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Effect of base oil polarity on the micropitting behaviour in rolling-sliding contacts

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Abstract

An automated micropitting test rig which uses the proven three point contact configuration was applied to study the effect of base oil polarity on micropitting behaviour in rolling-sliding contacts. The tribological tests using one polar (Ester) and one non-polar (PAO) base oil mixed with four different additives were firstly done in a micropitting rig to study the friction, wear and micropitting performance. The tested specimen after tribological tests were examined by an optical microscope to study the micropitting on the surface. The X-ray Photoelectron Spectroscopy (XPS) was applied to obtain the related tribochemical information from the reaction layer. The results showed that higher wear and less micropits formed when testing with Ester based lubricants. This was related to the higher affinity to the steel surface of polar base oil molecules which can compete with additives to attach to the surface, resulting in a thinner reaction layer and shorter chain phosphates.

Key words: Base oil polarity; Wear; XPS; Reaction layer thickness; Phosphate chain length

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1. Introduction

Micropitting is a commonly seen surface failure in machine elements (e.g. rolling element bearings) which work under heavy loading and rolling-sliding lubricated conditions. This phenomenon is acknowledged to be affected by material, surface roughness, lubricant, load, temperature, speed and slide to roll ratio (SRR). Oila et al. [1] studied these parameters and pointed out that load affected the initiation of micropitting most, while speed and slide to roll ratio showed the largest impact on the propagation of micropitting. The asperity contact stress was also considered to be a main factor to promote the formation of micropits [1], thus this contact fatigue phenomenon can be retarded by the increase of lambda ratio or reduce of surface roughness. However, recently Soltanahmadi et al. [2-3] found out that more micropits formed with enhanced reaction layer thickness between the contacting surfaces.

Several studies have focused on the relationship between friction/wear coefficient and micropitting [1,4-7]. The reduction of frictional tractions during rolling/sliding can have an effect on reducing micropitting, mainly through reduced frictional heating [1]. However, Maya-Johnson et al. [4] reported that the addition of a friction modifier (a commercial friction modifier based on synthetic oils) into the lubricated contacts would in fact accelerate the rolling contact fatigue. Morales-Espejel et al. [5] summarized the relationship between wear and micropitting as follows: micropitting phenomenon was worsen with decreasing reaction layer thickness and increasing sliding once the wear was negligible, while micropitting area was reduced once the wear cannot be ignored as the rolling sliding contacts can be dominated by wear which was able to remove the asperity peaks and reduce the contact asperity. Brizmer et al. [6] researched the micropitting performance of different base oil/additives combinations in lubricated rolling contacts, and concluded that the micropitting phenomenon can be predicted by focusing on friction and wear performance although tribochemistry was expected to be the main impacting factor. A recent study by the authors [7] showed that the degree of micropitting cannot be evaluated only by friction and wear performance, and that the combination effect of wear and reaction layer thickness as well as chemical reaction products (e.g. iron oxide) in the layer should be considered.

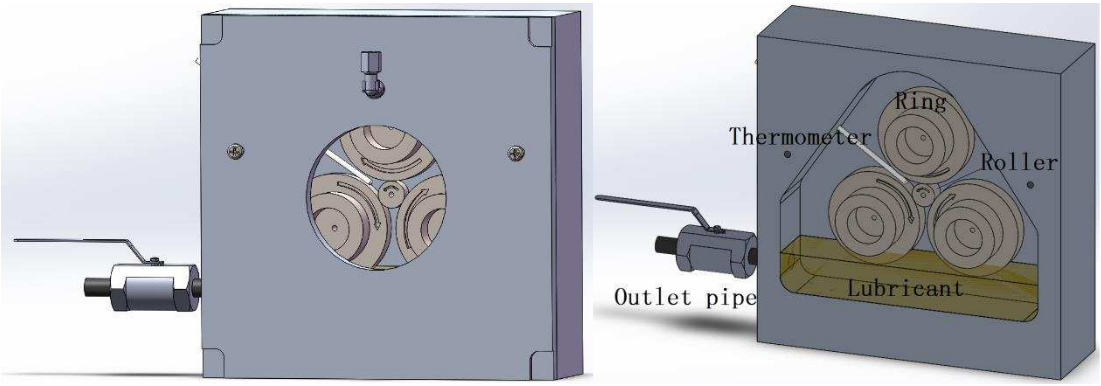
All the parameters mentioned above can change the physical properties of the contacting surfaces as well as the chemical nature of the system making an impact on the micropitting formation process. Base oil polarity is one of the least studied parameters on micropitting. However, commercial lubricants with base oils of different polarity can have different micropitting mechanisms. Naveira-Suarez et al. [8-9] studied the influence of base oil polarity on the tribological performance and derived reaction layer by testing base oil with different polarities blended with zinc dialkyl dithiophosphate (ZDDP) under mixed rolling-sliding conditions. They found that the derived reaction layer was thicker when ZDDP was blended with non-polar base oil, which was because that polar base oil molecules were more prone to attach to the contacting surface than the non-polar base oil molecules [8]. Base oil can then compete with the additive molecules to attach to the substrate, which would change the tribochemistry during the rubbing process. They came to a conclusion that base oil polarity should be considered to describe the base oil-additive interactions to study the tribological and tribochemical behaviours within the rolling-sliding contacts [9]. Naveira-Suarez et al. [8-9] and Jablonka et al. [10] reported that the reaction layer thickness can be affected by base oil polarity, but this was not related to the micropitting behaviour. In this study, one polar (Ester) and one non-polar (PAO) base oil mixed with four surface-active additives were tested in a micropitting rig to study the effect of base oil polarity on micropitting in the rolling-sliding contacts.

2. Experimental

2.1 Micopitting rig

The micropitting test rig in this study can be used under controlled slide-to-roll ratio, temperature, load, speed and different lubrication conditions. A detailed information on the micropitting test rig applied in this study has been provided in a previous paper by Cen et al. [7]. The overall appearance of the rig is shown in Fig. 1. A syringe was applied to fill the tested lubricants into the test chamber up to the level of ¼ of the bottom ring. Through the rotation of the bottom two rings, the lubricants can be dragged to the contacts between the centre roller and three surrounding rings. Load was applied onto the top ring and distributed into three contact loads. The roller and rings can be finished by grinding to desired roughness. A strain gauge located on the shaft which is connected to the top ring was used to measure the friction in the lubricated conditions. Friction signal was recorded during the test and the average value of last 30 minutes (when the signal was really stable) was considered as the friction coefficient of the test. An example of the recorded friction coeffient is shown in Fig. 2 where the average value of 630-770 K cycles (the last 30 minutes of the test, after 770 K cycles the data was recorded when the system started to unload and speed down).

The depth profile of the wear scar on the tested roller was obtained through Bruker's NPFLEX Wyko technology, based on which the cross-section area of the wear scar can be calculated, and the whole wear volume equalled to the perimeter of the roller multiplies by the cross-section area (assuming the cross-section area was the same across the circumference of the roller wear scar). For each wear volume of the roller, three depth profiles were obtained by Wyko measurement and the average value was used to calculate the wear volume. Before the wear measurement, the residual lubricant on the roller was removed by ultrasonic cleaning with acetone for 30 minutes. Details of the friction and wear acquisition process were shown in a previous paper by Cen et al. [7].



(a) (b)

Fig. 1. Micropitting rig: (a) chamber door closed for test; (b) chamber door open for illustration.

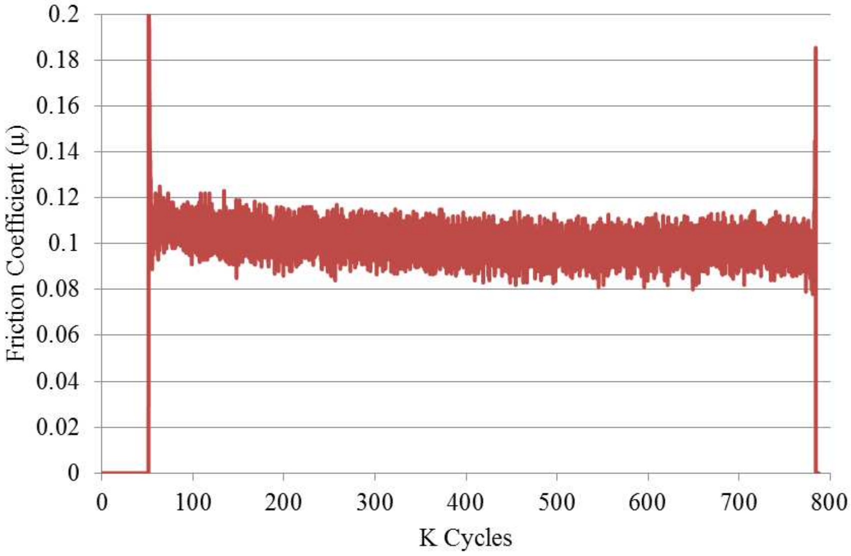


Fig. 2. An example of the recorded friction coeffient during the test

2.2 Materials and test conditions

The roller and three identical rings are disassembled from SKF bearings. Information of the roller and rings applied in this study are shown in Table 1.

Table 1. Details of roller & rings used in the tests

	Bearing code	Diameter (mm)	Roughness (Rq nm)-transverse to the rolling direction	Material (Steel code)	Hardness (HRC)
Roller	SKF SRB 21309E	12.05	<50	AISI 52100	59-66
Ring	SKF CRB NU 209EC	54.15	500±10		

The lubricants used in this study are composed of one polar base oil (Ester) and one non-polar base oil (PAO) as well as four additives which are ZDDP, S, P and Moly. Details of the base oil and additives are shown in Table 2. The ZDDP additive used in this research was solid powder thus the viscosity could not be obtained. The S, P additive did not contain phosphorus and sulphur respectively. The Moly additive contained neither phosphorus and sulphur content. The base oils and additives were all provided by SKF ERC, Netherlands and information other than the parameters in Table 2 were confidential from the supplier. Only one base oil (98wt%) and one additive (2wt%) were mixed together to get different test lubricants (wt%—the mass percentage of base oil, additive over the lubricant mixture). The mixture was obtained by in a glass beaker with a magnetic stirrer for 2 hours at 75°C just before the micropitting tests. The mixtures were observed to be clear and with no deposits, which was considered that the additives were totally dissolved in the base oil. The micropitting test conditions [7] are shown in Table 3, where the conditions were set to simulate the industrial working condition of rolling element bearings. Each test consisted of 720,000 contacting cycles which was 2.5 hours in total and the friction and wear results were the mean values of three repeats. Lambda ratio (λ) which can be used to identify the lubrication regime, is the ratio of minimum reaction layer thickness over the square root of the summation of square roughness of the two contacting surfaces (Eq.1).

$$\lambda = \frac{h_{min}}{\sqrt{R_{q,a}^2 + R_{q,b}^2}} \qquad \text{Eq. 1}$$

where $R_{q,a}$ and $R_{q,b}$ represent the average roller roughness and average roughness of the three rings, respectively. The initial lambda ratio λ of the test was 0.16 which indicated a boundary lubrication regime which was the most common seen lubricating condition for heavy loaded bearings. Initial contact pressure P_{max} was calculated from Hertzian initial line contact equation. The minimum reaction layer thickness h_{min} was obtained by applying Dowson and Higginson equation (Eq.2) [7].

$$\frac{h_{min}}{R} = 2.65 \times (2\alpha E')^{0.54} \times \left(\frac{U_e \eta_0}{2E'R}\right)^{0.7} \times \left(\frac{W}{2E'RL}\right)^{-0.13} \qquad \text{Eq.2}$$

where h_{min} is minimum reaction layer thickness, R is effective radius of curvature, α is the pressure–viscosity constant of the lubricant, E' is the effective modulus of elasticity, U_e is the entrainment speed, η_0 is the dynamic viscosity of the lubricant, W is the applied load, and L is contacting length.

Table 2. Details of base oils & additives used in the tests

Base Oil & Additive		Kinematic viscosity at 40°C (mm^2/s)	Kinematic viscosity at 100°C (mm^2/s)	Sulphur content (wt%)	Phosphorus content (wt%)
Description	Designation				
Fully synthetic Group IV	PAO	24.6	5.1	0.00055	<0.00030
Synthetic ester	Ester	26.8	5.2	0.00052	<0.00030
Iso-butyl-zinc dithiophosphate	ZDDP	-	-	23.400	11.300
Sulphurized fatty acid methylester	S	260±20	-	16±1	-
Phosphoric acid ester	P	180±20	-	-	13±1
Molybdenum Ester	Moly	280±20	-	-	-

Table 3. Test conditions

P_{max} (GPa)	Temperature (°C)	SRR（%）	Entrainment speed (m/s)	lambda ratio (λ)	N, K Cycles
1.5	75	2	1	0.16	720 (2.5hours)

2.3 Surface analysis techniques

The roller surface images after tribological tests were firstly captured by a Leica stereo microscope to examine the micropitting level. The residual oil on the roller surface was gently removed by a tissue with isopropanol before the capture. Then, XPS measurements were carried out on the roller surface in a PHI 5000 VersaProbe^{TM} X-ray photoelectron spectrometer (Ulvac-PHI Inc, Chanhassen, MN, US) with a monochromatized Al Kα X-ray (1486.6eV) source [7]. The residual oil on the roller surface was removed by ultrasonic cleaning with n-heptane for 3 minutes prior to the XPS test. In XPS, a surface-sensitive quantitative spectroscopic technique is applied to obtain the composition of different elements as well as the chemical and electrical state of the elements within the tested material. Through irradiating a material with a beam of X-rays, the XPS spectra can be obtained and the kinetic energy and number of electrons that escape from the top 0 to 10 nm of the material can be measured simultaneously [2]. The residual chamber pressure was always below 1×10^{-7} Pa during spectra acquisition.

Scanning X-ray Image (SXI) was applied to look for specific features on the surface which identifies the wear track. Survey spectra and detailed spectra were collected only within the roller wear scar with a beam diameter of 100 μm, and the whole acquisition time was less than 120 minutes. Pass energy of 117.4 eV and 46.95 eV, step size of 1 eV and 0.1 eV were applied in the survey and detailed spectra acquisition process, respectively. An

Argon ion source with 2 keV energy and 1 μA sputter current over an area of 2×2 mm^2 was applied during the depth profiling acquisition (etching process) to estimate the reaction layer thickness on the roller surface. The etching process was terminated once the element concentration of O 1s signal becomes less than 5%. CASA XPS software (CasaXPS software version 2.3.15 Ltd., UK) was used to process the XPS data. The detailed spectra were fitted with Gaussian-Lorentzian curves with a Linear background. All peaks were charge corrected by shifting C 1s to 285.0 eV.

3. Results and discussion

3.1 Friction and wear results

The two different base oils, as well as their combinations with four additives, were tested in the micropitting rig for 2.5 hours. The friction and wear data are shown in Fig. 3 (some of the error bars appear missing out because of the scale). It is quite clear that the polar base oil Ester (and its combination with additives) show higher wear than those of the non-polar base oil PAO. The friction of Ester pure and PAO pure are similar, while friction of PAO+ZDDP is higher than Ester+ZDDP. This is because that ZDDP reaction layer is known to increase the friction [12,13], where this friction increasing behaviour of ZDDP is reduced in polar base oil as Ester molecules can compete with ZDDP molecules to attach to the surface. Except blending with ZDDP additive, the friction of Ester series blended with other additives is higher than the friction of PAO series. This friction behaviour is in line with Tomala et al. [14] who showed that the friction coefficient of polar base oil (diethylenglycol) is higher than that of non-polar base oil (hexadecane). Besides, the friction coefficient of polar base oil Ester to Ester+all tested additives experienced an increase, while that of non-polar base oil PAO experienced an increase with ZDDP and P additives but a decrease with S and Moly additives. Especially, adding friction modifier (Moly) into Ester base oil increased the friction significantly, compared to PAO where Moly additive reduced the friction a lot. This could be attributed to polar Ester molecules competing with the Moly additive to attach to the surface, thus limiting the availability of this additive on the surface to form a friction reduction layer. This friction behaviour will be related to the micropitting performance later in this study.

Fig. 3 also shows that wear of base oils with additives was higher than the wear of base oil alone, with the exception that the addition of ZDDP and S into Ester base oil had limited effect in changing the wear. Naveira Suarez et al.[8,9] explained that the higher wear of polar base oil with ZDDP compared to non-polar base oil with ZDDP is due to that the polarity of base oil influences the adsorption rate of ZDDP on the surface. This is because polar base oil can compete with ZDDP to attach to the surface which limits the anti-wear performance of

ZDDP. The higher wear with polar base oil was also seen in pure sliding tests performed by Zhang et al.[15,16]. These studies [8,9,14-16] give an indication that additives blended with polar oil have less access to the surface to form a protective reaction layer. This will be discussed with the XPS etching results later in this paper. Besides, the addition of P additive into base oils experienced a huge increase. This can be related to the acidity of the P additive that has an aggressive impact on the steel surface, which has been shown in pure sliding tests shown in a previous research [17].

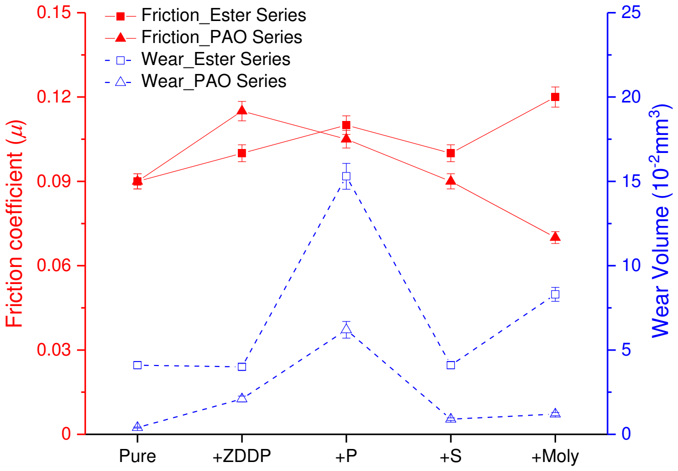
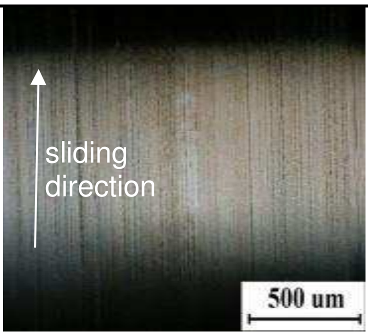
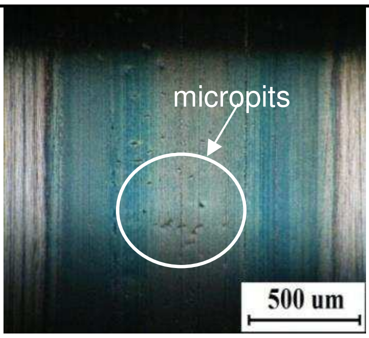
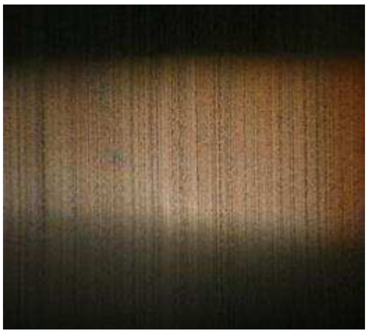
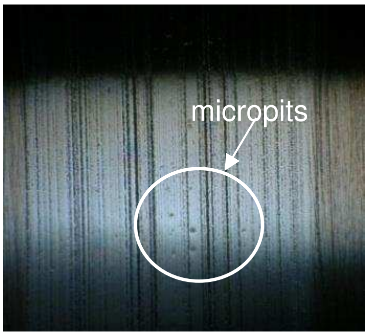
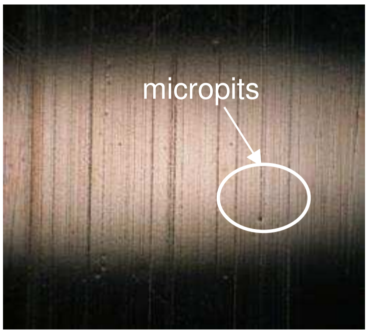
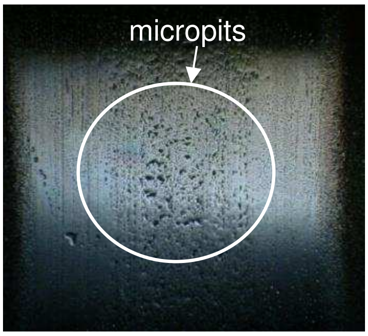
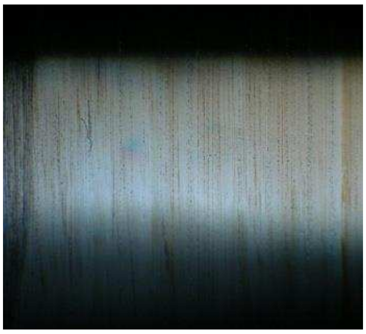
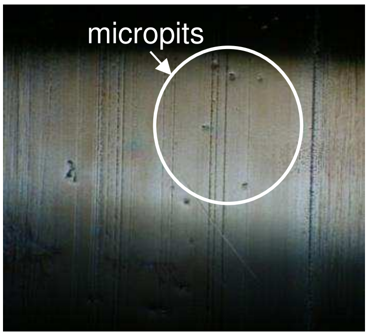
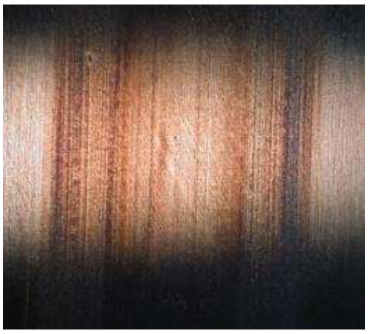
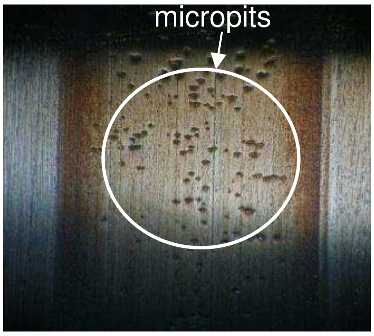


Fig. 3. Friction and wear results for the tested lubricants

3.2 Micropitting results

Table 4 shows the optical microscope images of rollers after tribological tests, which indicate the micropitting level on roller surfaces. The colours on the images are due to the presence of transparent surface films including boundary films, oxides, and traces of lubricant or solvent [18]. Seldom micropits were observed on the roller surface after the tests with Ester series, while few micropits were found with PAO Pure/+ZDDP/+S and a large amount of micropits were found with PAO+P/Moly. It can be concluded that non-polar base oil PAO and its combination with additives promote more micropits compared to polar base oil Ester. A possible explanation could be that the wear of Ester series is higher than PAO series (shown in Fig. 3) and the micropits formed during the rubbing process can be removed by the high wear, which has been proved by Morales-Espejel et al.[19]. Moreover, anti-wear additives like ZDDP can promote micropitting because they can slow down the removing speed of initial roughness on the surface as shown in previous researches [5,20-22]. But when these additives were blended with polar base oil Ester, their micropitting promoting effect would be reduced because of the competition of polar base oil and additive molecules to attach onto the surface. Thus, it is not surprising to see less or even no micropits when Ester series were tested.

Table 4. Optical microscope images of rollers after micropitting tests

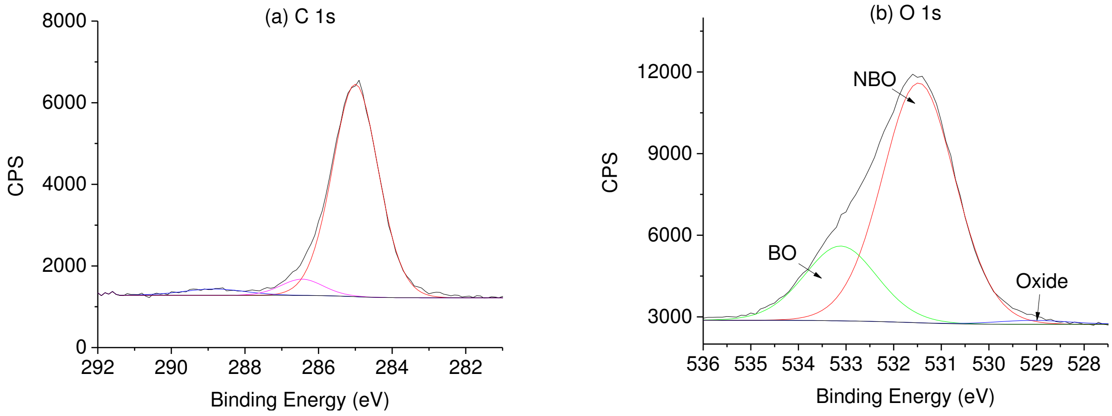
Oil Type	**Ester**	**PAO**
Pure		
+ZDDP		
+P		
+S		
+Moly		

However, both Lainé et al. [18] and Morales-Espejel et al.[19] found that fewer micropits formed with a lower friction coefficient, and this is considered to be due to the reduction of the local tensile stress within the contact area. In the current study, Ester base oil blended with other additives showed higher friction but resulted in fewer micropits on the wear scar than PAO series. This is a clear indication that micropitting behaviour cannot only be determined by friction and wear performance, and that the tribochemistry within the process should be considered.

3.3 Surface chemical properties

XPS was applied to study the tribochemical aspect of the micropitting formation process. As the effect of anti-wear additives on micropitting has been extensively studied, the roller surface after micropitting tests with Base oil+ZDDP/+P (P additive containing lubricants were chosen because PAO+P showed large quantities of micropits) were examined in XPS to study the tribochemistry involved. Both survey and detailed high-resolution spectra were obtained within the roller wear scar. Spectra from the survey scans were used to identify different peaks and to verify the contamination.

Figs. 4-7 show the detailed spectra of carbon 1s, oxygen 1s, sulphur 2p, phosphorus 2p linked with zinc 3s and zinc 2p from the reaction layer generated from Ester+ZDDP, PAO+ZDDP, Ester+P and PAO+P respectively. The summary of binding energies of elements/components of the reaction layers and atomic concentrations of the layer elements from Figs. 4-7 are shown in Table 5.



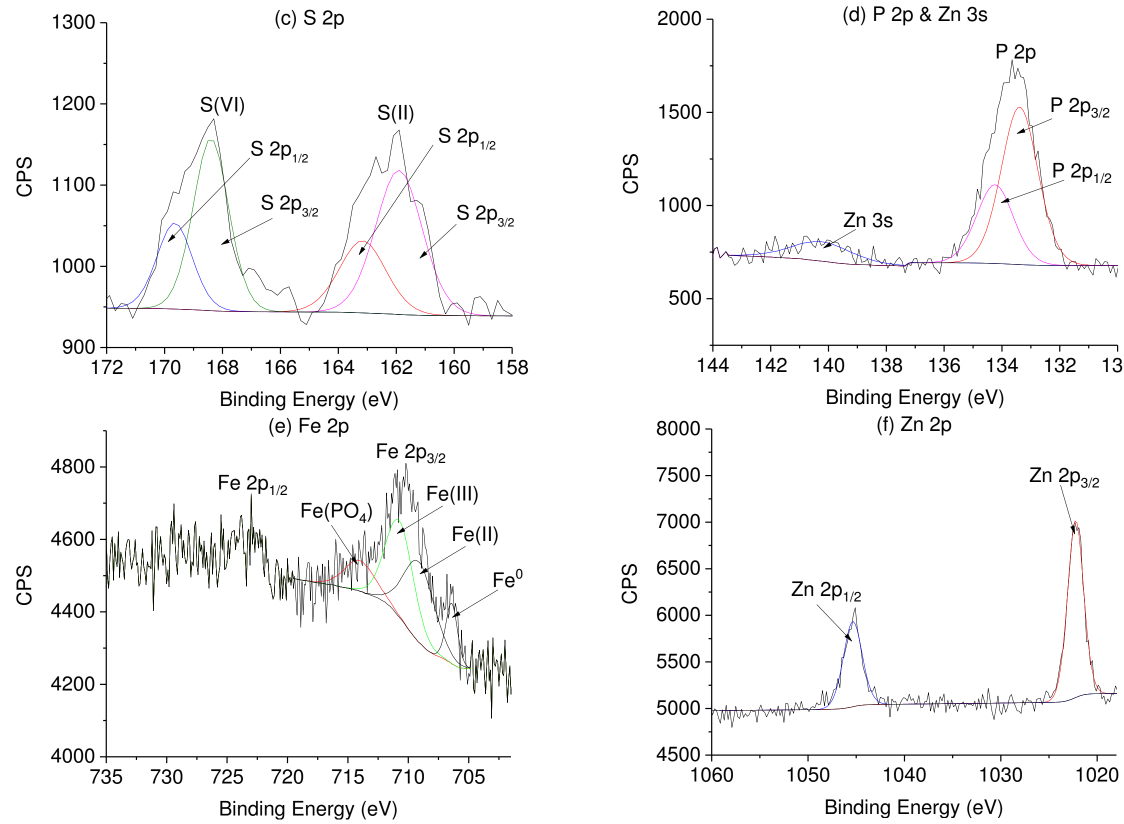
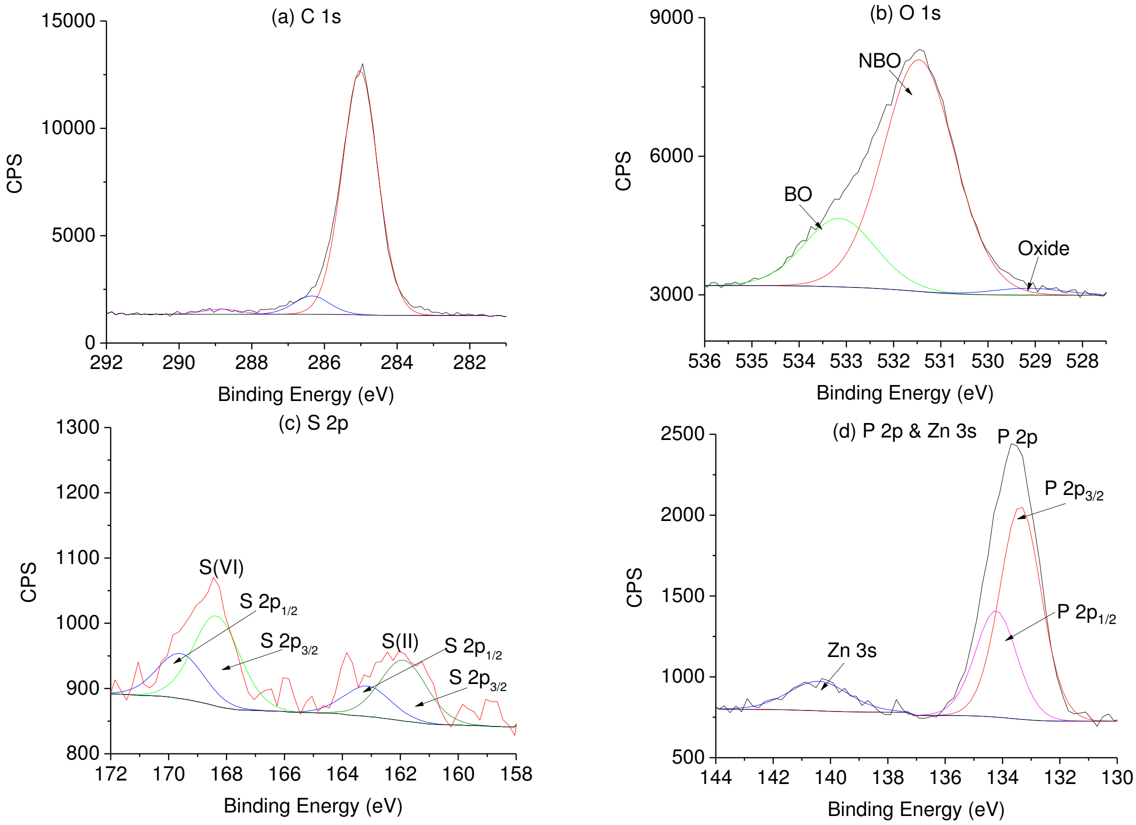


Fig. 4. XPS detailed spectra of (a) C1s, (b) O1s, (c) S2p, (d) P2p & Zn3s, (e) Fe2p and (f) Zn2p of the reaction layer derived from Ester+ZDDP roller sample



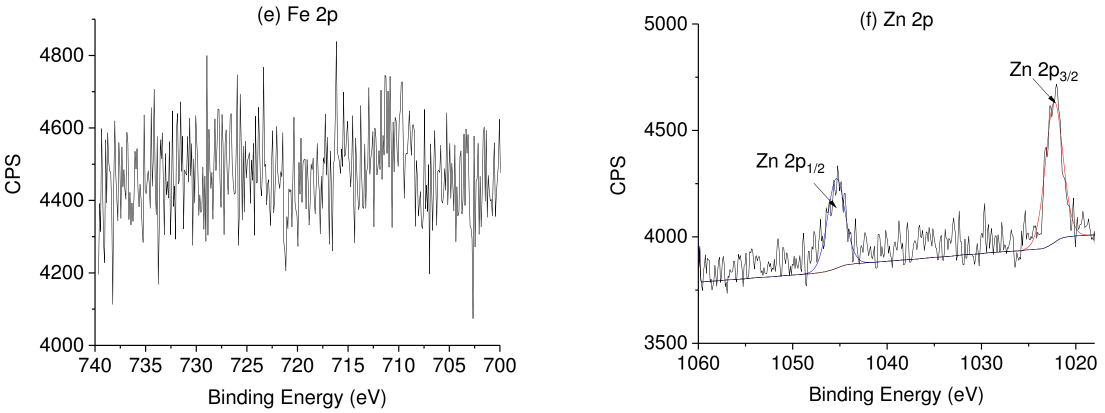


Fig. 5. XPS detailed spectra of (a) C1s, (b) O1s, (c) S2p, (d) P2p & Zn3s, (e) Fe2p and (f) Zn2p of the reaction layer derived from PAO+ZDDP roller sample

For ZDDP containing lubricants derived reaction layers (Figs. 3-4), C 1s signal was originally found at 285.4 eV and 285.5 eV for Ester+ZDDP (Fig. 4) and PAO+ZDDP (Fig. 5) which were both calibrated to 285.0 eV (C-C, C-H) and this processing was applied to all the regions and components generated. The second component generated from C 1s was found at 286.5±0.1 eV for Ester+ZDDP and at 286.4±0.1 eV for PAO+ZDDP which can be referred to C-O-P bond [23-24]. The third peak from C 1s was found at 288.8±0.1 eV for both Ester+ZDDP and PAO+ZDDP which can be referred to C-S bond [8].

The O 1s peak was curve fitted to three components of fixed FWHM of 1.8 eV for both Ester+ZDDP and PAO+ZDDP. The three components are a) non-bridging oxygen (NBO) at 531.5±0.1 eV for both Ester+ZDDP and PAO+ZDDP which originated from the phosphate chain –P=O and P-O-M (where M is metal Zn or Fe), b) bridging oxygen (BO) of P-O-P and sulphates at 533.2±0.1 eV for Ester+ZDDP and 533.1±0.1 eV for PAO+ZDDP, and c) a small peak of iron or zinc oxide at 529.2±0.1 eV for Ester+ZDDP and 529.1±0.1 eV for PAO+ZDDP [23-24]. NBO always contributes to short chain phosphates while BO contributes to long chain phosphates [25-27].

The S 2p peaks were curve fitted to two doublets of S $2p_{3/2}$ and S $2p_{1/2}$, where the area ratio and binding energy difference delta were fixed at 2:1 and 1.25 eV [8]. One S $2p_{3/2}$ peak was found at 161.9±0.1 eV for both Ester+ZDDP and PAO+ZDDP which can be related to oxidation state of S(II) and is believed to be Zn sulphide (ZnS) or (polythio)phosphate [28-30], while it is difficult to distinguish (thio)phosphate and metal sulphide in XPS analysis [2]; another S $2p_{3/2}$ peak found at 168.4±0.1 eV for Ester+ZDDP and 168.3±0.1 eV for PAO+ZDDP of oxidation state of S(VI) and is referred to sulphates [28-30]. The role of sulphate and its presence in the ZDDP reaction layer was also confirmed by previous studies [2,29].

The P 2p peak was curve fitted to a doublet of P 2p$_{3/2}$ and P 2p$_{1/2}$, where the area ratio and binding energy difference delta were fixed at 2:1 and 0.85 eV [8]. The P 2p$_{3/2}$ peak found at 133.4±0.1 eV for both lubricants can be referred to phosphates [27]. There was also a peak originated from Zn 3s found at 140.4±0.1 eV for Ester+ZDDP and 140.2±0.1 eV for PAO+ZDDP. This component was considered in the element quantification of zinc rather than only considering Zn 2p [2].

The Fe 2p signal of Ester+ZDDP (Fig. 4) consisted of two main peaks which are Fe 2p3/2 at 711±0.1 eV and Fe 2p1/2 at 723±0.1 eV. Curve fitting was only performed on Fe 2p3/2 peak, of which the main components are iron in the metallic state (Fe^0) at 706.5±0.1 eV, Fe(II) as oxide at 709.2±0.1 eV, Fe(III) as oxide at 710.8±0.1 eV and iron phosphate(FePO$_4$) at 713.9±0.1 eV which also contributed to the (poly)phosphate P 2p$_{3/2}$ peak at 133.4±0.1 eV [26-27]. Thus, the small peak of metal oxide at 529.2±0.1 eV for Ester+ ZDDP can be assigned to iron oxide. The Fe 2p signal of PAO+ZDDP (Fig. 5) showed a very low signal-to-noise ratio thus could not be analysed by curve fitting. The main component Zn 2p3/2 contributed from Zn 2p was found at 1022.2±0.1 eV for Ester+ ZDDP and 1022.3±0.1 eV for PAO+ZDDP.

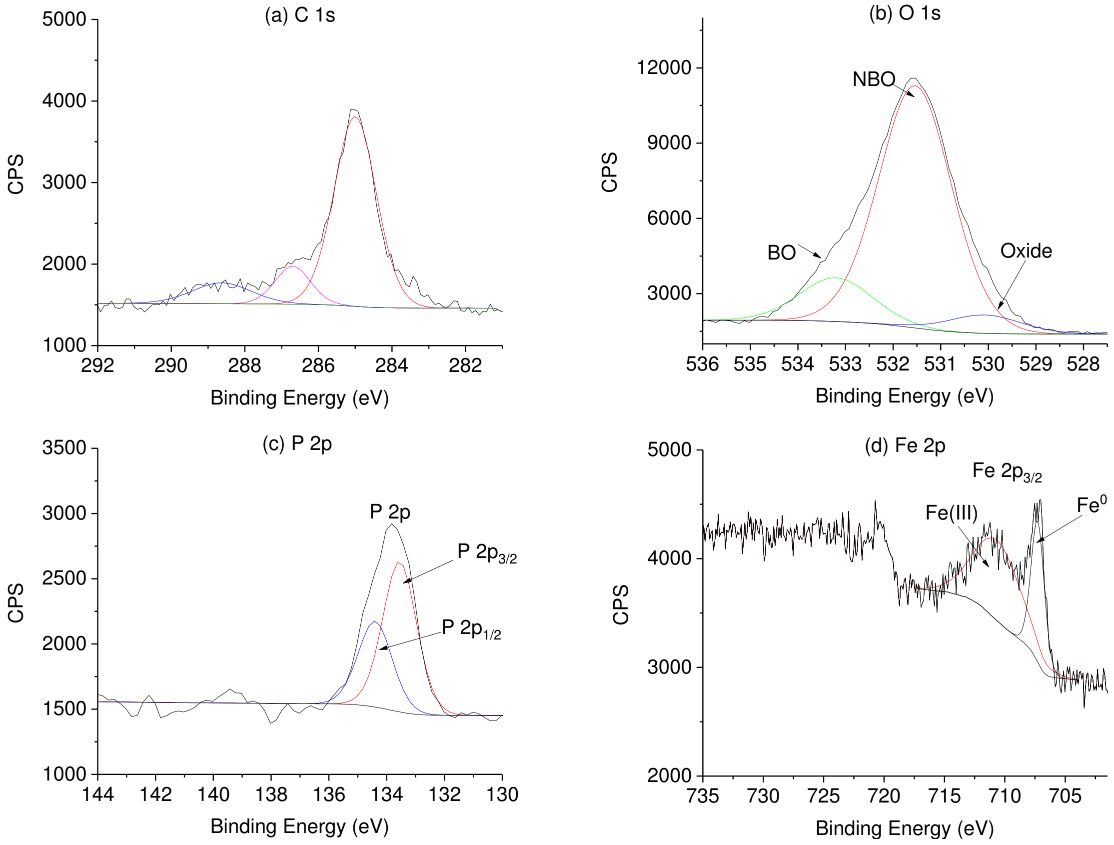


Fig. 6. XPS detailed spectra of (a) C1s, (b) O1s, (c) P2p and (d) Fe2p of the reaction layer derived from Ester+P roller sample

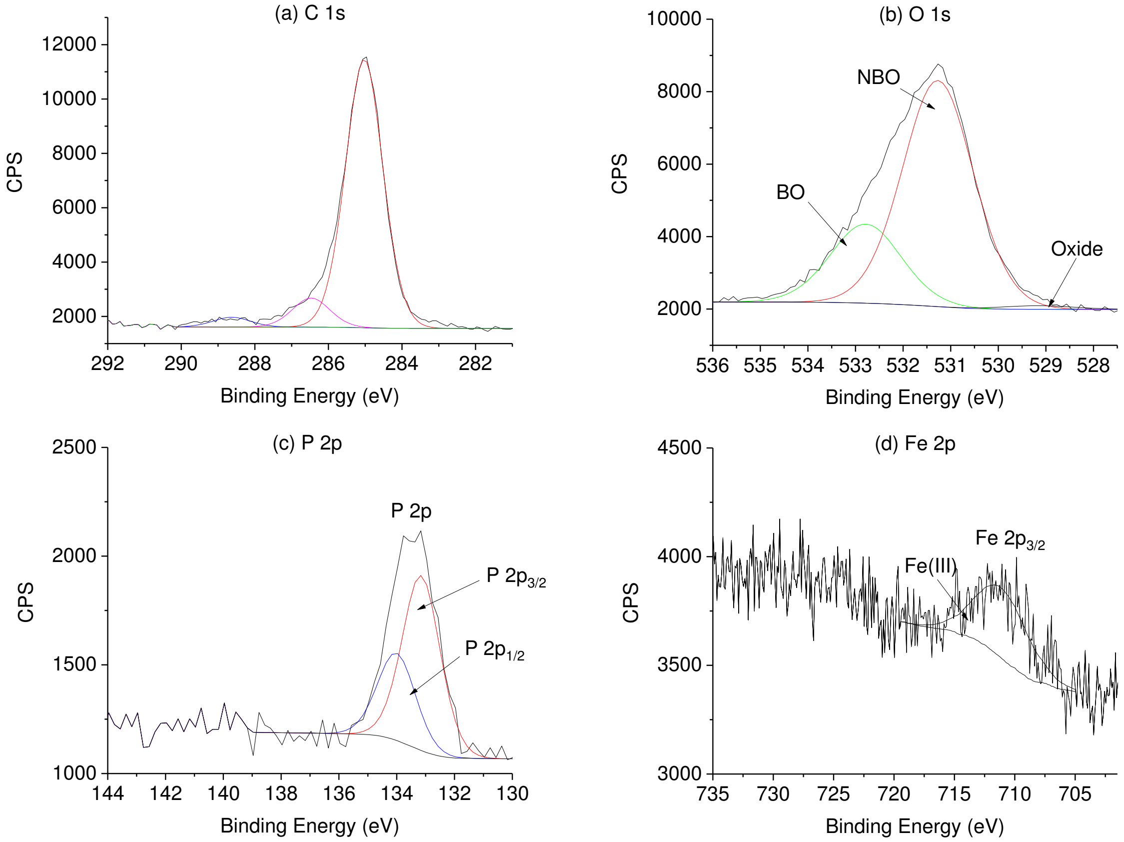


Fig. 7. XPS detailed spectra of (a) C1s, (b) O1s, (c) P2p and (d) Fe2p of the reaction layer derived from PAO+P roller sample

For P containing lubricants derived reaction layers (Figs. 5-6), C 1s signal was originally found at 285.4 eV and 284.8 eV for Ester+P (Fig. 6) and PAO+P (Fig. 7) which were both calibrated to 285.0 eV (C-C, C-H), thus all peaks were shifted accordingly. The C-O-P and C-S bonds for Ester+P and PAO+P were found at 286.7±0.1 eV,288.6±0.1 eV and 286.5±0.1 eV, 288.8±0.1 eV respectively. The O 1s peak was curve fitted to NBO, BO and oxide at a fixed FWHM of 1.8 eV for both Ester+P and PAO+P. The P 2p peak for P containing lubricants derived layers were curve fitted with the same procedures as for ZDDP tribofilms shown in Figs. 3-4. The P $2p_{3/2}$ peak was found at 133.4±0.1 eV and 133.3±0.1 eV for Ester+P and PAO+P, respectively. The Fe $2p_{3/2}$ peak was fitted to two components for Ester+P which were 707.3±0.1 eV, assigned to metallic iron Fe^0, and 710.6±0.1 eV assigned to oxidised Fe(III). Fe $2p_{3/2}$ peak detected on the PAO+P tribofilm was small, mainly dominated by the peak at 710.8±0.1 eV assigned to oxidised Fe(III).

The chain length of polyphosphate has been reported to affect the tribological performance in rolling-sliding contacts by Martin et al.[31] and Nedelcu et al.[32]. BO/NBO ratio was reported by them [31-32] to evaluate the chain length of the phosphate. It is clear from Table 5 that BO/NBO values for polar base oil Ester+ZDDP/P derived layers were lower than those of non-polar base oil PAO+ZDDP/P, which indicates that phosphate chain length derived from PAO containing lubricants were longer than Ester containing lubricants [31-32]. However, Soltanahmadi et al. [2] reported that BO/NBO ratio is not enough to evaluate the phosphate chain length as other non-phosphate peaks such as hydroxides can contribute to NBO peak, and binding energy of P-O-C can also overlap the BO peak region. Therefore, they [2] introduced the ratios of Zn/P, Fe/P and O/P to enhance the evaluation. Higher Zn/P, as well as O/P ratio, indicate a higher ratio of metal oxide/P_2O_5 which could be related to a shorter chain length of phosphate, and this phenomenon was also observed together with BO/NBO ratios [2]. Moreover, higher Fe/P ratio in iron phosphate reaction layer could be related to a shorter chain length of phosphates [33].

Table 5 shows that the ratios of metal (Zn, Fe)/P and O/P from Ester based lubricants were higher than those of PAO based lubricants, which confirms that phosphate chain length with PAO based lubricants were longer than those of Ester based lubricants. Moreover, this finding was also confirmed by the O/P values of Ester based lubricants that were quite close to 4:1 (refer to PO_4) which is the ratio of short chain length phosphate [28].

XPS depth profiling was applied to estimate the reaction layer thickness formed on the roller surface after micropitting tests. The etching process was terminated once the atomic concentration of O1s became lower than 5% [2,32]. The depth profiles of the reaction layers derived from the tested lubricants are shown in Fig. 8. Comparing Ester+ZDDP and PAO+ZDDP as well as Ester+P and PAO+P, it is quite clear that more etching time was spent to achieve a lower than 5% atomic concentration of O 1s signal for PAO based lubricants. Therefore, it can be concluded that the reaction layer thicknesses derived from Ester based lubricants were lower than those of PAO based lubricants, which is in line with the findings from Suarez et al. [8-9]. This could also be confirmed by the XPS detail scan results shown in Figs. 3-6 where stronger Fe 2p signal and metallic iron Fe^0 were only found in reaction layers derived from Ester based lubricants, which also indicates a thinner reaction layer formed on the surface [27].

Table 5. Binding energies of elements/components of the reaction layers and atomic concentrations of the layer elements(Zn, O, S) normalised to P

			Ester+ZDDP	PAO+ZDDP	Ester+P	PAO+P
Binding energy (eV)	C 1s	C-C,C-H	285.0 (90.1%)	285.0 (91.2%)	285.0 (75.7%)	285.0 (86.1%)
		C-O-P	286.5 (6.3%)	286.4 (6.9%)	286.7 (12.7%)	286.5 (11.3%)
		C-S	288.8 (3.6%)	288.8 (1.9%)	288.6 (11.6%)	288.8 (2.6%)
	O 1s	BO	533.2 (22.6%)	533.1 (23.5%)	533.2 (18.1%)	532.8 (25.3%)
		NBO	531.5 (76.0%)	531.5 (75.3%)	531.5 (73.8%)	531.3 (73.4%)
		Oxide	529.2 (1.4%)	529.1 (1.2%)	530.1 (8.2%)	529.2 (1.3%)
		BO/NBO ratio	0.297	0.312	0.245	0.350
	P $2p_{3/2}$		133.4	133.4	133.4	133.3
	Zn 3s		140.4	140.2	-	-
	S $2p_{3/2}$	Sulphide	161.9 (35.0%)	161.9 (26.9%)	-	-
		Sulphate	168.4 (31.7%)	168.3 (39.8%)	-	-
	Fe $2p_{3/2}$	Fe^0	706.5 (10.3%)	-	707.3 (34.8%)	-
		Fe (II)	709.2 (36.5%)	-	-	-
		Fe (III)	710.8 (39.5%)	-	710.6 (65.2%)	710.8
		$FePO_4$	713.9 (13.7%)	-	-	-
	Zn $2p_{3/2}$		1022.2	1022.3	-	-
Atomic concentration ratio (normalized to P)	Zn/P		2.7	1.6	-	-
	Fe/P		0.08	-	0.13	0.03
	O/P		3.5	1.8	3.9	1.6
	S/P		0.28	0.14	-	-

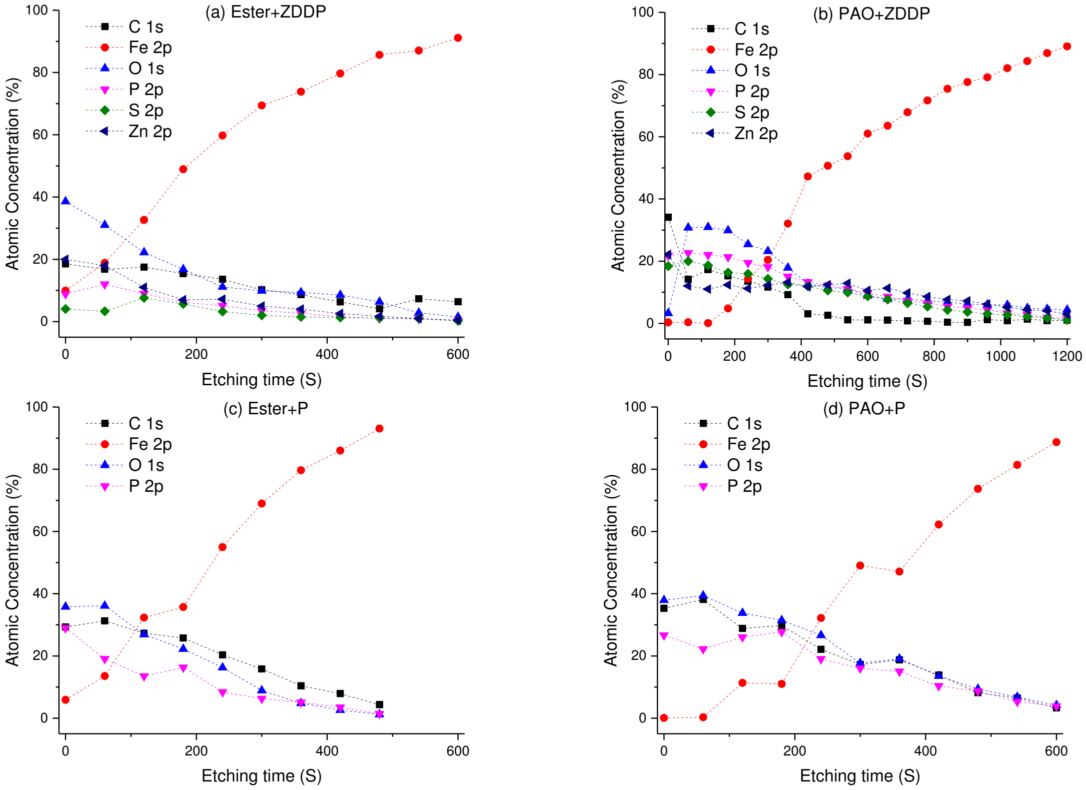


Fig. 8. XPS depth profile of the reaction layer derived from roller samples tested with: (a) Ester+ZDDP, (b) PAO+ZDDP, (c) Ester+P, (d) PAO+P.

Thicker reaction layer and longer phosphate chain length can digest the hard Lewis acid iron oxide wear particles according to the hard and soft acids and bases (HSAB) theory by Ho and Pearson [34-35]. Thus, it is not surprising to see the lower wear with PAO based lubricants (Fig. 3) because of the thicker reaction layer and longer phosphate chain length than Ester based lubricants. However, the thicker reaction layer which contains longer chain length phosphates formed on the roller surface tested with PAO based lubricants showed more micropits (Table 5). Pidduck et al. [36] showed that the top layer containing polyphosphates were viscous and soft, which can accommodate the shear stress inside the reaction layer during the rolling/sliding process rather than transferring it to the steel substrate [37]. Moreover, Spikes et al. [38] showed that short chain metal (poly)phosphates were more shear resistant and could be harder than the long chain phosphates, which enabled to accumulate more local stresses. Therefore, the local stress on the substrate shall be lower when the roller was tested with Ester based lubricants, thus the initiation and propagation processes of micropitting [39] can be hindered, resulting in less micropits on the surface.

The thinner reaction layer and shorter phosphate chain length formed with Ester based lubricants than PAO based lubricants was a result of the base oil polarity. Suarez et al. [8-9] explained that the higher affinity of the polar base oil molecules for the steel surface can limit the access of the additive molecules to the surface which restrains additives' ability to attach and form a protective reaction layer. This means that additive molecules mixed with polar base oil will have less access to form the reaction layer during the running in period. As a result, a thinner reaction layer can be expected with polar base oil. Meanwhile, limited access of additive molecules to participate in the reaction layer formation process could not provide the initially formed reaction layer with more source of additive to enhance the reaction layer, when the initially formed reaction layer (containing a lot of long chain phosphates) are experiencing severe decomposition at mean time. Therefore, long chain phosphates would experience a severer depolymerisation process and generate more short chain phosphates with polar base oil. This can be the reason that shorter chain length phosphates formed on the roller with polar base oil containing lubricants.

Fig. 8 also shows that more etching time was spent to achieve a lower than 5% atomic concentration of O 1s signal for ZDDP-containing lubricants than that of P-containing lubricants, which indicates that thinner reaction layer formed with P-containing lubricants. Table 5 shows that BO/NBO with Ester+ZDDP is higher than that with Ester+P, while this ratio is lower with PAO+ZDDP than that with PAO+P. However, the O/P ratio gives a opposite trend. Both the two ratios indicate that longer chain phosphates formed with Ester+ZDDP compared to Ester+P, while shorter chain phosphates formed with PAO+ZDDP compared to PAO+P. Thus, a universe trend can not be derived on the chain length of phosphates when comparing the ZDDP-containing lubricants with P-containing ones. Moreover, the Fe/P ratio is always lower with ZDDP-containing lubricants than that of P-containing lubricants, which indicates that less iron can participate in the phosphate formation process with ZDDP-containing lubricants, where Zn can compete with Fe to form (polythio)phosphate. Meanwhile, P-containing lubricants always show higher wear (Fig. 3) but more micropits (Table 4) than ZDDP-containing lubricants tested with same base oil. Thus, ZDDP is proved to be more supreme than P additive in terms of wear and micropitting performance. However, Morales-Espejel et al.[19] stated that the micropits formed during the rubbing process can be removed by the high wear, which is in contrary to the findings from this study. Again, it can be concluded that micropitting behaviour cannot be judged by tribological performances alone.

4. Conclusions

One polar base oil (Ester) and one non-polar base oil (PAO) blended with several additives were tested in a micropitting rig to study the effect of base oil polarity on the micropitting behaviour. It was shown that higher wear but fewer micropits formed on the roller surface when tested with Ester based lubricants. The following conclusions can be addressed from this study:

- Higher friction but fewer micropits with Ester series compared to PAO series indicates that micropitting behaviour cannot only be evaluated by tribological performances (e.g. friction, wear, roughness), tribochemistry needs to be considered.
- Higher wear and fewer micropits formed with Ester based lubricants were resulting from the affinity of the polar base oil which can compete with additives to attach to the surface which limited the ability of additives to form a protective reaction layer.
- Thinner reaction layer formed on the surface with polar base oil (Ester) containing lubricants, where the chain length of phosphates in the reaction layer were also shorter than those derived from non-polar base oil (PAO) containing lubricants.
- Short chain (poly)phosphates can be more shear resistant and harder than the long chains, which enable the reaction layer to endure more local forces, thus postpone the initiation and propagation of micropitting formation process.

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References

[1]. A. Oila, S.J. Bull, Assessment of the factors influencing micropitting in rolling/sliding contacts, Wear. 258 (2005) 1510–1524. doi:10.1016/j.wear.2004.10.012.

[2]. S. Soltanahmadi, A. Morina, M.C.P. Van Eijk, I. Nedelcu, A. Neville, Investigation of the effect of a diamine-based friction modifier on micropitting and the properties of tribofilms in rolling-sliding contacts, J. Phys. D. Appl. Phys. 49 (2016) 505302. doi:10.1088/0022-3727/49/50/505302.

[3]. S. Soltanahmadi, A. Morina, M.C.P. van Eijk, I. Nedelcu, A. Neville, Experimental observation of zinc dialkyl dithiophosphate (ZDDP)-induced iron sulphide formation, Appl. Surf. Sci. 414 (2017) 41–51. doi:https://doi.org/10.1016/j.apsusc.2017.04.023.

[4]. S. Maya-Johnson, J. Felipe Santa, A. Toro, Dry and lubricated wear of rail steel under rolling contact fatigue - Wear mechanisms and crack growth, Wear. 380-381 (2017) 240–250. doi:10.1016/j.wear. 2017.03.025.

[5]. G.E. Morales-Espejel, P. Rycerz, A. Kadiric, Prediction of micropitting damage in gear teeth contacts considering the concurrent effects of surface fatigue and mild wear, Wear. 398–399 (2018) 99–115. doi:https://doi.org/10.1016/j.wear.2017.11.016.

[6]. V. Brizmer, H.R. Pasaribu, G.E. Morales-Espejel, Micropitting Performance of Oil Additives in Lubricated Rolling Contacts, Tribol. Trans. 56 (2013) 739–748. doi:10.1080/10402004.2013.790097.

[7]. H. Cen, A. Morina, A. Neville, Effect of slide to roll ratio on the micropitting behaviour in rolling-sliding contacts lubricated with ZDDP-containing lubricants, Tribol. Int. 122 (2018) 210–217. doi:10.1016/ j.triboint.2018.02.038.

[8]. A. Naveira Suarez, M. Grahn, R. Pasaribu, R. Larsson, The influence of base oil polarity on the tribological performance of zinc dialkyl dithiophospate additives, Tribol. Int. 43 (2010) 2268–2278. doi:10.1016/ j.triboint.2010.07.016.

[9]. A. Naveira-Suarez, A. Tomala, M. Grahn, M. Zaccheddu, R. Pasaribu, R. Larsson, The influence of base oil polarity and slide-roll ratio on additive-derived reaction layer formation, Proc. Inst. Mech. Eng. Part J J. Eng. Tribol. 225 (2011) 565–576. doi:10.1177/1350650111405115.

[10]. K. Jablonka, R. Glovnea, J. Bongaerts, G. Morales-Espejel, The effect of the polarity of the lubricant upon capacitance measurements of EHD contacts, Tribol. Int. 61 (2013) 95–101. doi:10.1016/j.triboint. 2012.11.016.

[11]. H. Cen, A. Morina, A. Neville, R. Pasaribu, I. Nedelcu, Effect of water on ZDDP anti-wear performance and related tribochemistry in lubricated steel/steel pure sliding contacts, Tribol. Int. 56 (2012) 47–57. doi:10.1016/j.triboint.2012.06.011.

[12]. L.J. Taylor, H.A. Spikes, Friction-enhancing properties of zddp antiwear additive: Part I—friction and morphology of zddp reaction films, Tribol. Trans. 46 (2003) 303–309. doi:10.1080/10402000308982630.

[13]. L.J. Taylor, H.A. Spikes, Friction-Enhancing Properties of ZDDP Antiwear Additive: Part II—Influence of ZDDP Reaction Films on EHD Lubrication, Tribol. Trans. 46 (2003) 310–314. doi:10.1080/ 10402000308982631.

[14]. A. Tomala, A. Naveira-Suarez, I.C. Gebeshuber, R. Pasaribu, Effect of base oil polarity on micro and nanofriction behaviour of base oil + ZDDP solutions, Tribol. - Mater. Surfaces Interfaces. 3 (2009) 182–188. doi:10.1179/175158310X481709.

[15]. 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, Tribol. Lett. 19 (2005) 211–220. doi: 10.1007/s11249-005-6148-2.

[16]. Z. Zhang, E.S. Yamaguchi, M. Kasrai, G.M. Bancroft, X. Liu, M.E. Fleet, Tribofilms generated from ZDDP and DDP on steel surfaces: Part 2, chemistry, Tribol. Lett. 19 (2005) 221–229.doi: 10.1007/s11249-005-6149-1.

[17]. H. Cen, A. Morina, A. Neville, Effect of lubricant ageing on lubricant physical and chemical properties and tribological performance. Part I: effect of lubricant chemistry, Ind. Lubr. Tribol. 70 (2018) 10.1108/ ILT–03–2017–0059. doi:10.1108/ILT-03-2017-0059.

[18]. E. Lainé, A. V. Olver, M.F. Lekstrom, B.A. Shollock, T.A. Beveridge, D.Y. Hua, The effect of a friction modifier additive on micropitting, Tribol. Trans. 52 (2009) 526–533. doi:10.1080/10402000902745507.

[19]. G.E. Morales-Espejel, V. Brizmer, Micropitting modelling in rolling–sliding contacts: Application to rolling bearings, Tribol. Trans. 54 (2011) 625–643. doi:10.1080/10402004.2011.587633.

[20]. S. Maya-Johnson, J. Felipe Santa, A. Toro, Dry and lubricated wear of rail steel under rolling contact fatigue - Wear mechanisms and crack growth, Wear. 380-381 (2017) 240–250. doi:10.1016/j.wear.2017.03.025.

[21]. S. Hutt, A. Clarke, H.P. Evans, Generation of Acoustic Emission from the running-in and subsequent micropitting of a mixed-elastohydrodynamic contact, Tribol. Int. 119 (2018) 270–280. doi:https://doi.org/10.1016/j.triboint.2017.11.011.

[22]. E. Lainé, A.V. Olver, T.A. Beveridge, Effect of lubricants on micropitting and wear, Tribol. Int. 41 (2008) 1049–1055. doi:https://doi.org/10.1016/j.triboint.2008.03.016.

[23]. Y. Shimizu, H.A. Spikes, The Influence of Slide–Roll Ratio on ZDDP Tribofilm Formation, Tribol. Lett. 64 (2016) 19. doi:10.1007/s11249-016-0738-z.

[24]. M.A. Nicholls, T. Do, P.R. Norton, M. Kasrai, G.M. Bancroft, Review of the lubrication of metallic surfaces by zinc dialkyl-dithiophosphates, Tribol. Int. 38 (2005) 15–39. doi:https://doi.org/10.1016/j.triboint.2004.05.009.

[25]. J.M. Martin, C. Grossiord, T. Le Mogne, S. Bec, A. Tonck, The two-layer structure of Zndtp tribofilms: Part I: AES, XPS and XANES analyses, Tribol. Int. 34 (2001) 523–530. doi:https://doi.org/10.1016/S0301-679X(01)00029-9.

[26]. R. Heuberger, A. Rossi, N.D. Spencer, XPS study of the influence of temperature on ZnDTP tribofilm composition, Tribol. Lett. 25 (2007) 185–196. doi:10.1007/s11249-006-9166-9.

[27]. 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, Tribol. Lett. 15 (2003) 181–192. doi:10.1023/A:1024800900716.

[28]. A. Rossi, M. Eglin, F.M. Piras, K. Matsumoto, N.D. Spencer, Surface analytical studies of surface-additive interactions, by means of in situ and combinatorial approaches, Wear. 256 (2004) 578–584. doi:10.1016/j.wear.2003.10.001.

[29]. A. Morina, H. Zhao, J.F.W. Mosselmans, In-situ reflection-XANES study of ZDDP and MoDTC lubricant films formed on steel and diamond like carbon (DLC) surfaces, Appl. Surf. Sci. 297 (2014) 167–175. doi:10.1016/j.apsusc.2014.01.116.

[30]. P. Parsaeian, A. Ghanbarzadeh, M.C.P. Van Eijk, I. Nedelcu, A. Neville, A. Morina, A new insight into the interfacial mechanisms of the tribofilm formed by zinc dialkyl dithiophosphate, Appl. Surf. Sci. 403 (2017) 472–486. doi:https://doi.org/10.1016/j.apsusc.2017.01.178.

[31]. J.M. Martin, Antiwear mechanisms of zinc dithiophosphate: A chemical hardness approach, Tribol. Lett. 6 (1999) 1–8. doi:10.1023/A:1019191019134.

[32]. I. Nedelcu, E. Piras, A. Rossi, H.R. Pasaribu, XPS analysis on the influence of water on the evolution of zinc dialkyldithiophosphate-derived reaction layer in lubricated rolling contacts, Surf. Interface Anal. 44 (2012) 1219–1224. doi:10.1002/sia.4853.

[33]. A. Rossi, F.M. Piras, D. Kim, A.J. Gellman, N.D. Spencer, Surface reactivity of tributyl thiophosphate: effects of temperature and mechanical stress, Tribol. Lett. 23 (2006) 197–208. doi:10.1007/s11249-006-9051-6.

[34]. T. Hard, O. Chemistry, The hard soft acid bases (HSAB) principle and organic chemistry, Chem. Rev. 75 (1975) 1-20.

[35]. R.G. Pearson, Chemical Hardness–Applications from Molecules to Solids, VCH, (1997).

[36]. A.J. Pidduck, G.C. Smith, Scanning probe microscopy of automotive anti-wear films, Wear. 212 (1997) 254–264. doi:10.1016/S0043-1648(97)00081-1.

[37]. 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, in: Proc. R. Soc. London A Math. Phys. Eng. Sci., The Royal Society, 1999: pp. 4181–4203. Doi:10.1098/rspa.1999.0497.

[38]. H. Spikes, The history and mechanisms of ZDDP, Tribol. Lett. 17 (2004) 469–489. doi:10.1023/B:TRIL.0000044495.26882.b5.

[39]. S. Hutt, A. Clarke, H.P. Evans, Generation of Acoustic Emission from the running-in and subsequent micropitting of a mixed-elastohydrodynamic contact, Tribol. Int. 119 (2018) 270–280. doi:10.1016/j.triboint.2017.11.011.