two different mechanisms. First, the long chains of metal phosphate can align along the rubbing direction and thus lower the shear stress and consequently friction [41]. Second, the long phosphate chains, which have lower packing density than the shorter ones [42], can form less compact layers and thus less puckering occurs at the asperity contacts. Similarly, a number of previous studies [43–45] showed that for a single layer adhering loosely to the substrate, friction was maximum as compared to strongly adhered bulky layers. Therefore, the drop occurring between 20 and 60 minutes can be partially attributed to the enhanced

packing density of the chains arranged in the direction of rubbing, in addition to the smoothening of the contacting surfaces after the running-in period.

4.2 Effect of water on the rate of ZDDP decomposition reaction

The impact of water on the atomic concentrations of the decomposition products of O, P, Zn and S is presented in Fig. 7. The extent to which water affects these concentrations appears to vary depending on the decomposition products and their proximity to the metal surface. Water can have a small short-term effect limited to the running-in stage such as of O and S or a large long-term effect such as of P and Zn. During the running-in period, the concentrations of all the decomposition products change substantially, whereas less change occurs in the later stages. Each component starts with an initial concentration, which as rubbing continued exponentially approaches steady state. When water is present in the oil, the steady state concentrations of O and S were nearly unchanged. However, water decreased the equilibrium con-

centration of P and increased that of Zn by about 38%.

The initial exponential change in the concentration of the tribofilm components followed by steady state indicates that the kinetics of ZDDP decomposition is first-order, as detailed elsewhere [3, 17, 46]. This indicates that at the beginning of the test near the metal surface more reactants are available to generate the tribofilm layers than at the end of the tribotest away from the metal surface.

For all the components of the tribofilm, water appears to increase the reaction rate, i.e. how fast the atomic concentrations reached equilibrium; the faster the concentrations reach this equilibrium, the faster the decomposition reaction. The increased ZDDP decomposition rate in the oil containing water contradicts the widely perceived idea that water competes with the ZDDP molecules on the metal surface and thus decreases the decomposition rate [11]. It should be noted that this idea was mainly based on the observed delay in the tribofilm thickness growth (Fig. 2b) not the evolution of the decomposition products. Water indeed was found to hinder the formation of thick durable tribofilms. This apparent dis-

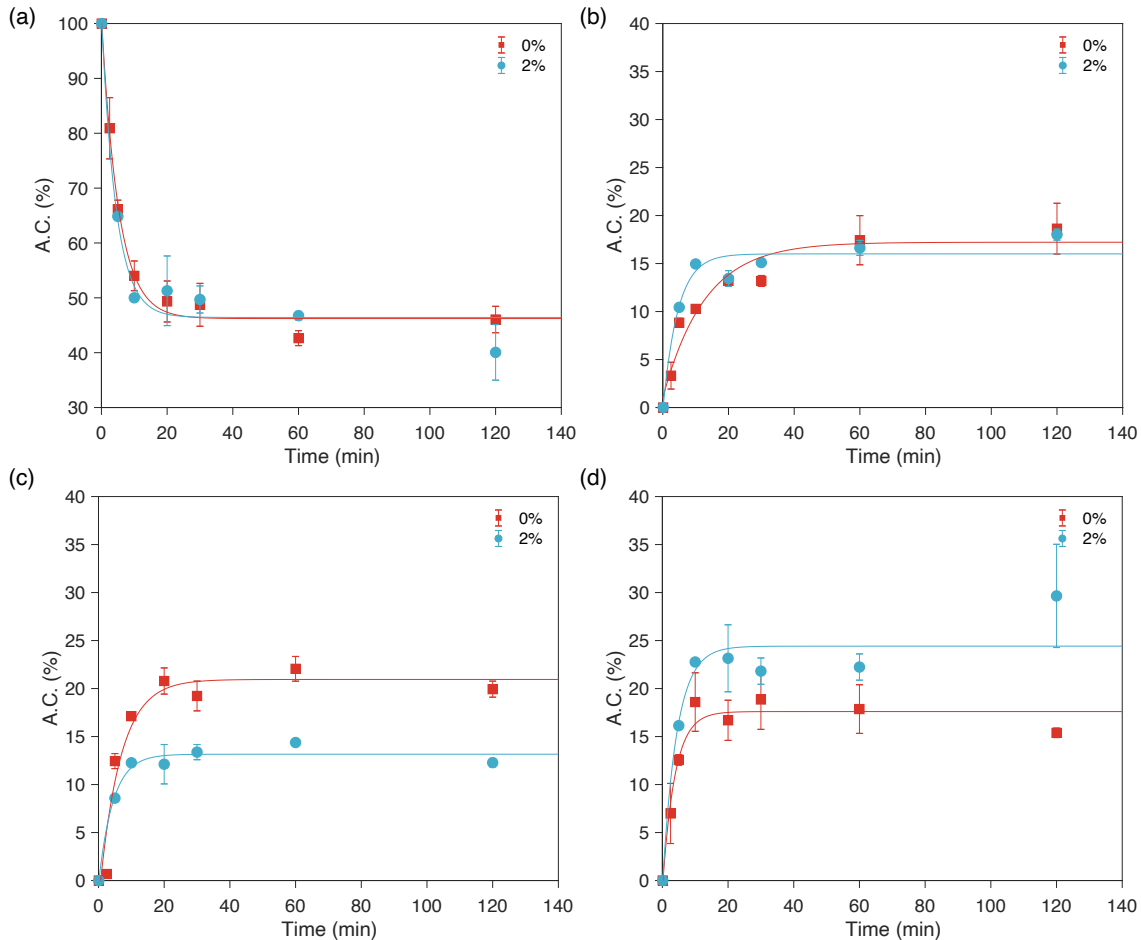


Figure 7. Effect of water on the atomic concentrations of a) O, b) S, c) P and d) Zn of the ZDDP tribofilm over the rubbing time.

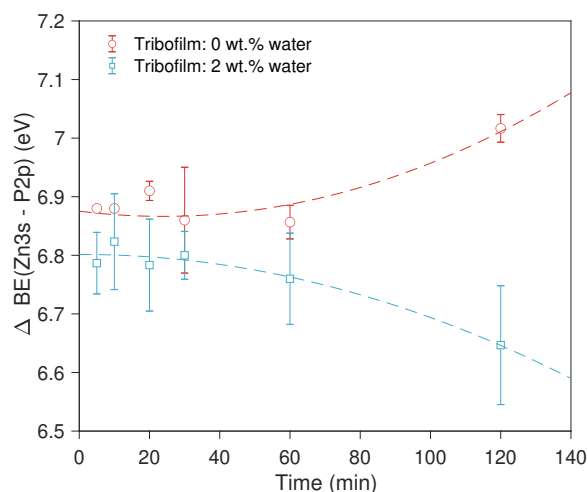


Figure 8. Effect of water on the Zn3s and P2p difference in binding energy (Δ) in the top 5–10 nm of the tribofilm over rubbing time.

crepancy can be explained as follows. Initially, water and ZDDP molecules compete on the available steel surface. The ZDDP molecules that succeed in reaching the surface appear to undergo fast initial decomposition reaction in the presence of water, which leads to a faster decrease in the concentration of the initially formed decomposition products. This leads to an early termination of the reactions forming the subsequent layers of the tribofilm, which is evident from the early approach to the steady state concentrations. This means that water does not completely hinder the formation of the early base layers on the metal surface. However, it can largely impede the formation of the subsequent layers. As rubbing and heating continue, more water evaporates and more ZDDP molecules adsorb to metal surface, which increases the formation of more phosphate layers.

4.3 Effect of water on the tribofilm composition

Several previous studies [3, 47] indicated that the formation of ZDDP starts as a nucleation-growth event, which is mechanically and thermally assisted. The initial growth starts on several activation sites with high energy on the formed nascent surface due to the presence of dangling bonds resulted from the initial wear and smear of asperities, or on dislocations and contamination sites on the substrate. Increasing either the contact pressure, temperature or both was reported [3, 47] to increase the formation rate significantly as they can reduce the energy barrier of the decomposition reaction. The presence of water can interfere with this effect as it can conceal the initial nucleation sites or simply hinder the accessibility of the adsorbed ZDDP molecules to the substrate. This becomes evident by noticing that water largely affects the concentrations of P, Zn and S as shown in Fig. 7, which are the main elements forming the tribofilm's layers

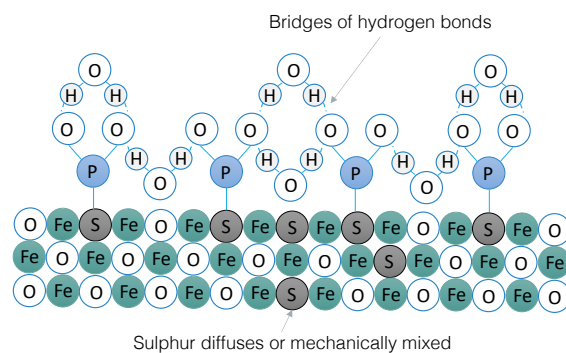


Figure 9. Schematic of the caging effect of water on the initially formed phosphate species and the subsequent formation of a single and multiple bridges of hydrogen bonds between water molecules and PO_2^- groups of the decomposed ZDDP.

of zinc phosphate [6] or zinc (thio)phosphate [17]. When mixed water exists, the concentrations of Zn and S was increased, whereas that of P was decreased. These changes can be explained by examining the progression of Δ , which is the Zn3s and P2p difference in binding energy, over rubbing time as shown in Fig. 8. As Zn3s is insensitive to changes in the composition [20, 21, 28], Δ can help determine the chemical changes associated with P while avoiding any uncertainties related to the calibration of the spectra [21]. In the absence of water, initially the binding energy appears to be constant but then increased with the continued rubbing. This indicates that a transformation occurs to the P species such as the polymerisation of the short phosphate chains. However, in the presence of water, the binding energy during the running-in period was constant, whereas the continued rubbing decreased the binding energy suggesting that a depolymerisation reaction occurs to the phosphate chains. The decrease in the binding energy when water existed was the general trend after long rubbing times. In contrast, Cen et al. [12] and Nedelcu et al. [11] reported that the binding energy of P2p does not change when water is mixed with oil, which suggested that it hinders the polymerisation of the short phosphate chains.

The transient behaviour observed in our results can be attributed to both the changes occurring in the tribofilm composition as well as the changes in the water concentration in the oil. Water initially hinders the transformation of P species during the running-in period. As water evaporates continuously from the oil (Fig. 2c), polymerisation starts to occur. However, the polymerisation reaction terminates earlier than the case in which water is absent, as shown in Fig. 7. Furthermore, the presence of water can induce defects in the formed phosphate chains that make them more susceptible to break, i.e. water catalyses chains scission. This is supported by the observation that in the presence of water, the concentration

of P never reaches the same terminal value as in the absence of water nor does its binding energy. This indicates that water does not only retard the polymerisation while it exists at high concentration in the oil but it also changes the formed tribofilm even after the concentration of water is minimal due to its continuous evaporation. Thus, the results indicate that the initial alteration of the ZDDP tribofilm occurring due to the presence of water during the running-in period cannot be reversed even if water is removed from the oil in the subsequent stages of the tribological test. The most probable explanation for this could be related to the formation of a single or multiple bridges between water molecules and the PO_2^- groups of the decomposed ZDDP, as shown in Fig. 9. This caging of the PO_2^- groups can hinder their chemical reactivity, which leads to the formation of short orthophosphate PO_4 segments. The short segments can be terminated easily by the available metal oxides on the substrate [48]. The evaporation of water from the oil reduces the number of bridges between water molecules, PO_2^- groups and PO_4 segments, which leads to the formation of longer phosphate chains. However, the increased concentration of Zn appears to oppose this effect by forming weak electrostatic interactions with the terminals of the short phosphate fragments to compensate their negative charge [48]. To confirm this effect, the BO/NBO ratio can be used to estimate the polymerisation number n , as follows [49]:

$$\text{BO/NBO} = \frac{1}{2} \frac{n-1}{n+1} \quad (1)$$

During the early stage of the tribotest, as water exists at high concentration, this ratio is likely to be prone to error. One way to check this is by calculating the BO/NBO ratio based on Δ , i.e. the $\text{Zn}3s$ and $\text{P}2p$ difference in binding energy [21], as follows:

$$\Delta = \Delta_0 - \frac{3}{2} \frac{\text{BO}}{\text{NBO}} \quad (2)$$

where Δ_0 is the binding energy difference for short orthophosphate chains, i.e. at the limit of BO/NBO approaches zero, which can be taken as a free fitting parameter. Fig. 10 compares the BO/NBO estimated from direct fitting of O1s signal and using Eq. (2). The ratios estimated based on these methods appear to follow the same trend over time. Therefore, it is possible to use the latter method to check the accuracy of the O1s signal fitting. This should reduce the uncertainty associated with the fitting and thus improve the accuracy of the chain length identification.

More insight into the changes in the chain length due to the presence of water can be found by following the evolution of the BO/NBO ratio, Δ and n simultaneously over rubbing time. The impact of water on this evolution is shown in Fig. 11. The small range of Δ and its small values due to the presence of water confirm that water significantly hinders the growth of the phosphate chains. This also confirms

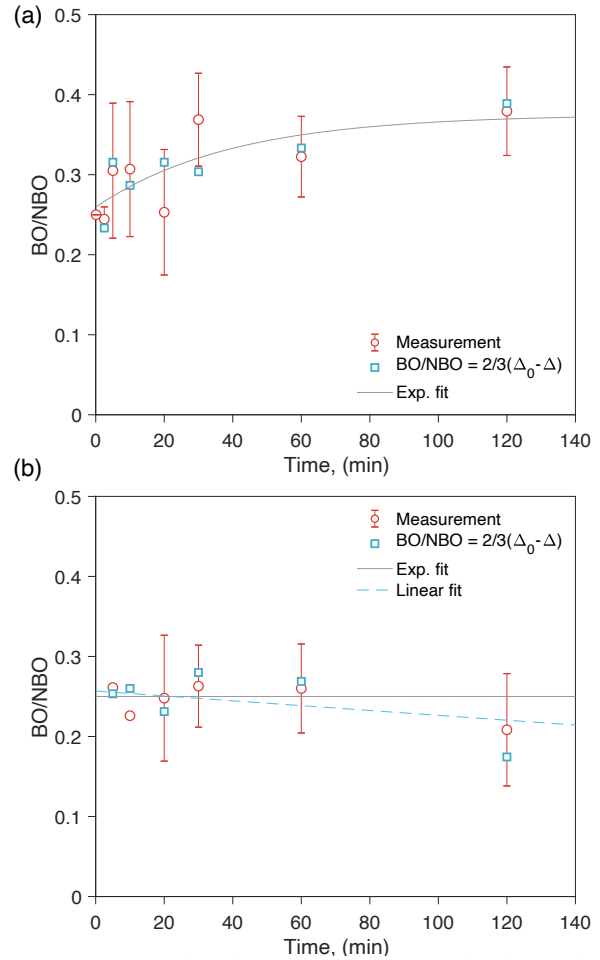


Figure 10. Comparison between the measured and calculated polymerisation number n ; a) in the absence of water in the oil and b) in case of 2% water is present in the oil.

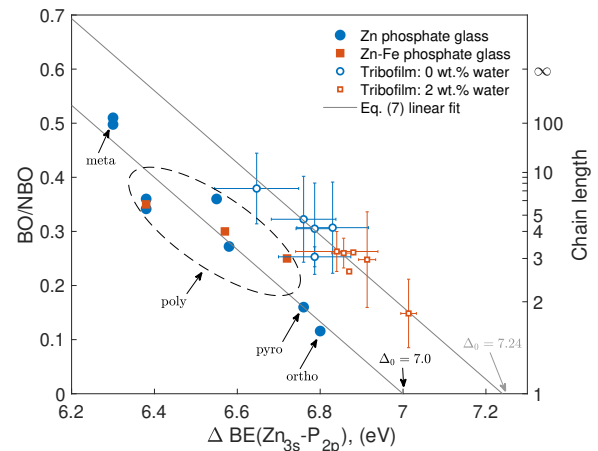


Figure 11. Effect of water on the temporal changes of the $\text{Zn}3s$ and $\text{P}2p$ binding energy difference (Δ), BO/NBO ratio, and chain length n over rubbing time, following Crobu et al. [21].

the previously discussed two effects of water on the phosphate growth. First, water can terminate the polymerisation reaction in the early stages of rubbing and hence the chain length does not grow. Second, water can result in weaker long chains that can be easily depolymerised into shorter ones. The trend of the chain length evolution suggests that the two mechanisms occur simultaneously.

5 Conclusion

This study examined the impact of water on the reaction kinetics of secondary ZDDP decomposed on 52100 bearing steel under 80 °C and 1.2 GPa contact pressure in the boundary lubrication regime. It also examined, under these conditions, the ultimate effect of water on the friction and composition of its antiwear tribofilm. Based on the XPS surface analysis, the following main conclusions can be drawn:

- Water initially accelerates the decomposition of ZDDP, which follows first-order reaction kinetics.
- The effect of water on the concentrations of the decomposition products can vary between a small short-term effect limited to the running-in period, such as for O and S, and a large long-term effect such as in the case of P and Zn.
- The first formed layer of the tribofilm is rich in zinc and sulphur, which appears to be a precursor for the subsequent layers of zinc phosphate.
- Water can hinder the polymerisation reaction in the early stages of rubbing forming predominantly short chains, which was related to the formation of a caging effect of water molecules on the initially formed PO_2^- groups of the decomposed ZDDP.
- This caging effect along with the initial alteration of the tribofilm occurring due to the presence of water during the running-in period cannot be reversed even if water is removed from the oil by evaporation in the subsequent stages.

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