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# **A New Insight into the Interfacial Mechanisms Involved in the Formation of Tribofilm by Zinc Dialkyl Dithiophosphate**

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## **Abstract**

Understanding the true interfacial mechanisms involved in the growth of tribofilms generated by Zinc Dialkyl Dithiophosphate (ZDDP) is important because it is the most widely used anti-wear additive and there is legislative pressure to find efficient environmentally-friendly replacements. The main focus of this study is to investigate the durability of the ZDDP tribofilm and correlate it to the chemical and physical properties of the glassy polyphosphates. A novel experimental method has been developed to study the effect of lubricant temperature and contact load on tribofilm growth and durability. Results show that physical parameters such as temperature and pressure significantly influence the tribofilm durability. XPS analyses were carried out before suspending the test and after changing the oil to assess the difference in chemical structure of the tribofilm before and after stopping the test. The chemical analyses suggest that there are different chemical properties across the thickness of the tribofilm and these determine the durability characteristics.

Keywords: Boundary lubrication, Tribochemistry, Tribofilm durability, ZDDP, XPS

## **1 Introduction**

### **1.1 Boundary lubrication**

The Boundary Lubrication (BL) regime is the regime where the fluid lubricant is not able to sustain the load between surfaces. The surfaces are not wholly separated by a viscous lubricant film and direct asperity-asperity interactions occur. The severity of the contact is high and the probability of adhesion, abrasion and fatigue, and therefore wear, is increased. Frictional

heating and rubbing of surfaces induces tribochemical reactions at the interfaces and the result is the formation of a very thin reacted film on the substrate called a tribofilm.

Antiwear additives have been commonly used in oil to reduce the wear of boundary-lubricated contacts by forming a protective layer on the surface which prevents the direct asperity-asperity contact thus reducing wear. There are also different mechanisms in which the additives react with the surface to form the tribofilm [2].

## **1.2 ZDDP as an anti-wear additive**

Zinc Dialkyl Dithiophosphate (ZDDP) is the most commonly used antiwear additive in engine oils. Considering new environmental legislation on reducing the amount of metals, Phosphorous and Sulphur in engine oils, the concentration of ZDDP in lubricant oils is continually decreasing. Alternatives to ZDDP are urgently required. The design of new antiwear chemistries requires an understanding of the principle modes by which ZDDP acts to provide antiwear function.

It is reported that adsorption of the ZDDP molecules on the substrate is necessary prior to the formation of any surface films [3, 4]. Surface studies show that ZDDP thermal films are different from tribofilms [5-7]. The tribofilm, unlike thermal films, needs asperity-asperity contact and sliding to be formed on the surface and generally they form at much lower temperatures than the thermal films [3, 8-10]. The thickness of the tribofilm is reported to be in the range of 50-150 nm on steel surfaces [9, 11, 12]. ZDDP tribofilms grow initially on small single patches and with time cover the surface in pad-like structures [13].

## **1.3 Mechanical properties and durability of ZDDP tribofilm**

Several works have studied the mechanical properties of ZDDP tribofilms formed in boundary lubricated contacts [13-19]. These have demonstrated that the properties of the ZDDP tribofilm layers are dependent on applied load [20, 21].

Mosey et al [20] developed a new theory for the functionality of ZDDP tribofilms at the molecular level. They suggested that pressure-induced cross-linking is the reason for chemically-connected networks and many aspects of experimentally-observed behaviour of ZDDP can be explained by this theory. It was reported that the high pressure at the surface of the film will lead to higher cross-linking and result in longer chain phosphates. The different mechanical properties of long and short chain polyphosphates were simulated and reported in

the work. All these studies give good insights of mechanical characteristics of ZDDP tribofilms under severe conditions.

It was suggested by Morina et al [22] that the durability of tribofilm can be evaluated by the chemistry of the tribofilm formed on the surface. The experiments were based on investigating the formation, stability and removal of the tribofilm by changing the oils during the tests and monitoring the friction coefficient. The concept of tribofilm removal was also reported by Lin et al [23]. Based on the experimental wear results, they suggested that a comparison between the rate of formation and removal of the tribofilm can characterise wear in boundary lubrication.

#### **1.4 Chemistry of ZDDP tribofilm**

The chemical composition of the ZDDP tribofilm in boundary lubrication conditions on steel surfaces has been extensively characterized. The general conditions is that there is a viscous layer of physically -adsorbed additive on the top layer of the tribofilm which can be easily removed by means of solvents and washing. Underneath this viscous layer, there is a chemically adsorbed layer of amorphous zinc and iron polyphosphates with different chain lengths [3, 24-26]. The ZDDP tribofilm has a layered structure with different chain lengths at different positions in the layer [24, 26]; shorter chain polyphosphate layers are present at the bottom adjacent to the substrate interlinked with the iron oxide. The top layer is reported to be thinner consisting of mainly longer chain polyphosphates. The interfaces is present between the layers are most likely to be gradual changes in the structure of the tribofilm.

Crobu et al. [1, 24] characterised the surface chemistry of zinc polyphosphates using XPS and Time-of-Flight Secondary-Ion Mass Spectroscopy (ToF-SIMS) by assessing the intensity ratio of bridging oxygen (P-O-P) and non-bridging oxygen (P=O and P-O-M) and. The chain length of the glassy phosphates in the tribofilm can be identified by a combined use of bridging oxygen/non-bridging oxygen (BO/NBO) intensity ratio and the difference in binding energies between the Zn3s-P2p<sub>3/2</sub> peaks from XPS and a modified Auger parameter. This combined method allows characterisation of polyphosphate chain composition ranging from zinc orthophosphate to zinc metaphosphate (Figure 1).

	Phosphate Glass	BO/NBO
Longer chain	Metaphosphate	0.48±0.02
	Polyphosphate	0.37±0.05
	Pyrophosphate	0.20±0.05
Shorter chain	Orthophosphate	----

**Figure 1 Identification of different composition of zinc polyphosphates [1]**

### 1.5 Growth of ZDDP tribofilm

An important aspect in the study of ZDDP tribofilms is the growth rate and the steady state thickness. The growth of ZDDP tribofilm on contacting surfaces has been subject of several studies [13, 19, 27-31]. Fujita et al [32, 33] studied the growth of ZDDP tribofilm using a Mini Traction Machine (MTM) and Spacer Layer Interferometry Method (SLIM). The experimental results were then used to extract semi-empirical relationships for the growth of the tribofilm.

It was suggested [32, 33] that ZDDP tribofilms are very durable when rubbed in base oil once they are formed. A base oil containing dispersant was found to be essential to remove the tribofilm patches. It was shown that secondary ZDDPs reach to a maximum film thickness very rapidly and then a removal of the tribofilm occurs due to different surface phenomena. They suggested that a combined model of formation and removal can explain such a behaviour. It was hypothesized that the removal process only begins after some time of rubbing. [32, 33]. There was a difference between the growth patterns for primary and secondary ZDDPs. Results revealed that primary ZDDP generally follows a straightforward increase in the thickness while secondary ZDDP grows to a maximum value and then levels out to a steady-state.

Recently Gosvami et al [34] designed an experiment to monitor the growth of the ZDDP tribofilm in a single asperity contact. They used Atomic Force Microscopy (AFM) to generate the tribofilm and monitor the growth in-situ. It was reported that temperature and stress play a significant role in the initiation of the tribochemical reactions.

Authors of the current manuscript recently reported a theoretical model with a hypothesis that formation and removal of the tribofilm happen simultaneously [35]. The hypothesis was based on the experimental observations of removal of the tribofilm and wear of the system even in the presence of fully-formed tribofilms [17, 31, 36]. The wear hypothesis was then validated against some wear measurements in experiments [37, 38] and has shown good agreement. Testing the model in different conditions suggests that the removal of the tribofilm is time dependent [22, 32].

The aim of this study is to investigate the effect of different physical parameters such as temperature and load on the durability and chemical characteristics of the ZDDP tribofilm. XPS analyses were carried out to be able to evaluate the tribofilm chemical characteristics. The change in the tribofilm thickness was correlated to the chemistry of the glassy polyphosphates. This study will open new insights into the real mechanisms in which ZDDP acts as antiwear additive by correlating its durability to the chemical structure. This will help to better understand the growth mechanism and the kinetics of the tribochemical reaction. The durability of such films is an important parameter to consider in the design of new lubricants containing antiwear additives.

## **2 Experimental Procedure**

### **2.1 Tribology test rig**

A Mini Traction Machine (MTM) is used to simulate a sliding/rolling contact in boundary lubrication. One of the key points in using MTM is that slide-to-roll ratio (SRR) can be changed in the experiments over the wide range of ( $0 < \text{SRR} < 5$ ) [39].

In the standard configuration the test specimens are a 19.05mm steel ball (AISI 52100) and a 46 mm diameter steel disc. Using standard samples has also an advantage that the results can be compared with the existing results in the literature in terms of tribofilm thickness. The ball is loaded against the face of the disc and the ball and disc are driven independently to create a mixed rolling and sliding contact. The frictional force between the ball and disc is monitored by a force transducer. The applied load, the lubricant temperature and the electrical contact resistance between the specimens and wear scar are monitored by sensors.

## 2.2 Spacer Layer Interferometry

The Spacer Layer Interferometry Method (SLIM) was used to measure tribofilm thickness in-situ [40]. The glass disc is coated with a thin layer of silicon oxide which has a semi-reflective layer of chromium on top. The contact of the ball with the glass is shined by white light through the microscope and the coated glass. Part of the light is returned back from the semi-reflective chromium layer on top of the coated glass and other part goes through the silicon oxide layer and tribofilm formed on the surface and is reflected back from the steel ball. These light paths are captured by RGB colour camera and it can be analysed by the software to evaluate the tribofilm thickness during the experiments. This method is capable of measuring the film thickness of any reaction layer as they are being formed on the surface.

## 2.3 Material and test conditions

In this study balls and discs were both made from AISI 52100 steel with hardness of 6 GPa. New balls and discs were used for each experiment. They were cleaned before each test by immersing in isopropanol and petroleum ether in an ultrasonic bath for 20 minutes. The materials used in the experiments and working conditions are shown in Table 1 and Table 2 respectively. The roughness of the balls and the discs were measured using a White Light Interferometer and the measured values were compared with the data provided by the manufacturer (PCS instruments, UK). Experiments were carefully designed to investigate the effect of different parameters such as temperature, load, stopping time and running in on the tribofilm formation/removal and wear performance of the system. A small entrainment speed was chosen for this purpose to remain in the boundary lubrication regime.

The comparison between minimum Elastohydrodynamic film thickness and the composite roughness of the surfaces represents the severity of the contact known as the lambda ratio. The minimum EHL film thickness is calculated by using Hamrock-Dowson equation as the following:

$$h_{min} = 3.63R_x \left( \frac{U\eta_0}{E^*Rx} \right)^{0.68} (\alpha E^*)^{0.49} \left( \frac{W}{E^*R_x^2} \right)^{-0.073} (1 - e^{-0.68k}) \quad (1)$$

Where  $R_x$  is the radius of curvature in the x-direction (m),  $U$  is the entrainment speed (m/s),  $E^*$  the reduced Young's Modulus (Pa),  $\eta_0$  the dynamic viscosity of the lubricant (Pa.s),  $\alpha$  the pressure-viscosity coefficient (Pa<sup>-1</sup>),  $W$  the applied load (N),  $k=1$ . The entrainment speed of

the lubricant is an input into Equation 1. Smaller entrainment speed results in lower EHL film thickness which leads to contact moving towards boundary lubrication regime.

**Table 1 Material properties**

Material properties	Value
Hardness (GPa)	6
Elastic modulus (GPa)	210
Ball surface roughness $R_q$ (nm)	20
Disc surface roughness $R_q$ (nm)	10

**Table 2 Experimental working conditions**

Parameters	Value
Load (N)	30, 40, 60, 75
Temperature °C	80, 100, 120, 140
Entrainment speed ( $\frac{m}{s}$ )	0.1
SRR	5%
Test durations (min)	120
$\lambda$ ratios	0.03-0.06
Oil used	PAO+ZDDP
Ball diameter (mm)	19.05
Disc track diameter (mm)	32

## 2.4 Lubricating oil

In this study, Poly- $\alpha$ -olephin (PAO) +ZDDP and PAO were used to investigate the durability of the tribofilm. The lubricant properties are listed in Table 4.

## 2.5 Effect of temperature

The effect of temperature on viscosity is important and has been considered in the film thickness calculations. The viscosity values have been measured for the lubricating oil at different temperatures by using SVM 3000 Stabinger Viscometer and are reported in Table 3. The working conditions and the corresponding  $\lambda$  ratios are reported in Table 2. The methodology used to study the formation and removal behaviour of the tribofilm by using MTM SLIM is reported in detail in the experimental approach.

**Table 3 Viscosity values for the lubricating oil measured at different temperatures**

Temperature (°C)	Viscosity Values (cSt)
80	6.2
100	4.2
120	3.07
140	2.37

## 2.6 Tribofilm durability test – oil changing procedure

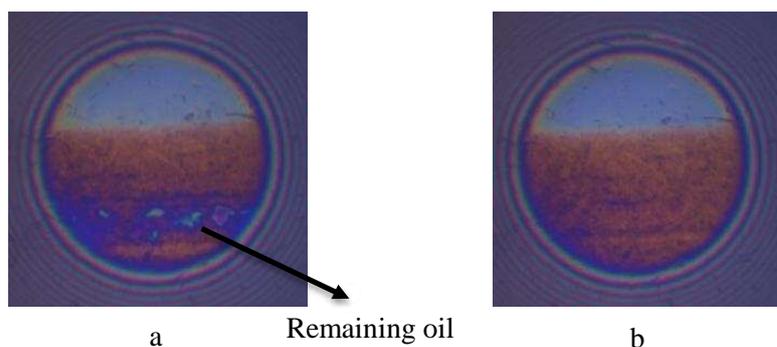
### 2.6.1 Clean up after suspending the test

Cleaning the oil bath and MTM accessories used for the test is important to study the durability of the tribofilm.

**Table 4 Lubricant properties**

Designation	Details
PAO+ZDDP (0.08 mass% phosphorus)	PAO+ZDDP
Base oil	PAO

The cleaning process was carried out in three different steps. First of all, MTM accessories were immersed in the ultrasonic bath for 30 minutes including 15 minutes in isopropanol and 15 minutes in petroleum-ether. Secondly, the disc was immersed in isopropanol in the ultrasonic bath to remove the attached ZDDP remaining additive from the disc. Thirdly, to avoid altering the tribofilm formed on the balls, they were cleaned by a tissue stained by isopropanol to remove the remaining ZDDP on the ball. To make sure that any tribofilm on the ball was not removed during the cleaning process by isopropanol, two images were taken by SLIM, one before suspending the test and one exactly before starting the rubbing again and the images are shown in Figure 2 as an example. Comparison between these two images shows that the thickness of the tribofilm before and after cleaning the ball is almost the same and the only thing which was removed from the ball is the excess unreacted oil (as shown in Figure 2). The difference in the images is the spots of oil remaining on the ball at the time of imaging.



**Figure 2 SLIM images taken (a) before suspending the test (b) immediately after suspending the test and before starting the rubbing**

## 2.7 Wear scar chemistry

In this research, X-ray Photoelectron Spectroscopy (XPS) was used to investigate the chemical characteristics of tribofilm under different conditions. The XPS measurements were carried out

in a PHI 5000 VersaProbe™ XPS (Ulvac-PHI Inc, Chanhassen, MN, US) with a monochromatized Al K $\alpha$  X-ray (1486.6eV) source.

XPS is a surface-sensitive quantitative spectroscopic technique which measures the elemental composition, chemical state and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 0 to 10 nm of the material being analysed. XPS requires high vacuum ( $P \sim 10^{-8}$  millibar) or ultra-high vacuum (UHV;  $P < 10^{-9}$  millibar) conditions.

Scanning X-ray Image (SXI) was used to find specific features on the surface to distinguish between wear track and outside. Survey spectra and detailed spectra were collected with a beam diameter of 100  $\mu\text{m}$ . Survey spectra were acquired with 117.4 eV pass energy and a step size of 1 eV when detailed spectra were acquired with 46.95 eV pass energy and a step size of 0.1 eV. The whole set of spectra (detailed and survey spectra) was acquired within 120 minutes. Samples were argon ion sputtered using 2kV ions over an area of  $2 \times 2 \text{ mm}^2$ .

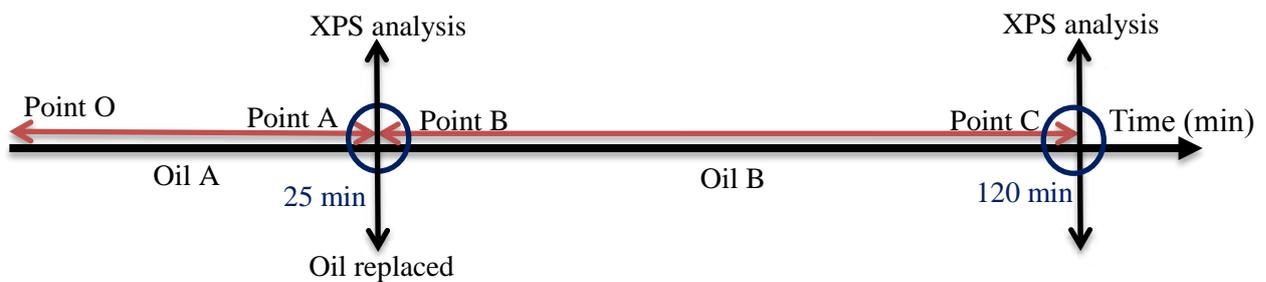
The data was then post processed using XPS software (CasaXPS) and the spectra were fitted using Gaussian-Lorentzian curves. The calibration was carried out by shifting C1s peak to 284.8 eV [41]. For the phosphorus and sulphur signals, the two peaks  $2p_{3/2}$  and  $2p_{1/2}$  arising from the coupling of the spin and the orbital angular momentum are close to each other, resulting in an asymmetric signal. The fitting parameter for the model curve leaves the ratio between the two peaks fixed at 1:2 and the difference in energy at 1.25 eV for the S signal and 0.85 eV for the P signal. The O 1s peak was curve fitted to bridging oxygen (BO) at  $532.6 \pm 0.5$  eV, non-bridging oxygen (NBO)  $531.2 \pm 0.5$  eV, and in some cases oxide at  $530.2 \pm 0.5$  eV [24]. The XPS analyses were carried out on the surfaces of the tribofilm on ball samples without any sputtering.

## 2.8 Methodology

It has been hypothesized that the balance between formation and durability of the tribofilm significantly affects the wear performance of the tribological system [23, 35, 37]. To investigate this, a set of experiments was designed to study the durability of the tribofilm. Tribofilm durability is assessed by measuring its thickness and how this changes once rubbed in base oil. In this scenario the rate of tribofilm formation is significantly lower than the loss of tribofilm thickness due to the lack of supply of ZDDP during the rubbing process in base oil. For this purpose, experiments were carried out for two hours in total; the first 25 minutes

run with PAO+ZDDP (oil A) to form the tribofilm and the rest of the test run by base oil (oil B). The test was suspended after different times and different removal behaviour was observed. In addition, a set of tests was conducted to assess the durability of the film formed after 3 hours of rubbing. The oil was replaced after 3 hours and the results were compared with the test when the oil was replaced at 25 minutes.

The experimental part of this study contains different steps. Tribological experiments were carried out by MTM in rolling/sliding conditions in boundary lubrication. Spacer Layer Interferometry was used to monitor tribofilm thickness during the experiments in-situ. The disc was then analysed using XPS to assess the chemical characteristics of the tribofilm. This experimental sequence leads to growth of the tribofilm and correlating its chemical and durability characteristics. This experimental approach is demonstrated schematically in Figure 3.



**Figure 3 Schematic of the experimental approach for replacing oil and surface analysis. Points A, B and C are used to identify the tribofilm analysed by XPS**

The first set of experiments was to study the tribofilm durability at different periods and was conducted in three sub-steps as following:

- I. Early-stage tribofilm durability (oil replaced at 25 minutes)
- II. Late-stage tribofilm durability (oil replaced at 3 hours)
- III. Multiple oil replacement durability test (oil replaced at 25 minutes and then replaced again at 1 hour)

The second part of the experiments also includes the following sub-steps:

- I. Study the effect of temperature on the durability and chemistry of the tribofilm
- II. Study the effect of load on the durability and chemistry of the tribofilm

The working parameters for the second part of the experiments are summarized in Table 5.

**Table 5 Working parameters of the experimental procedure**

Tests	Points	<i>O</i> → <i>A</i>	<i>B</i> → <i>C</i>
<b>I</b>	Temperature (°C)	100	80, 100, 120, 140
	Load (N)	60	60
	Oil	Oil A (PAO+ZDDP)	Oil B (PAO)
<b>II</b>	Temperature (°C)	100	100
	Load (N)	60	30, 40, 60, 75
	Oil	Oil A (PAO+ZDDP)	Oil B (PAO)

### 3 Results and discussion

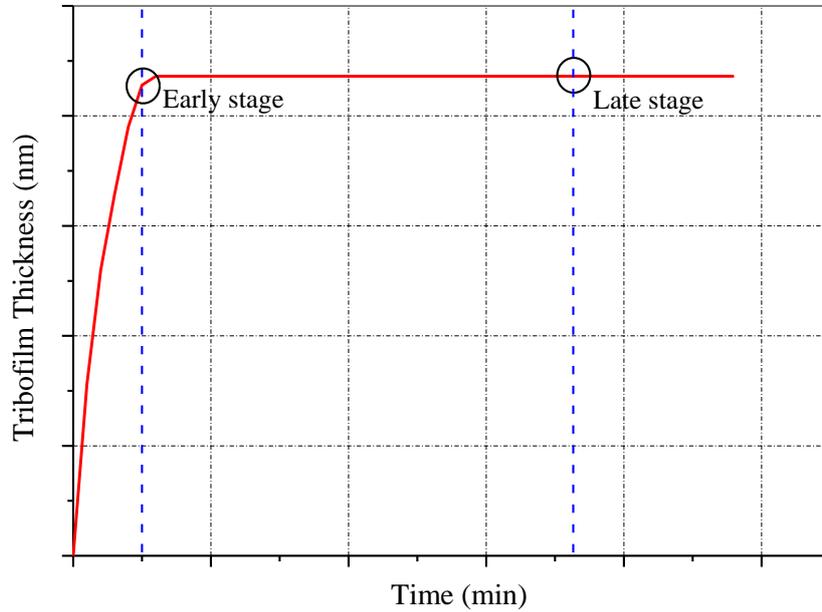
#### 3.1 Tribofilm evolution

To investigate the tribofilm durability throughout the time, oil was replaced at two different stages; early stage and late stage. Figure 4 illustrates the two stages in which the oil was replaced. In the early stage, the oil was changed after 25 minutes of starting the experiment whereas in the late stage, oil was replaced after 3 hrs of running the test. In both cases, two different experiments were conducted. Firstly, oil was replaced by a fresh ZDDP containing oil and secondly by base oil. The growth of the tribofilm for these two different points is reported in the next section as well as the chemistry of the tribofilm formed on the surfaces.

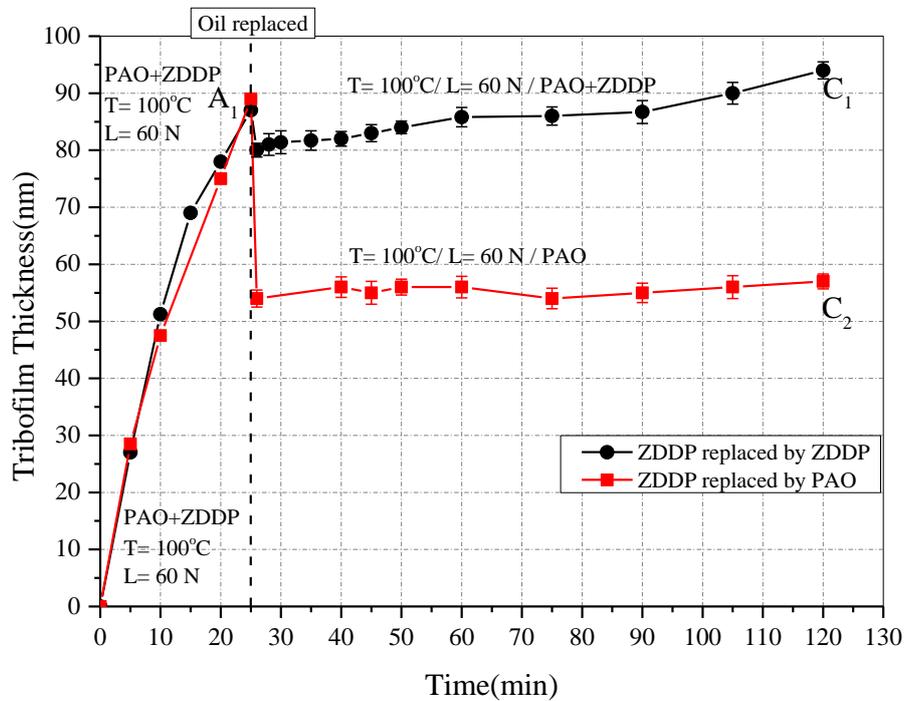
##### 3.1.1 Early stage tribofilm durability

The results of the tribofilm thickness measurements for the early stage oil replacement experiments are shown in Figure 5. It can be seen that if the lubricating oil is replaced by a fresh oil containing ZDDP, the tribofilm growth is not affected significantly by stopping the experiment and starting it again. There is a small drop in the thickness of the tribofilm due to the mechanical action. When the oil is replaced by base oil, there is a larger drop in the thickness of the tribofilm. Once the uppermost layer is removed, the tribofilm is durable and the thickness does not change. It should be noted that the drop in the thickness of the tribofilm is an instantaneous drop. It means that the top layer of the tribofilm is removed in the first few

load cycles after replacing the oil. It can also be related to the chemical properties of the top and bottom part of the glassy polyphosphates tribofilm formed on the surface.



**Figure 4 Schematic representative of two different stages of replacing the oil. Early stage after 25 minutes and late stage at 180 minutes.**

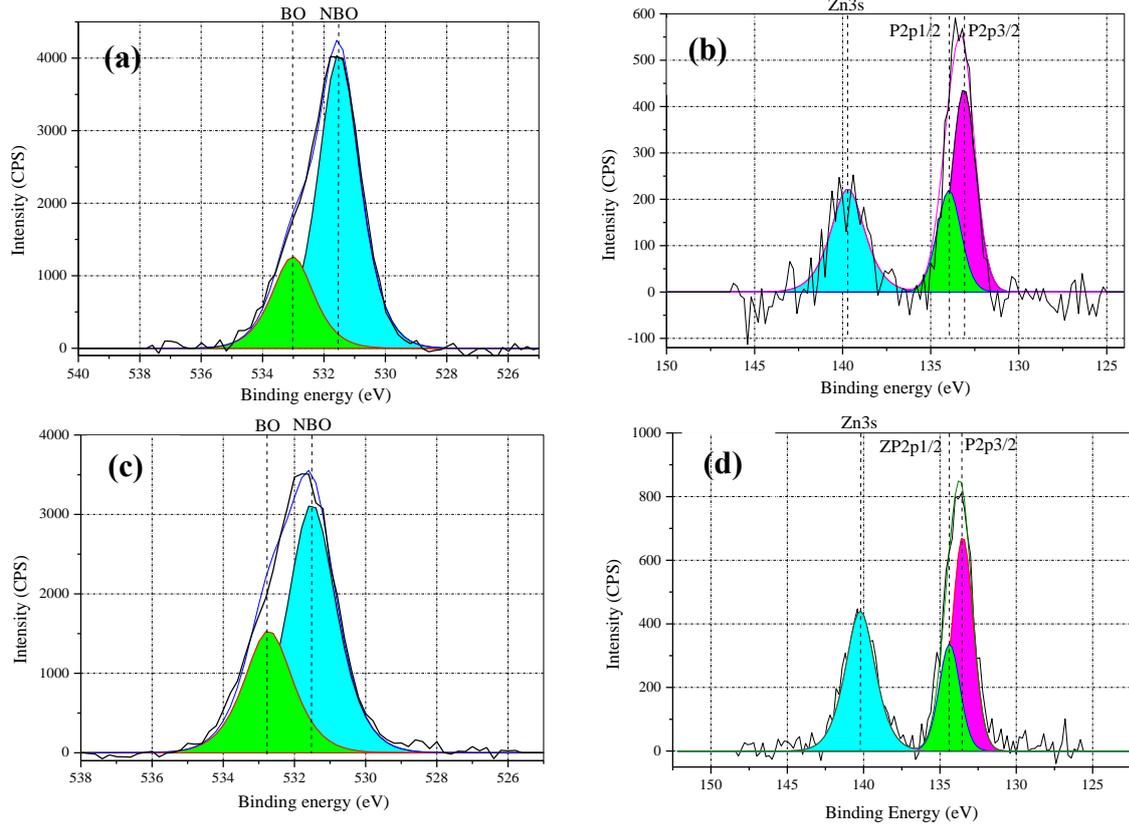


**Figure 5 Tribofilm thickness results for the early stage durability test**

### 3.1.1.1 Chemistry of the tribofilm

For the above mentioned experiments XPS analysis was conducted at the time of replacing the oil and at the end of each experiment. The oxygen and phosphorus peaks are plotted, to primarily identify the chain length for the glassy polyphosphates in the tribofilm. The ratio of bridging oxygen to non-bridging oxygen in the polyphosphate glass was calculated by dividing the intensity of BO and NBO peaks obtained from XPS analysis. This approach has been extensively used in literature [42-50]. Also the binding energy difference between the Zn3s and P2p peaks in the XPS spectra was used to give complementary information.

The BO/NBO ratio for the case of replacing the oil by base oil at 25 minutes of starting the test is identified as 0.31 at the end of the experiment (point C2 in Figure 5). According to the refs [1, 24], in this case the composition of the tribofilm is zinc pyrophosphate. This value is calculated to be 0.51 when the oil was replaced by a fresh ZDDP-containing oil (point C1 in Figure 5) and the tribofilm is mainly composed of metaphosphates (see Figure 6). The results suggest that the tribofilm consists of shorter chain polyphosphates in the case that oil was replaced by base oil. The tribofilm in this case is more durable and not easy to be removed. The BO/NBO ratio before replacing the oil was obtained as 0.47 ( Point A1 Figure 5) which shows a long chain polyphosphate in the tribofilm (metaphosphate) [1]. Calculation of the binding energy difference between Zn3s-P2p<sub>3/2</sub> peaks shows the same trend in identifying the chain length. The above mentioned results can be found in Table 6. Zn3s-P2p<sub>3/2</sub> binding energy difference increases when the tribofilm composition varies from metaphosphate (longer) to orthophosphate (shorter). (As shown in Figure 1).



**Figure 6 XPS spectra for the tribofilm formed at the end of the test when**  
**(a) the oil was replaced by base oil O 1s spectra (b) oil was replaced by base oil Zn3s,**  
**P2p spectra (Point C<sub>2</sub> in Figure 5)**  
**(c) oil was replaced by fresh ZDDP O1s spectra (d) oil was replaced by fresh ZDDP**  
**Zn3s, P2p spectra (Point C<sub>1</sub> in Figure 5)**

**Table 6 BO/NBO ratios and the difference between Zn3s and P2p peaks. Tribofilm thickness at points A<sub>1</sub>, C<sub>2</sub> and C<sub>1</sub> is shown Figure 5.**

Test	Both tests	ZDDP changed with base oil	ZDDP changed with fresh ZDDP
	Before changing the oil (Point A <sub>1</sub> )	End of the test (Point C <sub>2</sub> )	End of the test (Point C <sub>1</sub> )
<b>BO/NBO ratio</b>	0.47	0.31	0.51
<b>Zn3s – P2p binding energy difference (eV)</b>	6.57	6.70	6.4

### 3.1.2 Late stage tribofilm durability

It was reported previously that long chain polyphosphates convert to shorter chain polyphosphates due to rubbing [24]. The tribofilm evolution experiments were conducted with the same experimental configuration and the oil was replaced by base oil after 180 minutes of starting the test. The tribofilm growth results are plotted in Figure 7. Results suggest that lower reduction in the thickness of tribofilm occurs when the oil is exchanged after 3 hours than after 25 minutes. It is clear that the tribofilm is more resistant to rubbing and only a few nanometres of the film are removed. These results are in agreement with [22, 32] that report a durable ZDDP tribofilm once fully formed. XPS analysis was carried out to differentiate the chemical properties of the tribofilm formed on the surfaces at two different stages.

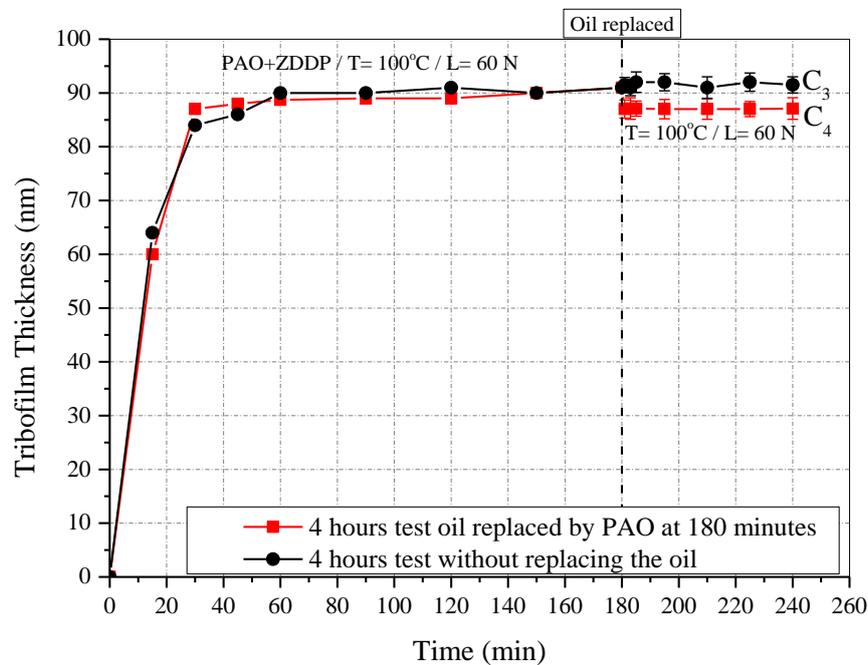
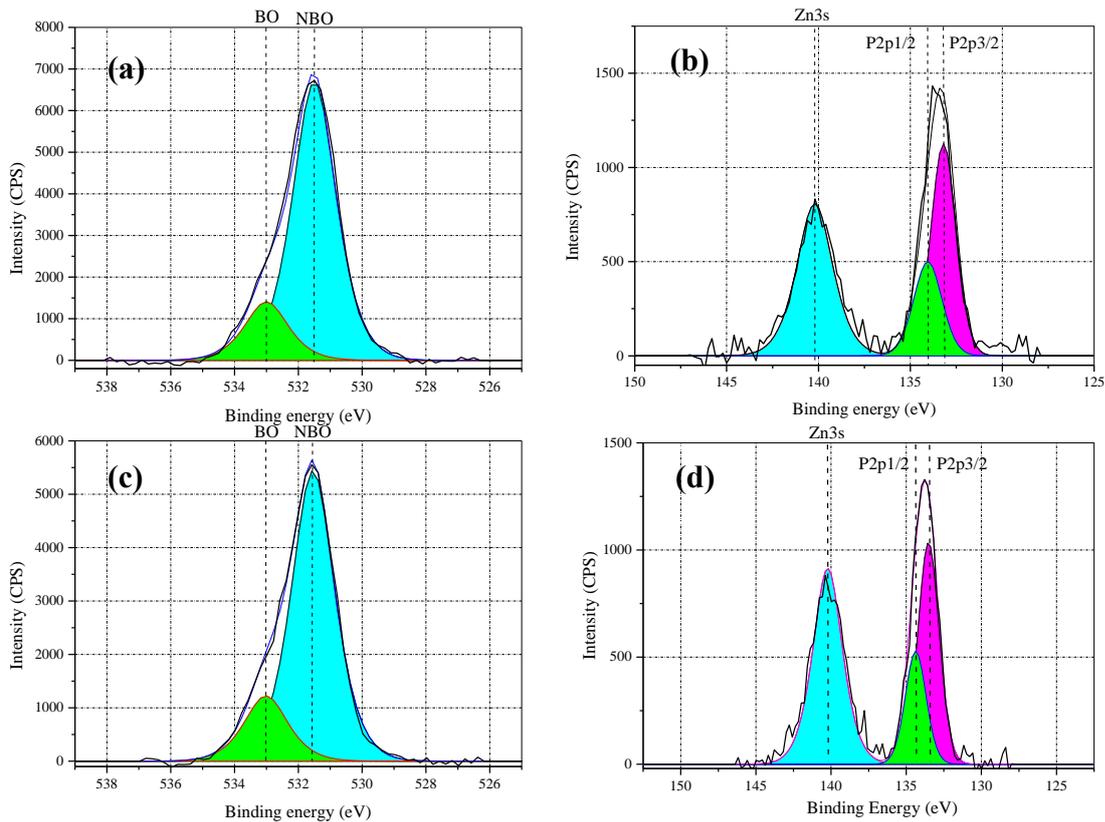


Figure 7 Tribofilm thickness results for the late stage durability test

#### 3.1.2.1 Chemistry of the tribofilm

The BO/NBO ratio and binding energy difference between Zn3s and P2p are calculated as 0.21 and 6.97 (eV) respectively (see Figure 8) for the case of replacing the oil at 3 hours of starting the test (point C<sub>4</sub> in Figure 7). The zinc polyphosphates composition can be recognised as pyrophosphate (short chain). These values are 0.23 (pyrophosphate) and 6.92 (eV) when the oil was not replaced (point C<sub>3</sub> in Figure 7) by base oil (see Table 7 in appendix and Figure 8). It suggests that short chain polyphosphates are present in the tribofilm. Comparing the chemical

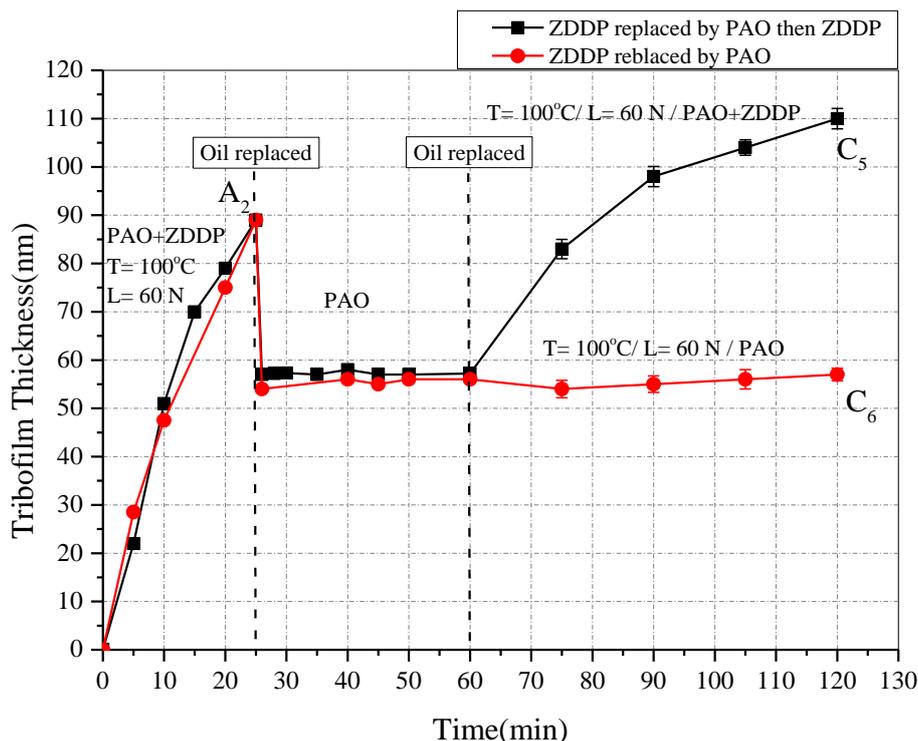
structure of the tribofilm when oil replaced after 25 minutes of the experiments and 3 hours with the same conditions shows that rubbing affects the structure and tribofilm contains more short chain polyphosphates at longer time of rubbing. Results are in agreement with the reports of literature [51]. The comparison between the experiments while the oil was exchanged after 25 minutes of rubbing with the one after 3 hours of rubbing suggests that more tribofilm loss happens in the former and it can be related to the chemical structure of the tribofilm.



**Figure 8 XPS spectra for the tribofilm formed at the end of the 4hrs test when (a) the oil was replaced by base oil at 3hrs O1s spectra (b) oil was replaced by base oil at 3hrs Zn3s, P2p spectra (Point C4 in Figure 7) (c) without replacing the oil O1s spectra (d) without replacing the oil Zn3s, P2p spectra (Point C<sub>3</sub> in Figure 7)**

### 3.1.3 Multiple replacement

This experiment was designed to assess whether when a tribofilm partially removed by rubbing in an oil without ZDDP can be replenished when the ZDDP is subsequently replenished. The oil was changed to base oil after 25 minutes of starting the test and the base oil was replaced again by a fresh ZDDP after 1hour of starting the test and the results are shown in Figure 9.



**Figure 9 Tribofilm thickness results for adding fresh ZDDP to the base oil**

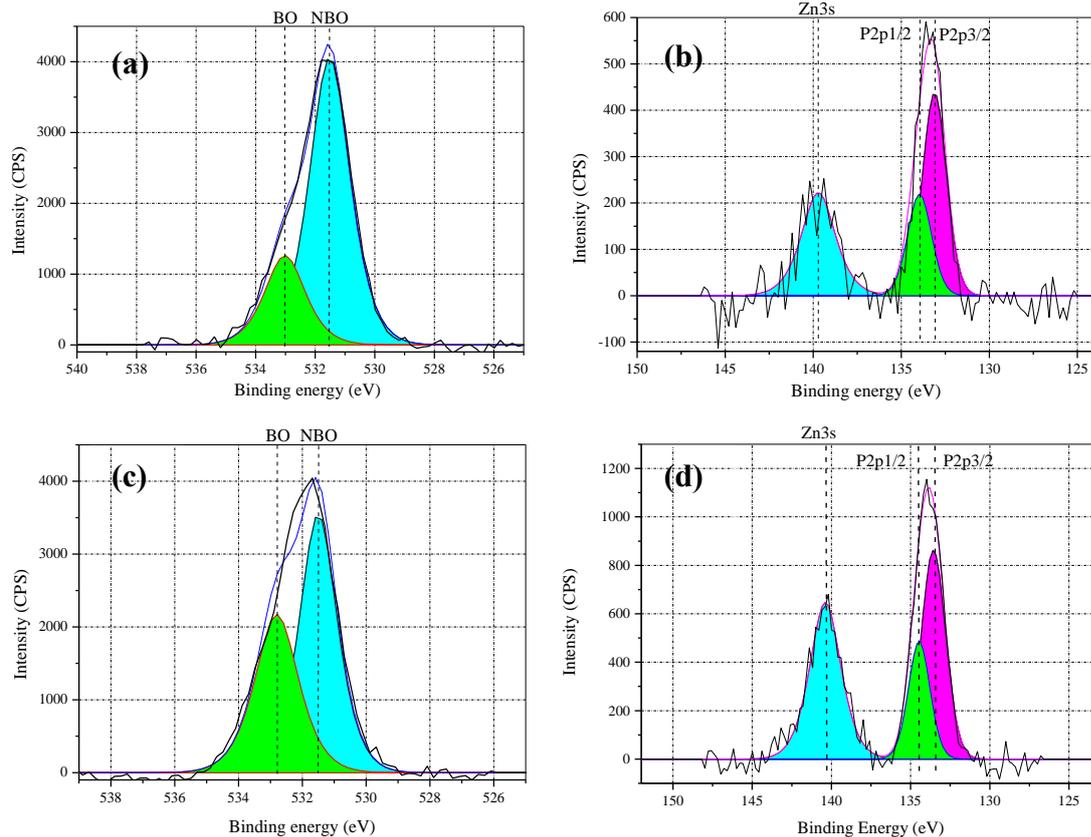
Results show that replacement of ZDDP in oil leads to continued growth of the tribofilm, the rate being slower than for a fresh clean surface. XPS analysis was carried out at different times of these experiments to correlate the chemistry of the tribofilm and the different layers.

### 3.1.3.1 Chemistry of the tribofilm

For the multi replacement experiments (Figure 9) in which the oil was replaced twice, XPS was carried out at the end of the experiment to compare it with the first test and the results are shown in Figure 10.

Results for BO/NBO ratio and binding energy difference between Zn3s and P2p are reported in Table 8 presented in the appendix. The value of BO/NBO ratio was 0.51 (metaphosphate) in case of ZDDP replaced by fresh ZDDP (point C<sub>1</sub> in Figure 5) and 0.62 (metaphosphate) when ZDDP changed with base oil and then replaced by fresh ZDDP again (C<sub>5</sub> in Figure 9). It has also been shown in the literature that unreacted ZDDP can be replenished in the contact areas and reform glassy polyphosphates [16]. The difference in the values of binding energy (eV) between Zn3s and P2p was 6.4 (point C<sub>1</sub> in Figure 5) and 6.32 (point C<sub>5</sub> in Figure 9), respectively. It can be interpreted from the values that longer chain polyphosphates are present in the tribofilm before exchanging the oil when the tribofilm is relatively thick. Once the oil is

exchanged and the tribofilm is partially removed, it is mainly consisting of shorter chain polyphosphates. It has been shown that the mechanical properties and chemistry of the ZDDP tribofilm varies from bulk to the surface [13, 16, 17, 24, 52]. This suggests that different chemistries can be correlated for mechanical properties of the film. Comparison between the two experiments shows that while the tribofilm forms again in the presence of the fresh ZDDP, more of longer chain polyphosphates are detected at the end of the experiment.



**Figure 10 XPS spectra for the tribofilm formed at the end of the test when (a) the oil was replaced by base oil O1s spectra (b) oil was replaced by base oil Zn3s, P2p spectra (Point C6 in Figure 9) (c) when the oil was replaced by base oil and then with ZDDP O1s spectra (d) when the oil was replaced by base oil and then with ZDDP Zn3s, P2p spectra (Point C5 in Figure 9)**

### 3.2 Effect of temperature

Temperature is reported to affect the tribological performance of ZDDP [53, 54]. To study the effect of temperature on the durability of the tribofilm, tribological tests were carried out with the same conditions to form the tribofilm on the surfaces. The tests were stopped after 25 minutes and the temperature was changed when the oil was replaced by base oil to see the

effect of temperature on the tribofilm durability. The tribofilm thickness was measured for four different temperatures after the suspension. Figure 11 demonstrates the tribofilm thickness measurements for different temperatures. It should be noted that the temperature is the same for all the tests before the suspension to form similar tribofilm and then it is changed at the time of the suspension. The amount of tribofilm removed at different temperatures in terms of the reduction in the thickness is reported in Figure 12. It can be seen that the removal of the tribofilm is changing with the oil bulk temperature. One would say these changes in the temperature can change the severity of the contact due to the effect of temperature on the viscosity of the oil. Smaller  $\lambda$  ratio for higher temperature might result in more tribofilm removal. For this reason,  $\lambda$  ratio was calculated for all four temperatures. It was observed that  $\lambda$  ratio varies between 0.03 and 0.06 for all these temperatures. All these conditions are severe and the ratio is small enough to be in boundary lubrication. Therefore the chemical properties of the tribofilms were analysed using XPS to see a correlation between the chemical characteristic of the film and the observed tribofilm durability.

Based on the results from Figure 11, there is a more prominent mechanism to support the fact that the higher temperature results in the higher reduction in the tribofilm thickness after changing the oil to base oil (oil B). Increasing the temperature can affect the mechanical properties of the tribofilm. Interpreting the results for different temperatures revealed that the higher temperatures could lead to a significant decrease in hardness of the tribofilm and therefore plastic flow of the tribofilm increases. Due to the lower hardness and higher plastic flow, more indentation occurs into the depth of the tribofilm and more tribofilm thickness reduction is observed. Results are in agreement with the previous study of the temperature effects on the mechanical properties of ZDDP [21, 55].

It should be noted that the stable thickness of the tribofilm at 120°C is larger than 140°C. The reason behind this is perhaps that the higher reduction in the thickness of the tribofilm results in re-entering more polyphosphates (removed tribofilm) to the interface which leads to higher concentration of such molecules hence reforming the tribofilm. For small drops in the thickness of the tribofilm (80°C and 100°C) there is no significant re-formation of the tribofilm due to the low concentration of polyphosphates (removed tribofilm) present in the oil. In addition, in the case of higher temperature (140°C), the re-formation of the tribofilm after removal is higher which can be attributed to the effect of higher temperature in inducing the chemical reaction. Interesting observation is the rate of tribofilm generation even at the absence of ZDDP additive

in the oil. Temperature is shown to affect not only the removal but also the rate of tribofilm regeneration. This needs further investigation to understand the mechanism.

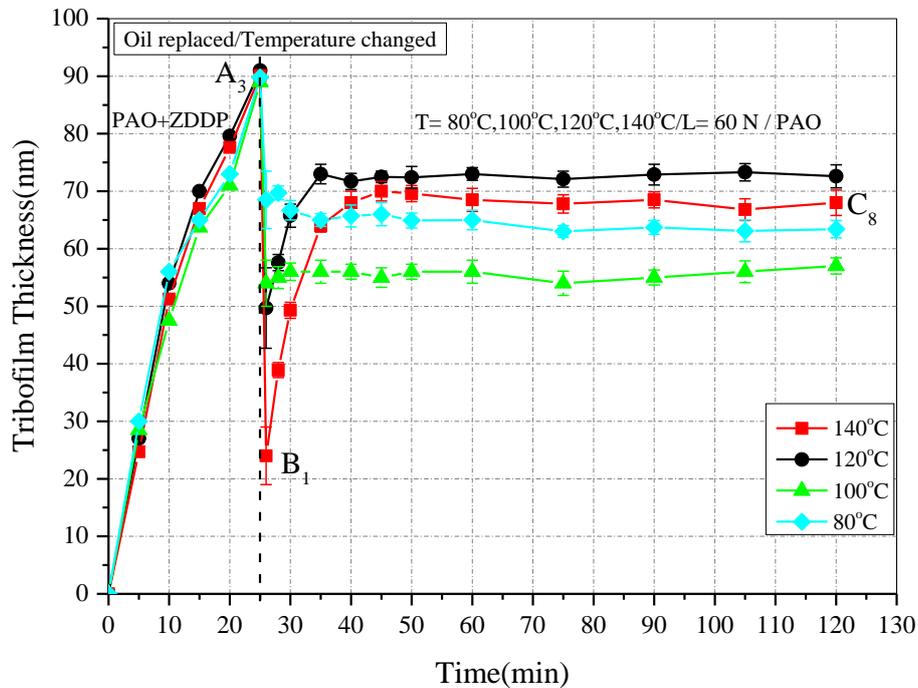
Based on the experimental results above, there is no clear pattern or regularity of the effect of temperature on the stable thickness of the tribofilm after replacing the oil which in fact is not the focus of the current study.

### 3.2.1 Chemistry of the tribofilm

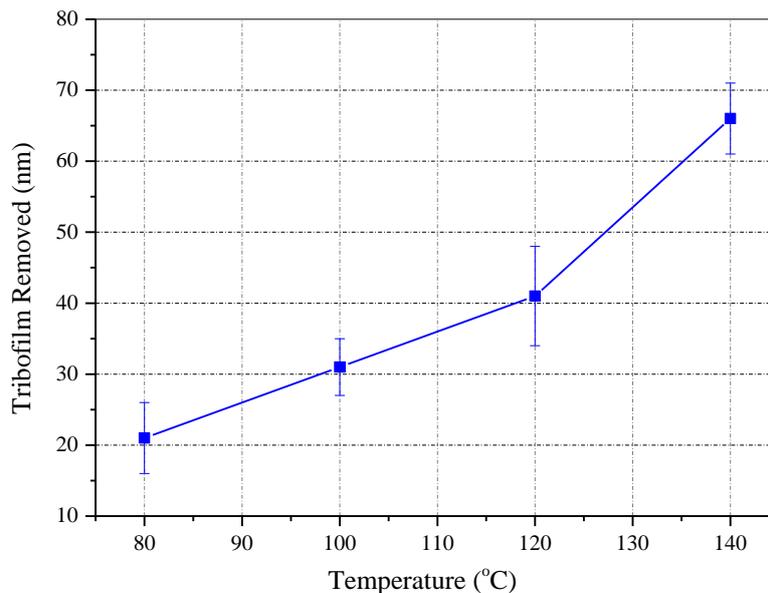
XPS is reported for the highest temperature for comparison reasons. The XPS was conducted before suspending the test, after 1 minute rubbing when the oil is changed and finally at the end of each experiment. The Oxygen and phosphorus peaks are reported in Figure 13 for three different points shown in Figure 11. The intensity ratio of BO to NBO is reported in Table 9 reported in the appendix as well as the binding energy difference for Zn3s and P2p. The results in Table 9 show that before suspending the test, the BO/NBO ratio is 0.47 (Point A3 in Figure 11) and the difference in binding energy for Zn3s and P2p is 6.57. This suggests that the tribofilm contains longer chain polyphosphates and mainly contains zinc metaphosphates [1, 24]. After the suspension of the test and once the oil is replaced, the softer top part of the tribofilm (consisting of long chain polyphosphates) is removed. This is also shown by XPS that the shorter chain polyphosphate (pyrophosphates) present in the tribofilm after the removal (Point B1 in Figure 11) (BO/NBO ratio of 0.19 and  $\Delta$  (Zn3s, P2p) of 6.76 eV). Once the tribofilm is again formed for the case of 140°C, longer chain polyphosphates are present in the tribofilm at the end of the experiments (Point C8 in Figure 11) where XPS analysis shows a BO/NBO ratio of 0.30 and binding energy difference of 6.70 eV for Zn3s and P2p (polyphosphate). The XPS results show that the top part of the tribofilm contains mainly the longer chain polyphosphates which can be removed easier than the shorter chain polyphosphates in the bulk of the tribofilm. The comparison between experiments for 80° C and 140° C shows that longer chain polyphosphates are present when tribofilm is removed in the case of 80° C compared to the 140° C. The removal of the tribofilm is more for the case of 140° C and XPS results confirm that shorter chain polyphosphates are present in depth of the tribofilm once it is removed. The difference between the binding energy for Zn3s and P2p also confirms the above mentioned observations (See Table 9 in the appendix).

The comparison between tribofilm growth results of Figure 11 suggests that increasing the temperature after replacing the oil results in more removal of the tribofilm. In addition XPS analysis results confirm that the top part of the tribofilm contains mainly longer chain

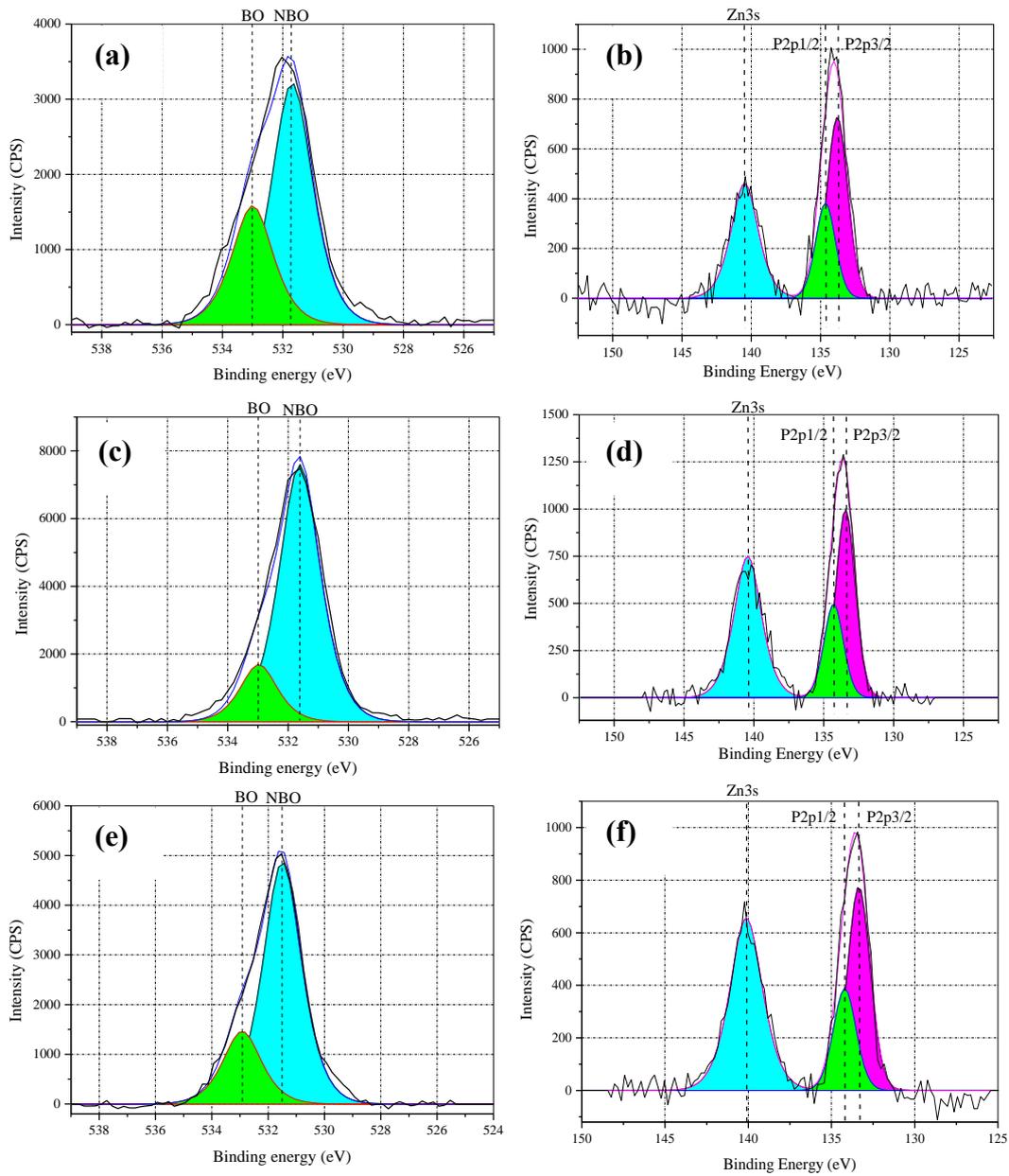
polyphosphates than the bulk [13, 16, 17, 24, 52]. It can be interpreted that higher temperature can result in changes in the structure of the tribofilm thus changing the mechanical properties of the glassy phosphates. The changes in the chemical and mechanical properties of the tribofilm due to changes in the temperature can be the reason for the different removal behaviour of the tribofilm.



**Figure 11 Tribofilm thickness results and removal behaviour for different temperatures after suspending the test**



**Figure 12 Tribofilm thickness reduction for different temperatures after one minute of rubbing when the oil is changed with base oil**



**Figure 13 XPS spectra for the tribofilm formed at 140°C**  
**(a) before suspending the test O 1s spectra (b) before suspending the test Zn3s, P2p spectra (Point A3 in Figure 11)**  
**(c) after suspending the test O 1s spectra (d) after suspending the test Zn3s, P2p spectra (Point B1 in Figure 11)**  
**(e) at the end of the test O 1s spectra (f) at the end of the test Zn3s, P2p spectra (Point C8 in Figure 11)**

### 3.3 Effect of load

One important parameter in the mechanical action of removing any material is the load applied on the surfaces. The load affects the penetration depth into the material and is responsible for the stress fields on the surface. Therefore it is reasonable to see the effect of load on the durability of the tribofilm. Similar to the experiments for the temperature, the tribological tests were conducted with the same conditions to form the tribofilm on the surfaces and the tests were stopped after 25 minutes. Four different loads were then applied after the suspension and images were taken after 1 minute of rubbing with the sequence of every 5 minutes. Figure 14 shows the results of the tribofilm thickness evolution for different loads. Higher load results in more thickness reduction of the tribofilm and this variation is plotted in Figure 15. Not surprisingly, reduction in thickness of the tribofilm is almost linear with the applied load. Similar to the temperature, variation of load may result in changes in the severity of the contact. For this purpose  $\lambda$  ratios have been calculated for all four loads and all the results are very close to 0.04. It shows that variation of loads from 30N to 75N does not change the severity of the contact significantly.

One important parameter in study of the boundary lubrication systems is the flash temperature due to the surface contacts. For this reason, flash temperature was calculated for different applied loads in this work (see Figure 16). According to Kennedy et al [56], flash temperature can be calculated from Equation 2.

$$\Delta T_{max} \approx \frac{2Qb}{K\sqrt{\pi(1+Pe)}} \approx \frac{1.122Qb}{K} \quad (2)$$

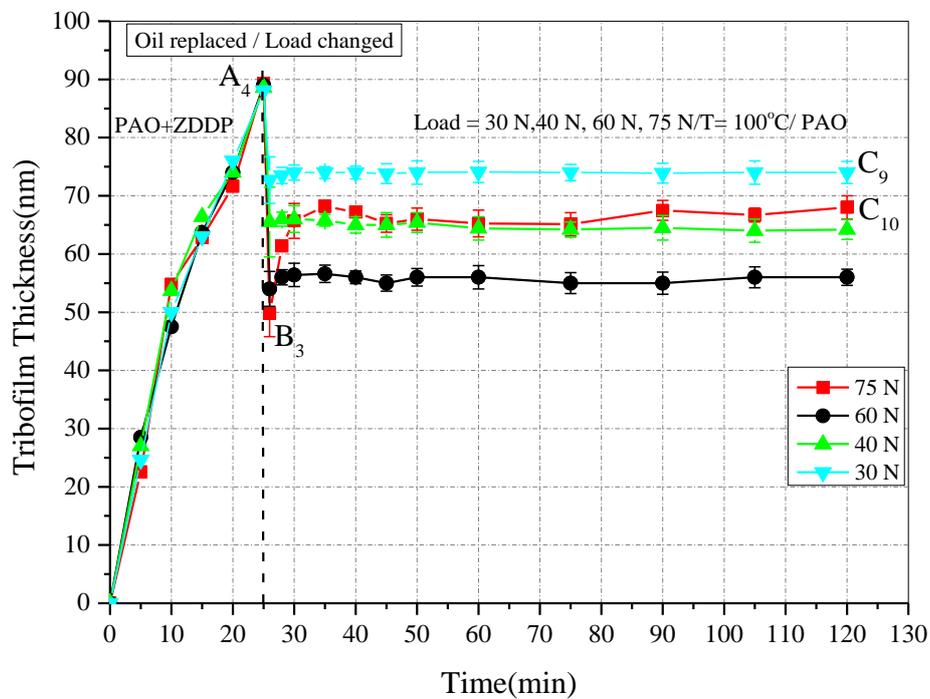
where  $b$  is the width of the contact and  $K = \frac{k}{\rho C}$  is the thermal diffusivity ( $k$  is the thermal conductivity,  $\rho$  is the density and  $C$  is the specific heat).  $Pe$  is the Peclet number.  $Q$  is the frictional heating [57] at the contact interface and is calculated from Equation 3.

$$Q = \mu PV \quad (3)$$

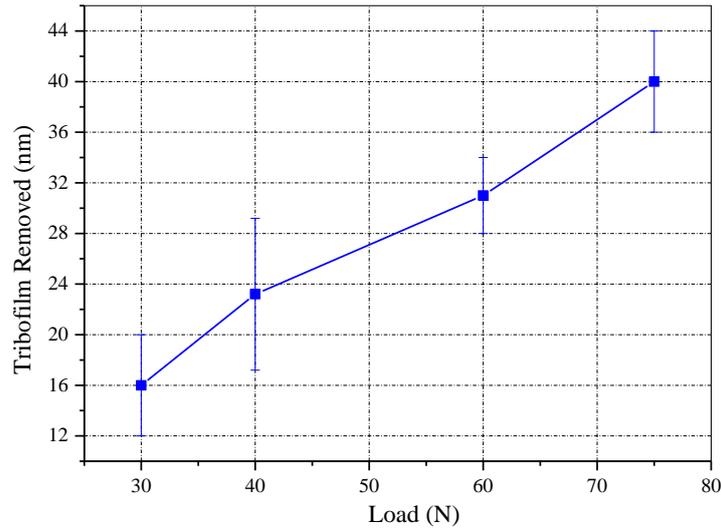
In which  $\mu$ ,  $P$  and  $V$  are the coefficient of friction, contact pressure and the relative sliding speed between surfaces respectively. Results showed that flash temperature is not significantly increased by load. This is because of the slight difference in the Hertzian contact pressure on the surfaces. The maximum contact pressure is calculated to be 1 GPa and 1.3 GPa for the loads of 30N and 75 N respectively. These pressures result in the flash temperature rise of around 12°C-14°C. This suggests that the changes in thickness due to the different applied load is not

because of variation of the flash temperature at these loads. For further investigations, the shear stress was calculated for different loads and is plotted in Figure 16. Higher loads lead to the higher shear stress in both substrate and tribofilm and it can affect the material removal of the tribofilm. It is also shown by Archard [58] that that the material removal is proportional to the real area of contact and load.

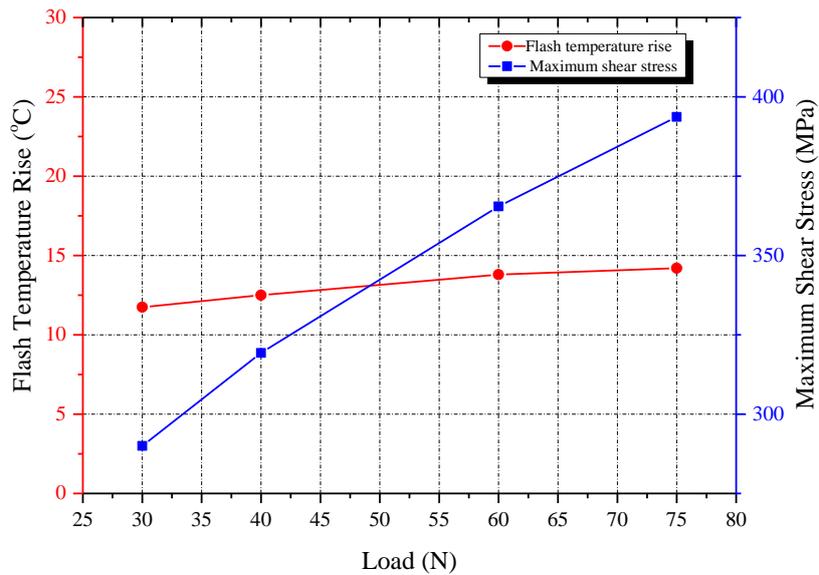
Very similar to the effect of temperature, if the amount of tribofilm thickness reduction is high (for example at 75 N) there would be more polyphosphates (removed tribofilm) re-entering the interface which leads to higher concentration of such molecules hence increasing the reaction rate. In this case, there is not also any clear pattern for the effect of load on the steady-state tribofilm thickness after replacing the oil.



**Figure 14 tribofilm thickness results and removal behaviour for different loads after suspending the test**



**Figure 15 Tribofilm thickness reduction for different loads after one minute of rubbing when the oil is changed with base oil**



**Figure 16 Effect of load on the flash temperature rise and the maximum shear stress on the surfaces**

### 3.3.1 Chemistry of the tribofilm

Analyses were carried out at three different times on the samples to see the change of the chemical structure of the tribofilm and the effect of load on its variations. The intensity ratio of BO to NBO as well as the difference between Zn3s and P2p are reported in Table 10 (see the appendix) for different positions of Figure 14. The results show that BO/NBO is 0.47 and the binding energy difference for Zn3s and P2p is 6.57 eV before suspending the oil (Point A4

in Figure 14), therefore longer chain polyphosphates (metaphosphates) are present in the tribofilm. BO/NBO ratio is 0.29 (Point B<sub>3</sub> in Figure 14) and the binding energy difference for Zn3s and P2p is 6.6 which suggest that the shorter chains (pyrophosphates) are present after the removal of the top layer of the tribofilm when the oil is replaced with base oil. The chain length at the end of the experiments is almost the same as the chain length after the removal process.

The comparison between high load and low load suggests that when the tribofilm is more removed for the case of higher load, there are shorter chain polyphosphates present in its bulk after the removal. Therefore higher load is able to remove more durable glassy phosphates in the bulk of the tribofilm and this behaviour is very similar to the temperature effect on the removal of the tribofilm. For the temperature, it is more reasonable that temperature changes the structure of the tribofilm therefore changing its durability and removal behaviour. On the other hand higher load results in more shear stress applied on the tribofilm which can lead to more removal of the film.

#### **4 Conclusions**

A methodology for studying the mechanical and chemical aspects of the durability of the tribofilm derived from ZDDP antiwear additive is reported for the first time in this work. The following conclusions can be drawn:

- The dynamic growth of the tribofilm on the contacting asperities is important for the antiwear mechanism of ZDDP on steel surfaces.
- The experiments suggest that chemical characteristics and durability of ZDDP tribofilm evolves in time. The results from XPS confirm that longer chain polyphosphates convert to shorter chains when rubbing occurs and tribofilm changes its structure. These changes in the structure are responsible for the increase in the durability of the tribofilm. When the oil was replaced at 25 minutes, the tribofilm mainly consisted of metaphosphates while the structure moved towards containing more pyrophosphates after 3 hrs.
- ZDDP tribofilm is less durable in the early stages of tribofilm formation. The durability of the ZDDP tribofilm is different at different stages of tribofilm evolution.
- Physical parameters such as temperature and load significantly affect the resistance of the film to the mechanical rubbing.

- It was observed that temperature can significantly affect the structure of the glassy polyphosphates in a way that the same applied load can remove more glassy polyphosphates at higher temperature. The structure of the ZDDP tribofilm evaluated by XPS shows that shorter chain polyphosphates (pyrophosphates) are found on the tribofilm when a high amount of tribofilm thickness reduction occurred. In contrast, relatively longer chain polyphosphates were found when the applied temperature was low and a relatively lower amount of tribofilm was removed.
- Variations in the temperature in this study affect the viscosity of the oil but the calculations of the severity of the contact and  $\lambda$  ratio is not significant.
- Higher lubricant temperature changes the structure of the glassy polyphosphates which results in higher tribofilm removal once tested in base oil. This observation was supported by XPS and different chain lengths of polyphosphates were found at different depths of the tribofilm.
- Not surprisingly, higher load results in higher tribofilm thickness reduction and this variation is almost linear. The flash temperature was calculated for different applied loads. It was found that the flash temperature is not varying significantly by the applied load due to the small differences in the maximum Hertzian contact pressures.

## **Acknowledgment**

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## 5 Appendix

**Table 7 BO/NBO ratio. Tribofilm thickness at points C<sub>4</sub> and C<sub>3</sub> is shown in Figure 7.**

Test	ZDDP changed with base oil	Without changing the oil
	at 3 hrs	
	End of the test (Point C <sub>4</sub> )	End of the test (Point C <sub>3</sub> )
<b>BO/NBO ratio</b>	0.21	0.23
<b>Zn3s – P2p binding energy difference (eV)</b>	6.97	6.92

**Table 8 BO/NBO ratios and the difference between Zn3s and P2p peaks. Tribofilm thickness at points A<sub>2</sub>, C<sub>5</sub> and C<sub>6</sub> is shown in Figure 9.**

Test	Both tests	ZDDP changed with base oil	ZDDP changed with base oil and then changed with fresh ZDDP
	Before changing the oil (Point A <sub>2</sub> )	End of the test (Point C <sub>6</sub> )	End of the test (Point C <sub>5</sub> )
<b>BO/NBO ratio</b>	0.47	0.31	0.62
<b>Zn3s – P2p binding energy difference (eV)</b>	6.57	6.70	6.32

**Table 9 BO/NBO ratios and the difference between Zn3s and P2p peaks. Tribofilm thickness at points A<sub>3</sub>, B<sub>1</sub> and C<sub>8</sub> is shown in Figure 11.**

Test	140°C		
	Before suspension (Point A <sub>3</sub> )	After suspension (Point B <sub>1</sub> )	End of the test (Point C <sub>8</sub> )
<b>BO/NBO ratio</b>	0.47	0.19	0.30
<b>Zn3s – P2p binding energy difference (eV)</b>	6.57	6.76	6.70

**Table 10 BO/NBO ratios and the difference between Zn3s and P2p peaks. Tribofilm thickness at points A<sub>4</sub>, B<sub>3</sub>, C<sub>9</sub> and C<sub>10</sub> is shown in Figure 14.**

Test	75 N		30 N	
	Before suspension (Point A <sub>4</sub> )	After suspension (Point B <sub>3</sub> )	End of the test (Point C <sub>10</sub> )	End of the test (Point C <sub>9</sub> )
<b>BO/NBO ratio</b>	0.47	0.29	0.27	0.45
<b>Zn3s – P2p binding energy difference (eV)</b>	6.57	6.6	6.58	6.54

## References

- [1] M. Crobu, A. Rossi, F. Mangolini, N.D. Spencer, Chain-length-identification strategy in zinc polyphosphate glasses by means of XPS and ToF-SIMS, *Analytical and bioanalytical chemistry*, 403 (2012) 1415-1432.
- [2] L.R. Rudnick, *Lubricant additives: chemistry and applications*, CRC Press, 2009.
- [3] H. Spikes, The history and mechanisms of ZDDP, *Tribology Letters*, 17 (2004) 469-489.
- [4] B. Dacre, C. Bovington, The adsorption and desorption of zinc di-isopropylidithiophosphate on steel, *ASLE TRANSACTIONS*, 25 (1982) 546-554.
- [5] F.M. Piras, A. Rossi, N.D. Spencer, Combined in situ (ATR FT-IR) and ex situ (XPS) study of the ZnDTP-iron surface interaction, *Tribology Letters*, 15 (2003) 181-191.
- [6] M.L.S. Fuller, M. Kasrai, G.M. Bancroft, K. Fyfe, K.H. Tan, Solution decomposition of zinc dialkyl dithiophosphate and its effect on antiwear and thermal film formation studied by X-ray absorption spectroscopy, *Tribology international*, 31 (1998) 627-644.
- [7] M. Fuller, Z. Yin, M. Kasrai, G.M. Bancroft, E.S. Yamaguchi, P.R. Ryason, P.A. Willermet, K.H. Tan, Chemical characterization of tribocoochemical and thermal films generated from neutral and basic ZDDPs using X-ray absorption spectroscopy, *Tribology International*, 30 (1997) 305-315.
- [8] E. Loeser, R. Wiquist, S. Twiss, Cam and tappet lubrication III—radioactive study of phosphorus in the EP film, *ASLE Transactions*, 1 (1958) 329-335.
- [9] H. Fujita, H. Spikes, The formation of zinc dithiophosphate antiwear films, *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology*, 218 (2004) 265-278.
- [10] L. Taylor, A. Dratva, H. Spikes, Friction and wear behavior of zinc dialkylidithiophosphate additive, *Tribology transactions*, 43 (2000) 469-479.
- [11] J. Palacios, Thickness and chemical composition of films formed by antimony dithiocarbamate and zinc dithiophosphate, *Tribology international*, 19 (1986) 35-39.
- [12] M.S. Fuller, L.R. Fernandez, G. Massoumi, W. Lennard, M. Kasrai, G. Bancroft, The use of X-ray absorption spectroscopy for monitoring the thickness of antiwear films from ZDDP, *Tribology Letters*, 8 (2000) 187-192.
- [13] M. Aktary, M.T. McDermott, G.A. McAlpine, Morphology and nanomechanical properties of ZDDP antiwear films as a function of tribological contact time, *Tribology letters*, 12 (2002) 155-162.
- [14] S. Bec, A. Tonck, J. M. Georges, R. C. Coy, J.C. Bell, G.W. Roper, Relationship between mechanical properties and structures of zinc dithiophosphate anti-wear films, *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Science*, 445 (1999) 4181-4203.
- [15] R.M. Gabi Nehme, Pranesh B. Aswath,, Effect of contact load and lubricant volume on the properties of tribofilms formed under boundary lubrication in a fully formulated oil under extreme load conditions, *Wear*, 268 (2010) 1129-1147.
- [16] M.A. Nicholls, P.R. Nortona, G.M. Bancroft, M. Kasrai, T. Dob, B.H. Frazerc, G.D. Stasio, Nanometer scale chemomechanical characterization of antiwear films, *Tribology Letters*, 17 (2004) 205-216.
- [17] M.A. Nicholls, T. Do, P.R. Norton, M. Kasrai, G.M. Bancroft, Review of the lubrication of metallic surfaces by zinc dialkyl-dithiophosphates, *Tribology international*, 38 (2005) 15-39.
- [18] A.L. G. Pereira, M.A. Nicholls, M. Kasrai, P.R. Norton, and G. De Stasio, Chemical characterization and nanomechanical properties of antiwear films fabricated from ZDDP on a near hypereutectic Al-Si alloy, *Tribology Letters*, 18 (2005) 411-427.
- [19] P.A. Ramoun Mourhatch, Tribological behavior and nature of tribofilms generated from fluorinated ZDDP in comparison to ZDDP under extreme pressure conditions—Part II: Morphology and nanoscale properties of tribofilms, *tribology international*, 44 (2011) 201-210.
- [20] N.J. Mosey, T.K. Woo, M. Kasrai, P.R. Norton, G.M. Bancroft, M.H. Muser, Interpretation of experiments on ZDDP anti-wear films through pressure-induced cross-linking, *Tribology Letters*, 24 (2006) 105-114.
- [21] K. Demmou, S. Bec, J.-L. Loubet, J.-M. Martin, Temperature effects on mechanical properties of zinc dithiophosphate tribofilms, *Tribology international*, 39 (2006) 1558-1563.

- [22] A. Morina, A. Neville, Tribofilms: aspects of formation, stability and removal, *Journal of Physics D: Applied Physics*, 40 (2007) 54-76.
- [23] Y. Lin, H. So, Limitations on use of ZDDP as an antiwear additive in boundary lubrication, *Tribology International*, 37 (2004) 25-33.
- [24] M. Crobu, A. Rossi, F. Mangolini, N.D. Spencer, *Tribochemistry of bulk zinc metaphosphate glasses*, *Tribology letters*, 39 (2010) 121-134.
- [25] Z. Yin, M. Kasrai, M. Fuller, G.M. Bancroft, K. Fyfe, K.H. Tan, Application of soft X-ray absorption spectroscopy in chemical characterization of antiwear films generated by ZDDP Part I: the effects of physical parameters, *Wear*, 202 (1997) 172-191.
- [26] J.M. Martin, C. Grossiord, T. Le Mogne, S. Bec, A. Tonck, The two-layer structure of Zn<sub>2</sub>P tribofilms: Part I: AES, XPS and XANES analyses, *Tribology international*, 34 (2001) 523-530.
- [27] A. Naveira-Suarez, A. Tomala, R. Pasaribu, R. Larsson, I.C. Gebeshuber, Evolution of ZDDP-derived reaction layer morphology with rubbing time, *Scanning*, 32 (2010) 294-303.
- [28] A.N. Suárez, *The Behaviour of Antiwear Additives in Lubricated Rolling-Sliding Contacts*, Luleå University of Technology, 2011.
- [29] S. Gonsel, H.A. Spikes, M. Aderin, In-Situ Measurement of ZDDP Films in Concentrated Contacts, *Tribology transactions*, 36 (1993) 276-282.
- [30] L. Taylor, H. Spikes, Friction-enhancing properties of ZDDP antiwear additive: part I—friction and morphology of ZDDP reaction films, *Tribology transactions*, 46 (2003) 303-309.
- [31] Z. Zhang, E.S. Yamaguchi, M. Kasrai, G.M. Bancroft, Tribofilms generated from ZDDP and DDP on steel surfaces: Part 1, growth, wear and morphology, *Tribology Letters*, 19 (2005) 211-220.
- [32] H. Fujita, R. Glovnea, H. Spikes, Study of zinc dialkyldithiophosphate antiwear film formation and removal processes, part I: Experimental, *Tribology transactions*, 48 (2005) 558-566.
- [33] H. FUJITA, H.A. SPIKES, Study of Zinc Dialkyldithiophosphate Antiwear Film Formation and Removal Processes, Part II: Kinetic Model, *Tribology transactions*, 48 (2007) 567-575.
- [34] N. Gosvami, J. Bares, F. Mangolini, A. Konicek, D. Yablon, R. Carpick, Mechanisms of antiwear tribofilm growth revealed in situ by single-asperity sliding contacts, *Science*, 348 (2015) 102-106.
- [35] A. Ghanbarzadeh, M. Wilson, A. Morina, D. Dowson, A. Neville, Development of a new mechano-chemical model in boundary lubrication, *Tribology International*, 93 (2016) 573-582.
- [36] J.S. McQueen, H. Gao, E.D. Black, A.K. Gangopadhyay, R.K. Jensen, Friction and wear of tribofilms formed by zinc dialkyl dithiophosphate antiwear additive in low viscosity engine oils, *Tribology International*, 38 (2005) 289-297.
- [37] A. Ghanbarzadeh, P. Parsaeian, A. Morina, M.C. Wilson, M.C. van Eijk, I. Nedelcu, D. Dowson, A. Neville, A Semi-deterministic Wear Model Considering the Effect of Zinc Dialkyl Dithiophosphate Tribofilm, *Tribology Letters*, 61 (2016) 1-15.
- [38] P. Parsaeian, A. Ghanbarzadeh, M. Wilson, M.C. Van Eijk, I. Nedelcu, D. Dowson, A. Neville, A. Morina, An experimental and analytical study of the effect of water and its tribochemistry on the tribocorrosive wear of boundary lubricated systems with ZDDP-containing oil, *Wear*, 358 (2016) 23-31.
- [39] J. Benedet, J.H. Green, G.D. Lamb, H.A. Spikes, Spurious mild wear measurement using white light interference microscopy in the presence of antiwear films, *Tribology Transactions*, 52 (2009) 841-846.
- [40] H. Spikes, P. Cann, The development and application of the spacer layer imaging method for measuring lubricant film thickness, *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology*, 215 (2001) 261-277.
- [41] H. Cen, *Effect of water on the performance of lubricants and related tribochemistry in boundary lubricated steel/steel contacts*, University of Leeds, 2012.
- [42] R. Brückner, H.-U. Chun, H. Goretzki, M. Sammet, XPS measurements and structural aspects of silicate and phosphate glasses, *Journal of Non-Crystalline Solids*, 42 (1980) 49-60.
- [43] R.K. Brow, An XPS study of oxygen bonding in zinc phosphate and zinc borophosphate glasses, *Journal of non-crystalline solids*, 194 (1996) 267-273.

- [44] E. Onyiriuka, Zinc phosphate glass surfaces studied by XPS, *Journal of non-crystalline solids*, 163 (1993) 268-273.
- [45] B.M. Smets, D. Krol, Group III ions in sodium silicate glass. Part. 1. X-Ray Photoelectron spectroscopy study, *Physics and chemistry of glasses*, 25 (1984) 113-118.
- [46] H. Liu, T. Chin, S. Yung, FTIR and XPS studies of low-melting PbO-ZnO-P<sub>2</sub>O<sub>5</sub> glasses, *Materials chemistry and physics*, 50 (1997) 1-10.
- [47] P. Shih, S. Yung, T. Chin, FTIR and XPS studies of P<sub>2</sub>O<sub>5</sub>-Na<sub>2</sub>O-CuO glasses, *Journal of non-crystalline solids*, 244 (1999) 211-222.
- [48] E. Khawaja, S. Durrani, F. Al-Adel, M. Salim, M.S. Hussain, X-ray photoelectron spectroscopy and Fourier transform-infrared studies of transition metal phosphate glasses, *Journal of materials science*, 30 (1995) 225-234.
- [49] M. Salim, G. Khattak, P. Fodor, L. Wenger, X-ray photoelectron spectroscopy (XPS) and magnetization studies of iron-vanadium phosphate glasses, *Journal of non-crystalline solids*, 289 (2001) 185-195.
- [50] A. Flambard, J.-J. Videau, L. Delevoye, T. Cardinal, C. Labrugère, C. Rivero, M. Couzi, L. Montagne, Structure and nonlinear optical properties of sodium-niobium phosphate glasses, *Journal of Non-Crystalline Solids*, 354 (2008) 3540-3547.
- [51] G. Canning, M.S. Fuller, G. Bancroft, M. Kasraj, J. Cutler, G. De Stasio, B. Gilbert, Spectromicroscopy of tribological films from engine oil additives. Part I. Films from ZDDP's, *Tribology letters*, 6 (1999) 159-169.
- [52] J.F. Graham, C. McCague, P.R. Norton, Topography and nanomechanical properties of tribochemical films derived from zinc dialkyl and diaryl dithiophosphates, *Tribology Letters*, 6 (1999) 149-157.
- [53] H. So, Y. Lin, The theory of antiwear for ZDDP at elevated temperature in boundary lubrication condition, *Wear*, 177 (1994) 105-115.
- [54] A Morina, A Neville, M Priest, J.H. Green, ZDDP and MoDTC interactions in boundary lubrication The effect of temperature and ZDDP MoDTC ratio, *Tribology international*, 39 (2006) 1545-1557.
- [55] A.K. Landauer, W.C. Barnhill, J. Qu, Correlating mechanical properties and anti-wear performance of tribofilms formed by ionic liquids, ZDDP and their combinations, *Wear*, 354 (2016) 78-82.
- [56] F. Kennedy, Frictional heating and contact temperatures, *Modern tribology handbook*, 1 (2001) 235-259.
- [57] H. Blok, The flash temperature concept, *Wear*, 6 (1963) 483-494.
- [58] J. Archard, Contact and rubbing of flat surfaces, *Journal of applied physics*, 24 (1953) 981-988.