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Synergism between bio-based oleate ester and low-concentration ZDDP under reciprocating contacts

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ABSTRACT

In this study, a bio-based ester was experimentally tested under a reciprocating contact in terms of the tribological performance to assess the potential of bio-based materials as boundary lubrication additives for low Sulphated Ash, Phosphorus, and Sulphur (SAPS) lubricants. A synergy in tribological performance has been observed when the ethyl oleate was used with a low concentration of ZDDP, showing both lower friction and wear loss, compared to only ethyl oleate or Zinc dialkyldithiophosphates (ZDDP) as single additives in base oil. SEM-EDX and ToF-SIMS analyses confirm that the additive combination of ester and low-concentration ZDDP generates a more evenly distributed tribo-film than that for only ZDDP as an additive. Although the tribo-film thickness of the ester/ZDDP lubricant combination, measured with AFM, issmaller than that for only low-concentration ZDDP, the combination shows superior wear protection ability over ZDDP. Mass spectra from ToF-SIMS show that the main component of the film formed by the additive combination is zinc polyphosphate, while the film generated from low-concentration ZDDP consists of short-chain iron phosphate. It is proposed that the ethyl oleate present in the additive combination alleviates severe shear in the contact, which promotes the formation of a uniform tribo-film composed of glassy zinc polyphosphate. The formed tribo-film enhances the adsorption of ester fragments, improving the tribological performance compared to using only ester as an additive. The obtained results demonstrate the potential of bio-based esters to reduce ZDDP usage and move towards greener lubricants.

1. Introduction

Boundary lubrication is a challenging working condition for many engineering applications, where high friction and severe wear occur due to unavoidable asperity-to-asperity contact. To improve the performance and increase the service life of mechanical components, many types of lubricant additives have been applied to protect the surfaces, especially targeting the performance in boundary lubrication regime. One of the most widely used anti-wear additives is ZDDP, due to its excellent wear protection ability. The research on ZDDP has been going on for decades and one comprehensive summary can be found in [1]. Another detailed discussion about the surface protection mechanism of ZDDP is given in [2]. To further understand the ZDDP tribo-film formation process, film growth has been investigated under an in-situ condition [3,4]. Although ZDDP can greatly reduce wear loss, its high boundary friction coefficient remains a concern. To improve the friction performance, ZDDP has been investigated together with various friction modifiers which have been comprehensively reviewed in works [5,6].

The Molybdenum Dithiocarbamate (MoDTC) is one of the most efficient friction modifiers in reducing friction, showing strong synergism with ZDDP [7–9]. However, the increasingly rigorous environmental regulation on engine oils requires lower concentration of additives containing Sulphur, Phosphorus and heavy metals. Therefore, there has been a great effort to apply organic friction modifiers which can be obtained from bio-based materials to replace traditional organo-metallic additives such as ZDDP and MoDTC. In [10], the tribology of systems using lubricating oil with around 0.8 wt% ZDDP together with various organic additives was evaluated under sliding/-rolling condition. In this study, the pre-formed ZDDP film responded more quickly to nitrogen-containing additives such as amine and amide, showing immediate friction reduction. Fatty acid also provided friction reduction but required longer rubbing time. When ZDDP and organic friction modifiers were tested simultaneously in [10], only amine and amide showed good friction reduction ability. A similar testing method

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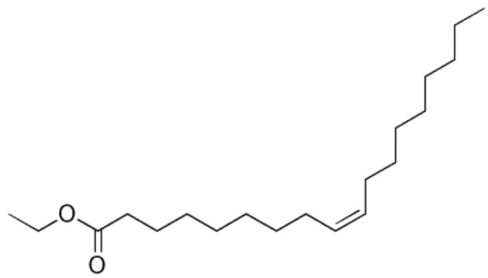


Fig. 1. Molecular structure of ethyl oleate.

Table 1
Lubricant sample composition.

Sample name	Component		
	ZDDP (wt%)	Ethyl Oleate (wt%)	Base oil
PAO	0	0	PAO4
Z1	1	0	
Z02	0.2	0	
E1	0	1	
E08Z02	0.2	0.8	

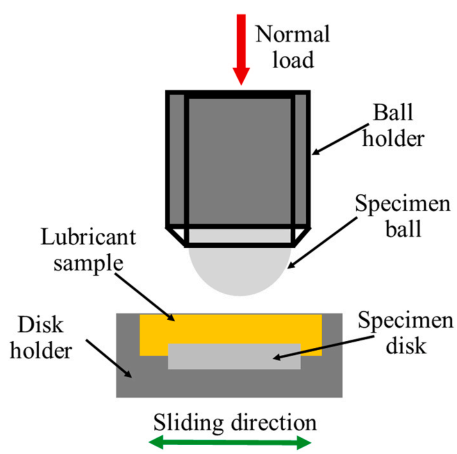


Fig. 2. Schematic figure of reciprocating contacts of TE77 tribo-meter.

was applied in [11,12], where additive mixtures containing both amine ethoxylates and 0.8 wt% ZDDP were studied. Results showed amine ethoxylates decrease both ZDDP film thickness and friction value, impacting the balance between friction reduction and maintaining the anti-wear film. In [13,14], the tribological performance of various bio-based amines was examined together with 0.8 wt% ZDDP under sliding/rolling configuration and results confirmed that all amines mitigated the pitchy effect of ZDDP, smoothened surface roughness and reduced friction, however amine with hydroxyl groups undermined wear protection of ZDDP in micro-pitting tests. A more recent study [15] focused on the combination of 1 wt% ZDDP and different types of amines with various chain lengths, unsaturation degrees and functional groups, under reciprocating movement. It was concluded that all amines provided reduced friction and wear to the systems lubricated with oils containing only ZDDP as an additive. The reduction ability depends on the chemical structures of amines. The best tribological performance is achieved when the molar ratio between ZDDP and amine is below 0.5 [15]. The summarised progress above was obtained with ZDDP concentration higher than 0.5 wt%. Amid environmental concerns, it is required to reduce the content of heavy metal, Sulphur and Phosphorus in lubricant. Therefore, lubricant formulations with low Sulphated Ash, Phosphorus, and Sulphur (SAPS) have attracted much attention [16–18].

Since ZDDP is a critical source of Sulphur and Phosphorus in the lubricant, it is important to remove ZDDP or reduce its concentration in engine lubricants by replacing it with bio-based materials. A concentration of as low as 0.2 wt% of ZDDP mixed with GMO [19] and oleamide [20] has shown detrimental behaviour under sliding/rolling conditions; 0.2 wt% ZDDP suppresses the friction reduction function of GMO whereas oleamide constrains ZDDP antiwear tribo-film formation for steel-steel contacts. On the other hand, ethoxylated fatty ester and oleyl amine have shown positive effects when combined with 0.2 wt% ZDDP. In particular, both organic friction modifiers reduce the boundary friction and decrease the phosphorus and zinc content in the tribo-film under sliding/rolling contacts[21], compared to results from tests with only ZDDP in the lubricant. As summarised in the former paragraph, the ZDDP concentration in previous studies is normally about 1 wt%, which is 5 times larger than the 0.2 wt% in studies[19–21]. Since the lowest concentration for ZDDP that can be found in the published works is also 0.2 wt%, this value is regarded as a low range for ZDDP as a lubricant additive. One promising application of bio-based material as a lubricant additive has been proved for methyl oleate, where 30% ZDDP and 70% volume methyl oleate possesses the lowest nano-level friction measured from the AFM technique[22,23]. This research indicates a potential synergistic tribological performance when using bio-based esters and ZDDP as lubricant additives. However, this progress only focuses on the nano-level experiments and the macro tribological performance has not been studied yet. Additionally, the properties of tribo-films generated from severe reciprocating contacts have not been fully revealed.

This study aims to experimentally evaluate the potential of combining the ethyl oleate which has been obtained from bio-based resources [24,25] and ZDDP in low-concentration to obtain low friction and wear under severe boundary lubrication conditions. The worn surfaces were examined by analysing the physical and chemical properties of the tribo-film, referenced to the film formed from lubricants containing only low-concentration ZDDP.

2. Materials and Experimental Methods

2.1. Materials

The ethyl oleate with its molecular structure shown in Fig. 1, was supplied by Sigma Aldrich with purity higher than 99%. ZDDP was provided by Infineum. PAO4 was used as base oil, supplied by Total Energies. The lubricant samples were prepared by first adding the desired amount of additive into the base oil, then heating the samples under about 50 °C while stirring the solution for 1 h with magnetic stirring, ensuring all lubricant samples were homogeneous. Table 1 shows the lubricant additive combinations tested in this study. According to the justification in the introduction section, this research focuses on the low-range concentration of ZDDP at 0.2 wt%. The total additive concentration in all lubricant samples was set at 1 wt% which was applied in many studies for bio-based additives[15,26–30]. Hence, there are 3 samples with 1 wt% additive in total, namely Z1 containing 1 wt% ZDDP, E1 containing 1 wt% ethyl oleate and E08Z02 containing 0.8 wt% ethyl oleate and 0.2 wt% ZDDP. A sample Z02 with only 0.2 wt % ZDDP was included as a reference to investigate the effect of the addition of ethyl oleate in the lubricant on the properties of the tribo-film generated from only Z02.

2.2. Methods

The tribological tests were conducted under reciprocating sliding with a TE77 tribometer, a widely used rig for testing lubricants in boundary and mixed lubrication regime. A schematic figure describing the contact configuration of TE77 is given in Fig. 2. This contact geometry generates severe conditions so that efficient comparison with shorter running time tests can be made to distinguish the performance of

Table 2
Tribological testing conditions.

Parameters	Values
Temperature (℃)	90
Frequency (Hz)	10
Stroke length (mm)	7
Running time (hour)	2
Max Contact pressure (GPa)	≈ 1.27
Surface roughness of pin and plate (R_a in nm)	≈ 500, 50
Hardness of pin and plate (HRC)	58-62

lubricant additives. Additionally, the reciprocating motion can also be found in many industrial applications such as combustion engines, reciprocating pumps and shaper machines. Therefore, TE77 was selected for tribological investigation.

A normal load of 80 N was applied on pins with a 10 mm radius against flat plates, generating an initial maximum contact pressure of 1.28 GPa. Both pins and plates are made of steel EN31. Before the tribology tests, both samples were cleaned with heptane in an ultrasonic bath to remove the impurities from manufacturing. The surface roughness values, *Ra*, for pins and plates were about 500 nm and 50 nm, respectively. The oscillating frequency was 10 Hz, and the stroke length was 7 mm. The lubricant container temperature was kept at 90 °C. With

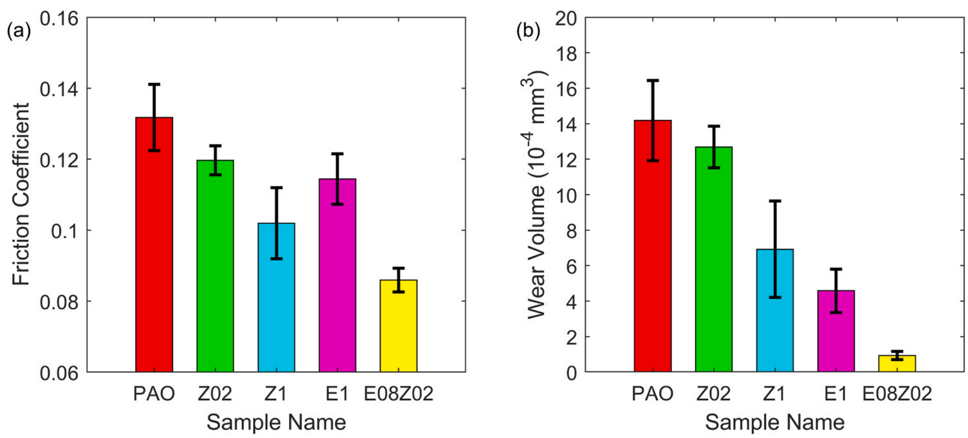


Fig. 3. Tribological results (a) friction coefficient and (b) wear volume under 1 GPa maximum contact pressure, 10 Hz reciprocating frequency, 7 mm stroke length and 90 °C for 2 h.

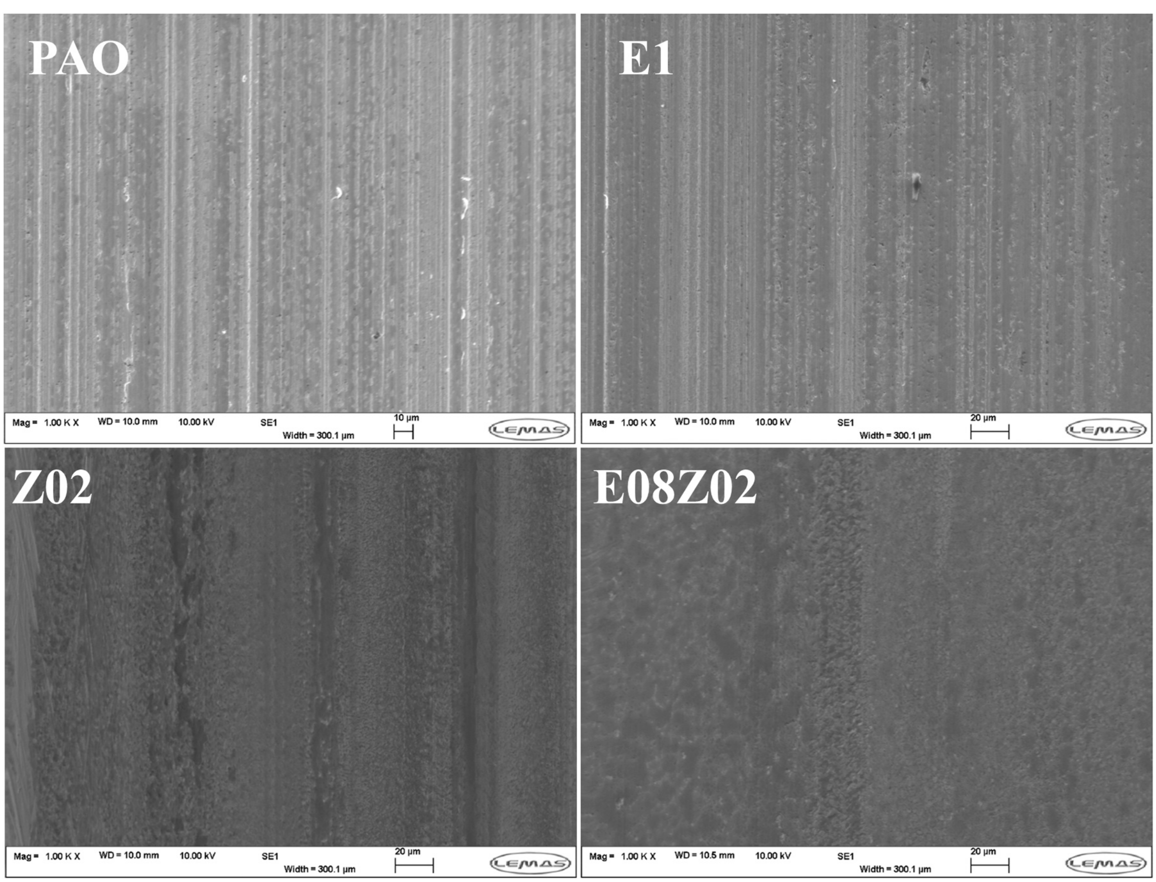


Fig. 4. SEM Images taken from the centre of the wear tracks on plates under 1000 magnification, 10 kV accelerating voltage.

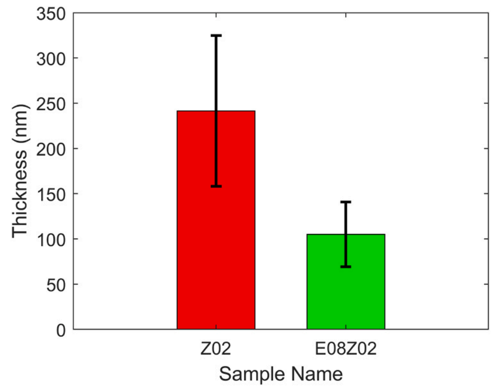


Fig. 5. Tribo-film thickness for Z02 (0.2 wt% ZDDP) and E08Z02 (0.8 wt% ethyl and 0.2 wt%) under 1 GPa maximum contact pressure, 10 Hz reciprocating frequency, 7 mm stroke length and 90 °C for 2 h.

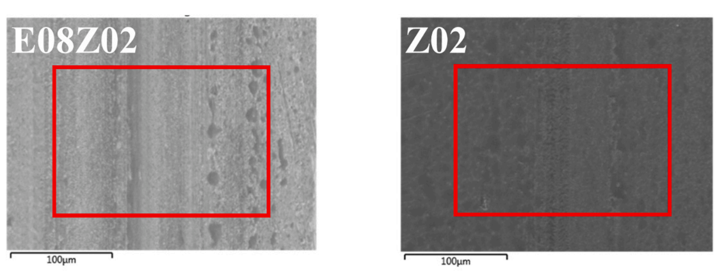
all the above conditions, the estimated lambda value was significantly smaller than 1, which ensured the contact was in boundary regime. Each test lasted for 2 h, equivalent to a total running distance of approximately 1000 m. The friction value during the last 20 min of each 2-hour test was averaged to deliver the steady state friction coefficient for each test. The repeatability was checked by conducting at least three repeats per tested lubricant. An average of three tests was regarded as the representative friction value for each testing condition. All testing conditions are summarised in Table 2.

The wear scar diameter of the pins was measured by an optical microscope from Leica Microsystems. For each wear scar, a diameter value was obtained by averaging two measurements of the circular scar taken perpendicularly. Then, an average of at least three wear scar diameter values was taken as the representative wear performance value for each tested lubricant sample. The wear volume V was calculated using the sphere cap Eq. (1), where $R=$ *10 mm is the* radius of the pin, and d is the wear scar diameter, obtained from measurements.

$$V = \pi * \left(R - \sqrt{R^2 - \left(\frac{d}{2}\right)^2}\right) * \left[3\left(\frac{d}{2}\right)^2 + \left(R - \sqrt{R^2 - \left(\frac{d}{2}\right)^2}\right)^2\right] \Big/ 3 \tag{1}$$

The wear mechanisms were determined by examination of the plates using SEM with a Carl Zeiss EVO MA 15 (Carl Zeiss AG), EDX from Oxford Instruments was then applied to detect chemical elements in terms of both concentration and distribution.

The tribo-film thickness was obtained through a method similar to that described in work [31]. First, a nano-indenter was used to create tetrahedral marks on the worn surface obtained from tribological tests. After this, a 50 × 50 μm^2 area containing the tetrahedral marks was scanned by AFM to obtain initial surface topography. The lowest point of the tetrahedral mark is regarded as the baseline, and the distance between the top point and the lowest point of this scanned area is measured. Then EDTA solution was used to etch the whole wear track, with the etching process described in [32,33]. After EDTA etching, the same area with tetrahedral marks was again scanned by AFM to measure the new distance between the new top point and the lowest point of the surface profile. The difference between the distances taken before and after the etching process was regarded as the tribo-film thickness value. A detailed procedure for acquiring the film thickness value is summarized in the supplementary materials. The AFM equipment is from Bruker, USA, and a standard RTESPA-300 AFM tip (Bruker, USA), made



Samples	P (wt. %)	S (wt. %)	Zn (wt. %)	Fe (wt. %)	O (wt. %)	C (wt. %)
E08Z02	5.75	1.72	15.12	60.70	11.61	2.99
Z02	3.84	2.62	9.25	72.92	7.61	2.72

Fig. 6. SEM-EDX analysis of worn surface from plates.

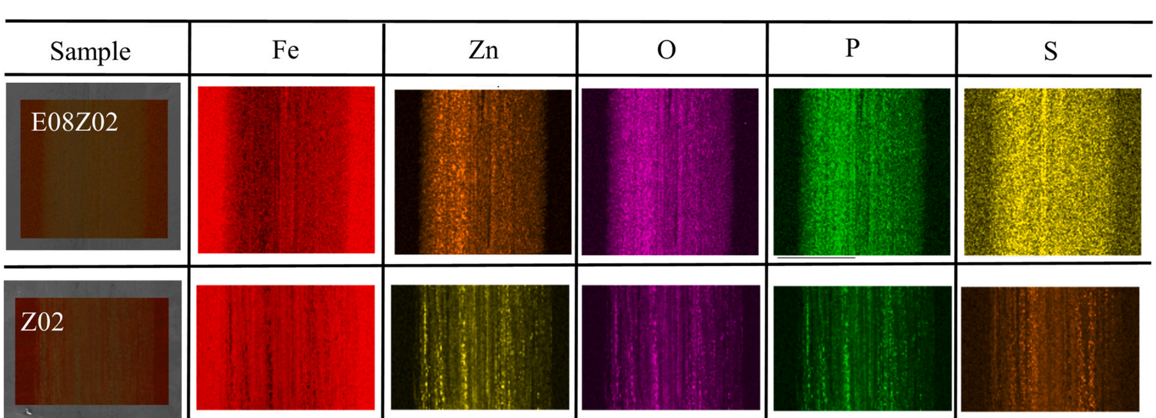


Fig. 7. SEM mapping for representative elements.

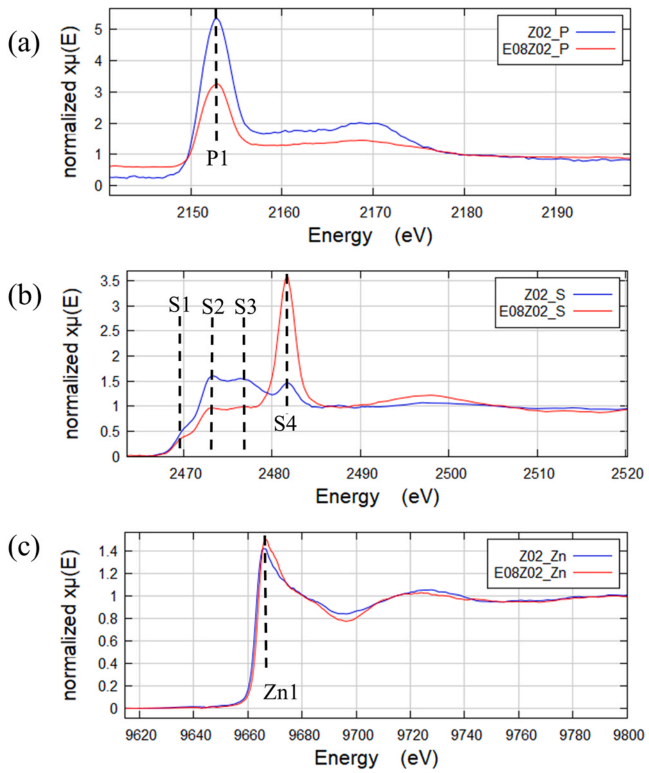


Fig. 8. XAS curves of three chemical elements (a) P *k*-edge, (b) S *k*-edge and (c) Zn *k*-edge.

of antimony (n) doped silicon, was applied. The cantilever is made from the same material as the tip and has a spring constant of 42 N/m. The data was collected using NanoScope v9 software (Bruker, USA), then analysed with software NanoScope Analysis 2.0.

The worn tracks on plates were also examined with X-ray Absorption Spectroscopy (XAS) technique and the experiments were conducted in the I18 microfocus spectroscopy beamline at the Diamond Light Source-Oxford, UK. One advantage of this XAS study is that the specimens are analysed in an ambient environment so that extremely deep cleaning on specimens is not necessary,. Hence, the tribo-films can remain in their original states to the maximum degree for an ex-situ study, without any potential influence of the ultra-high vacuum condition on the tribo-films [34]. The X-ray beamline has a resolution of 2 μm x 2 μm area and an energy ranging from 2.05 keV to 20.5 keV. Three types of elements, namely P, S and Zn were scanned, monitoring their fluorescence behaviour. The collected data was post-analysed with the software Athena. A more detailed experimental procedure can be found in [34].

Different from the application of the XAS technique in this work, which is monitoring the fluorescence behaviour of relevant chemical elements in the tribo-film to identify the *K*-edges of P and S, the specific organic molecules can be analysed using the ToF-SIMS technique. Therefore, as a complementary analysing method to XAS, ToF-SIMS was also utilised to study the worn surface. This can not only intuitively verify the existence of molecular fragments from the bio-based ester in the tribo-film, but also distinguish the different metal elements in phosphate salts in the tribo-film, which is difficult to achieve from the XAS technique. A ToF-SIMS IV instrument (ION-TOF GmbH., Münster, Germany) was used to study molecular fragments on the wear tracks. A current of 1 pA ion beam was shot from a bismuth liquid ion gun under 25 kV accelerating voltage. Three different places of 500 × 500 μm^2 on each wear track were scanned to ensure the reliability of results. The resolution is 256 × 256 pixels for 20 scans. Data analysis was conducted with the software SurfaceLab 7 (IONTOF GmbH). ToF-SIMS spectra were extracted from an area size 300 μm x 300 μm within the wear track, and the intensity of the species of interest was normalised by dividing the intensity of the ions of interest by the total ion intensity.

3. Results

3.1. Tribological performance

Fig. 3 shows the tribological performance of the tested samples under severe loading conditions. In Fig. 3(a), Z1 (1 wt% ZDDP) and E1 (1 wt% ethyl oleate) show a friction reduction from 0.13 for base oil PAO4 to 0.10 and 0.11, respectively. For Z02 with only low-concentration ZDDP as additive, less friction reduction is obtained, with the friction coefficient being around 0.12. The combination of 0.2 wt% ZDDP and 0.8 wt % Ester, E08Z02, shows the lowest boundary friction among all tested samples. In part (b) of Fig. 3, Z02 reduces the wear loss volume from $14 * 10^{-4}$ mm^3 for PAO4 to about $12 * 10^{-4}$ mm^3, and Z1 (1 wt% ZDDP) or E1 (1 wt% Ester) alone further improves the wear protection ability. A significant decrease in wear was witnessed for the additive mixture E08Z02, with a wear volume of only 20% of that for lubricant with 1 wt % Ester. Generally, these tribological results clearly show that the synergism between ethyl oleate and ZDDP in low concentration effectively promotes friction and wear reduction, and that the wear protection is greatly enhanced.

To compare the wear mechanisms, the wear tracks were examined with SEM and the images are given in Fig. 4. The surface lubricated with base oil PAO4 exhibits clear abrasive traces and E1, with 1 wt% ester as an additive also shows the appearance of abrasion. On the other hand, images from samples containing ZDDP such as Z02 and E08Z02, present surfaces with a patchy morphology, which evidence the ZDDP tribo-film formation during the tribological process. Additionally, less abrasive wear trace can be seen for these two samples.

3.2. Tribo-film thickness

The thickness of the tribo-film could be one of the important parameters to evaluate the surface protection ability of antiwear additives. Therefore, this work quantified this value based on one method described above in the experimental part, with the detailed implementing procedure provided in the Supplementary Material. Since this work focuses on the influence of the addition of ester to 0.2 wt% ZDDP on the tribo-film properties, the film thickness measurement was conducted on the wear track for E08Z02 and Z02. The tribo-film thicknesses for both E08Z02 and Z02 are shown in Fig. 5. The Z02 oil is shown to form a tribo-film of about 220 nm, while the additive mixture E08Z02 forms a thinner film, about 100 nm thick. Although E08Z02 produces thinner film, it demonstrates a better wear protection ability than Z02. Further investigation was conducted to understand this phenomenon.

3.3. Tribo-film chemical composition

To acquire the information of chemical elements in the tribo-film, wear tracks from E08Z02 and Z02 were analysed using SEM-EDX. The scanned area size is about 250 × 200 μm^2, located in the middle of the wear track. Relevant elements including P, S, Zn, Fe, O and C can be found in the tribo-film, as summarised in Fig. 6. The worn surface from E08Z02 shows higher P, O and Zn content compared to only 0.2 wt% ZDDP wear scar, while E08Z02 shows lower S and Fe content. Since the scanning electron beams penetrate all through the tribo-film, the obtained chemical element concentrations in Fig. 6 are not the exact values for the tribo-films. However, the direct comparison of element content, obtained from the same testing condition, still provides an indication that ethyl oleate facilitates the formation of Zn, P and O film on wear tracks, compared to results from the lubricant with only 0.2 wt% ZDDP (Z02).

The distribution of the representative chemical elements was mapped and shown in Fig. 7. All element images show clear boundaries

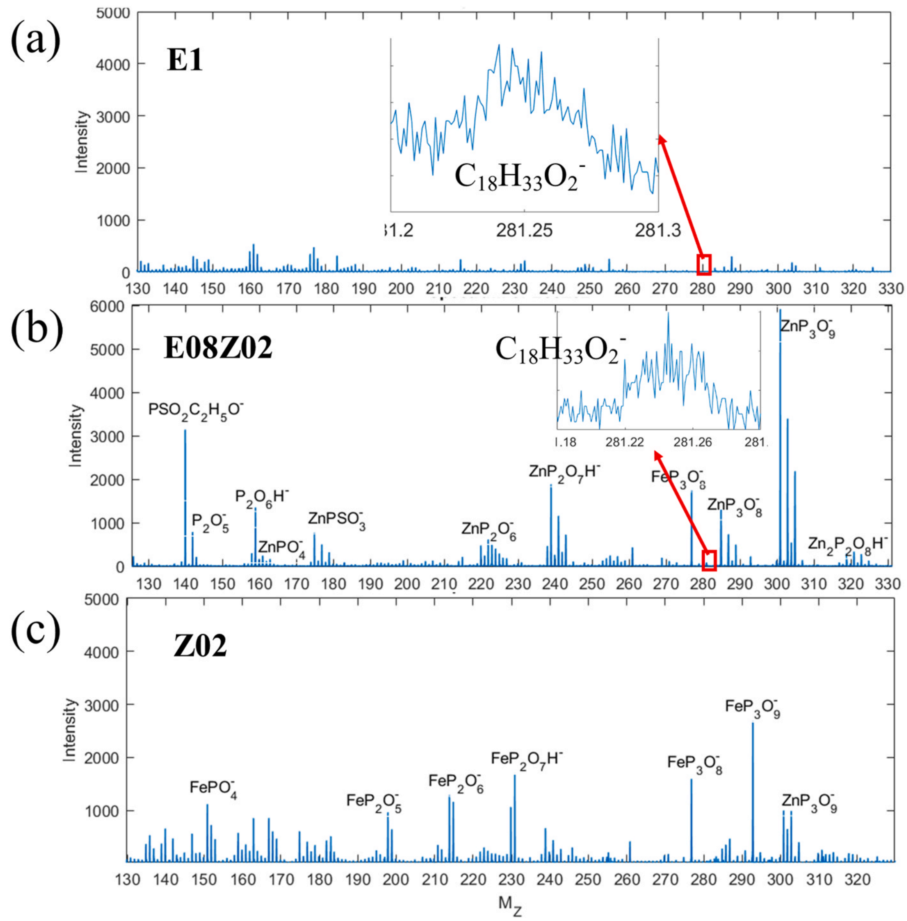


Fig. 9. Negative ions from ToF-SIMS analysis with ion mass from 130 to 330 u, (a) spectrum of worn surface lubricated 1 wt% ethyl oleate (E1), (b) spectrum of worn surface lubricated 0.8 wt% ethyl oleate and 0.2 wt% ZDDP (E08Z02), (c) spectrum of worn surface lubricated 0.2 wt% ZDDP (Z02).

between wear tracks and unworn surface. One easily distinguishable pattern for these two tracks is that the element distribution is much more uniform over the wear track for the additive mixture, E08Z02 than that for 0.2 wt% ZDDP tribo-film. Much higher contrast among different parts within the Z02 wear track can be easily identified, however, this phenomenon is not seen for E08Z02.

For a more detailed chemical characterisation of tribo-films, XAS results are shown in Fig. 8. The *k*-edge curves for P in Fig. 8(a) show almost identical patterns where the peak at the 2152.8 eV energy position can be assigned to metal phosphate [35–37], indicating that ethyl oleate has little influence on the oxidation state of phosphorus. Fig. 8(b) contains the k-edge curves for S, and there are 4 peaks for both samples. The S1, at 2469.6 eV energy position, is the pre-edge peak illustrating the existence of FeS [34]. The second peak, S2 at position 2473.0 eV is assigned to the compound ZnS [34]. The following peak S3 located at 2476.8 eV corresponds to the metal thiosulfate [38] and the last peak S4 at 2481.8 eV is assigned to the metal sulphate [37,39]. Although both samples share the same 4 peaks, the two curves have two very different shapes where E08Z02 has a much higher peak signal for S4, metal sulphate, but lower peaks for S1 and S2, metal sulphide, than those peaks for Z02. In Part (c), E08Z02 and Z02 have almost identical k-edge curves for Zn.

ToF-SIMS was applied to examine the specific molecular fragments on the wear tracks lubricated with E1 (1 wt% ester), E08Z02 (0.8 wt% ester and 0.2 wt% ZDDP) and Z02 (0.2 wt% ZDDP) respectively. One goal of ToF-SIMS analysis was to detect if oleate anion can be found at position 281.2 u, which is the fingerprint peak for ethyl oleate [19,40]. The spectra in Fig. 9 for E1 and E08Z02 indicate the presence of this peak. For both E08Z02 and Z02 in Fig. 9, one shared observation is that ion fragments for both samples contain PO_4, P_2O_5, P_2O_6, P_2O_7, P_3O_8 and P_3O_9 as negative parts, while the major difference lies in the metal element. For E08Z02, zinc phosphate including $ZnPO_4^-$, $ZnP_2O_6^-$, $ZnP_2O_7^-$, $ZnP_3O_8^-$, $ZnP_3O_9^-$ and $Zn_2P_2O_8^-$, are identified in the spectrum, with $ZnP_3O_9^-$ (zinc tri-metaphosphate) as the main fragment. On the other hand, for Z02, iron phosphate including $FePO_4^-$, $FeP_2O_5^-$, $FeP_2O_6^-$, $FeP_2O_7^-$, $FeP_3O_8^-$ and $FeP_3O_9^-$, are the main components, with $FeP_3O_9^-$ (iron tri-metaphosphate) as the main fragment.

Figs. 10 and 11 show the negative ion spectra, with ion mass from 330 to 730 u. With ester as the only additive, E1, no representative ethyl oleate fingerprint peaks can be identified. E08Z02 and Z02, both containing 0.2 wt% ZDDP, metal phosphate accounts for most of the tribo-film. Following a similar trend of ion mass from 130 to 330 u, the wear track from E08Z02 contains mainly zinc phosphate and the polymerisation of phosphate can be witnessed with monomer PO_3. As many as 6 phosphorus atoms in the phosphate fragments can be detected in Fig. 11 (b). On the other hand, in the Z02 spectrum, the detected ions are mainly iron phosphate with 3 phosphorus atoms in all fragments. So, the polymerisation of phosphate for Z02 is not as high as E08Z02. Additionally, the content of FeO gradually increases in the pattern of $FeP_3O_9^-(FeO)_n$ in the Z02 spectrum from Fig. 11 (c), which is not seen for E08Z02 in Fig. 11 (b).

ToF-SIMS also possesses the function to visualise the distribution of relevant ions and the results are given in Fig. 12, containing Zn^+, Fe^+, $ZnP_3O_9^-$ and $FeP_3O_9^-$ together with normalised intensity values for each ion fragment. The scanned images cover across the wear track for E08Z02 but only about half of the wear track for Z02, due to the width of the Z02 track being much larger than that of E08Z02. In the Zn^+ column, both E08Z02 and Z02 have almost all Zn^+ inside the wear track,

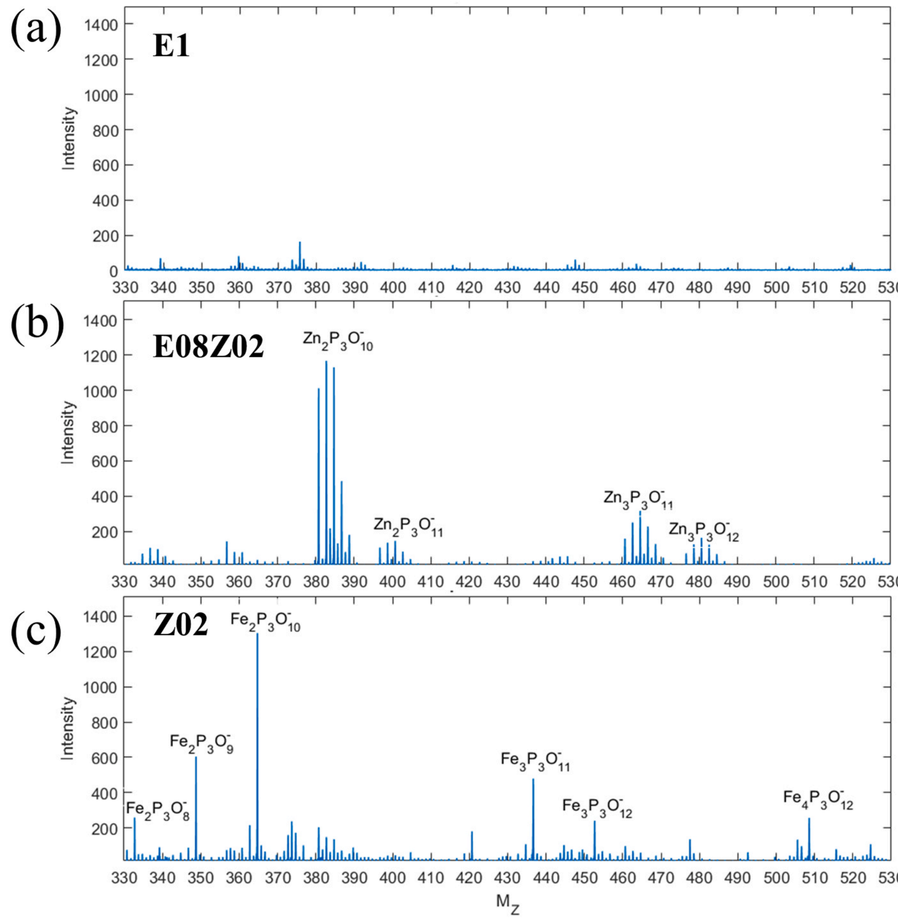


Fig. 10. Negative ions from ToF-SIMS analysis with ion mass from 330 to 530 u, (a) worn surface lubricated 1 wt% ethyl oleate (E1), (b) worn surface lubricated 0.8 wt% ethyl oleate and 0.2 wt% ZDDP (E08Z02), (c) worn surface lubricated 0.2 wt% ZDDP (Z02).

however Zn^+ distribution for E08Z02 is much more homogeneous than that for Z02. In the last line of Zn^+ column, the normalised intensity for the additive mixture is about 4 times larger than that for Z02, clearly indicating a significantly larger amount of Zn^+ in the E08Z02 tribo-film than Z02. In the Fe^+ column, the trend is the opposite. A clear boundary can be seen along the wear track for E08Z02 and there is a nearly undetectable amount of Fe^+ inside the wear track obtained from E08Z02. On the contrary, the whole scanned area for Z02 was covered with Fe^+ and the edge of the wear track cannot be identified. The results also show that the normalised intensity of Fe^+ from the E08Z02 tribo-film was only one-tenth of the value of that for Z02. Regarding the $ZnP_3O_9^-$ (Zinc tri-metaphosphate), the phenomenon follows the Zn^+ trend for both E08Z02 and Z02. The clear boundary again emphasises that the tribological process holds a more important role in forming the tribo-film than the thermal effect. In the last column, both the image analysis and normalised intensity results show that tribo-film from Z02 contains much more $FeP_3O_9^-$ (iron tri-metaphosphate) than that for E08Z02, which is exactly opposite to the trend of $ZnP_3O_9^-$ (zinc tri-metaphosphate). Generally, the worn surface for E08Z02 is mainly covered by evenly distributed zinc-containing compounds including $ZnP_3O_9^-$ with an easily distinguishable edge of wear track. At the same time, tribo-film from Z02 has much more iron-containing compounds located in stripe form, compared to zinc-containing compounds.

4. Discussion

In this study, strong synergism between 0.8 wt% ester and 0.2 wt% ZDDP was observed showing lower friction and wear than those obtained with either 1 wt% ester or 1 wt% ZDDP alone as an additive in base oil PAO4. These results have not been found in previous studies and highlight the potential of applying a bio-based ester to partially decrease the ZDDP usage, while improving friction and wear performance, especially for severe conditions under boundary regime. Moreover, the ester group is relatively chemically inert, so that it can stay stable in a fully formulated oil system without reacting with other components. This could again enlarge the possible future application in producing greener lubricants.

The importance of having ZDDP in the additive mixture lies in the formation of a strong protecting tribo-film to reduce wear loss and abrasion, proved by the SEM images in Fig. 4. SEM-EDX analysis shows that the ethyl oleate exhibits the function of promoting a zinc phosphate rich tribo-film formation rather than hindering the adsorption of ZDDP molecules. Additionally, a more uniform element distribution for E08Z02 from SEM mapping demonstrates that ester can homogenise the tribo-film generated from a low concentration ZDDP throughout the contact region, when compared with the concentrated stripe pattern presented in Z02 lubricated samples.

Film thickness measurements from AFM show that Z02 produced a thicker film than E08Z02. According to the obtained tribological results, E08Z02 shows only 10% wear loss of Z02, then it can be stated that caution should be taken when linking tribo-film thickness directly to wear protection performance. A previous study also gave a similar observation under reciprocating condition. Although the steady-state tribo-film thickness is thinner than the one obtained in the initial film formation process, upper stationary pins are well protected and little wear loss occurs [41]. This shows that the specific tribo-film composition shares an important role in wear protection, in Figs. 9, 10 and 11 that there exists a great difference in the tribo-film composition between

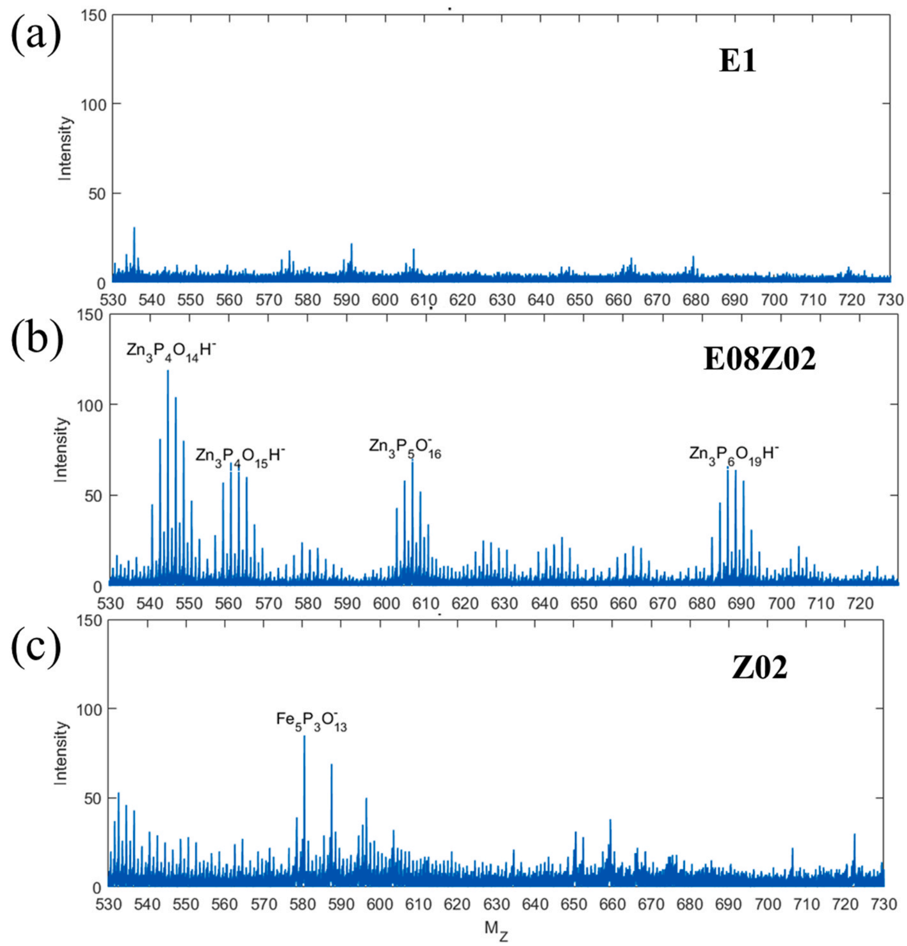


Fig. 11. Negative ions from ToF-SIMS analysis with ion mass from 530 to 730 u, (a) worn surface lubricated 1 wt% ethyl oleate (E1), (b) worn surface lubricated 0.8 wt% ethyl oleate and 0.2 wt% ZDDP (E08Z02), (c) worn surface lubricated 0.2 wt% ZDDP (Z02).

E08Z02 and Z02.

An examination on the tribo-film composition was conducted with the XAS technique. Both P and Zn in wear tracks from E08Z02 and Z02, show identical chemical states and curve shapes. Although E08Z02 and Z02 generated similar sulphur-containing compounds such as FeS, ZnS, metal thiosulphate and metal sulphate, most of the sulphur exists in the form of sulphate compound for E08Z02 whereas sulphide product accounts for a larger proportion of the sulphur-containing species in the Z02 tribo-film. In agreement with what was observed in this work, previous studies have shown a similar trend that under severe conditions such as high contact pressure, and high temperature, the ZDDP tribo-film is composed of a larger amount of sulphide and less sulphate compounds compared to milder conditions [34,36]. In the present work, a milder contact from the additive mixture is manifested by a lower friction coefficient in the tribological tests. This represents a shear force reduction from the reciprocating contact, enabling the ZDDP molecules to remain within the contact until the tribo-film is fully developed, leaving the S-containing species oxidized to the highest oxidation state (+6) in sulphate products. On the other hand, for Z02, when the contact condition is extremely harsh, the adsorbed additive molecules can be quickly rubbed away from the contact, together with the oxidised S species. Then, fresh additive molecule approaches contacts again together with a supply of sulphide compounds replacing the previous sulphate product. Therefore, the tribo-film shows a larger proportion of sulphide for Z02, without the assistance of ethyl oleate to mitigate shear.

For both E1 and additive mixture E08Z02, the fingerprint peak, oleate anion $C_{17}H_{33}COO^-$ for ethyl oleate was detected in the negative ion spectrum in Fig. 9(a) and (b). Considering the tribological results that friction for E08Z02 is much lower than for Z02, it indicates that tribo-film from ZDDP enhances the adsorption of ester fragments on the contact surface, consequently exhibiting lower friction. In addition, the additive combination processes a better tribology response than E1, 1 wt % ester although the ester fragment also exists on the wear tracks from E1. This implies that the interaction between ester fragments and iron surface is not the key factor to protect the surface against severe reciprocation, rather the high wear-resistance ZDDP tribo-film plays an essential role in stimulating the function of ester fragments to reduce friction. Although ToF-SIMS is powerful in post-analysis of worn surface, this technique misses the in-situ information for the contacts, especially for the dynamic adsorption process of ester fragments on the ZDDP film. Hence, it can be helpful to apply QCM (Quartz crystal microbalance) technique to study the absorbing behaviour of ester on the zinc phosphate surface in future investigations.

There is an important observation that E08Z02 tribo-film is composed of mainly zinc phosphate with representative fragment $ZnP_3O_9^-$ (zinc tri-metaphosphate), whereas iron phosphate is the main component of Z02 tribo-film with representative fragment $FeP_3O_9^-$ (Iron tri-metaphosphate). Moreover, the polymerisation of phosphate can be seen on the worn surface lubricated with E08Z02 which is not seen for Z02. Similar spectra for zinc meta-phosphate and iron meta-phosphate have been found in [42], although the surface in the referred study was chemically synthesised [42]. Comparing the negative spectra between E08Z02 tribofilm and zinc metaphosphate from [42], the same fragments were detected proving the correct identification of finger-print peaks within this work. For the spectra for iron meta-phosphate from [37] and Z02, although the $FeP_3O_9^-$ (Iron

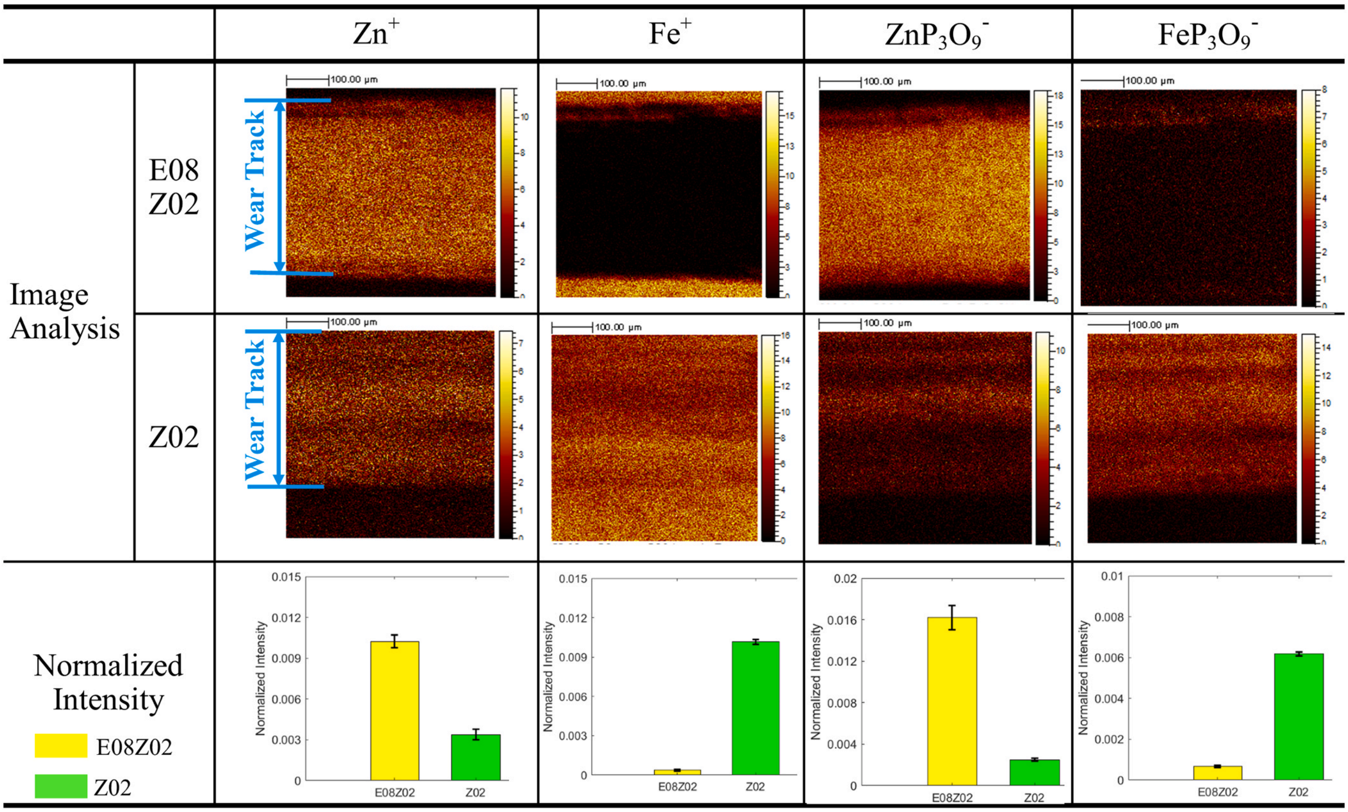


Fig. 12. ToF-SIMS image analysis to illustrate the distribution of representative ions. Note: the normalised intensity value was obtained for the isotope of 64 Zinc (Atomic mass unit 64).

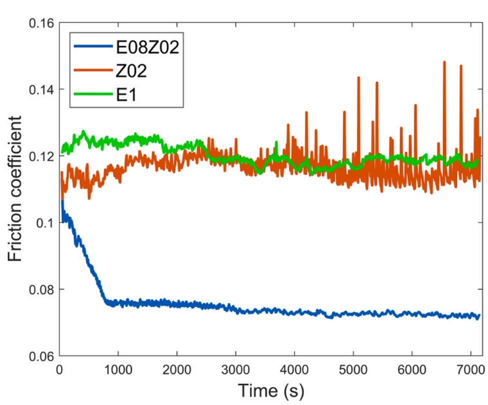


Fig. 13. Friction development against time under reciprocation contacts for additive combination E08Z02 (0.8 wt% ethyl oleate and 0.2 wt% ZDDP) in the left part and only 0.2 wt% ZDDP as additive.

tri-metaphosphate) has the highest peak for both cases, the polymerising phenomenon can be only seen for a chemically synthesised surface, not for the tribological surface obtained from the Z02 oil. This indicates that ethyl oleate leads the reaction of low concentration of ZDDP to a path resembling a chemical reaction or low-shear reaction process, where elements from only the low-concentration ZDDP in additive combination can fully participate in the tribo-film formation. On the other hand, with only 0.2 wt% ZDDP as additive, zinc and phosphorus cannot be heavily involved in the tribological reaction and only short-chain iron phosphate formation is favoured under severe shear condition. Another difference is that, with the increase of fragment weight, the content of FeO increases for Z02 rather than the PO_3 monomer for E08Z02. A similar phenomenon that higher FeO has a negative impact on the polymerisation phosphate can be also found in [4]. These two major divergences of the tribo-film above can explain why E08Z02 possesses much better wear protection than Z02. Glassy zinc polyphosphate formed from ZDDP contributes most to wear reduction for ZDDP [1], which is mainly found in the E08Z02 film. However, shorter-chain iron polyphosphate with more FeO for Z02 cannot perform as well as zinc polyphosphate.

Considering the tribo-film distribution, both SEM-EDX element mapping in Fig. 7 and ToF-SIMS image analysis in Fig. 12 correlate with each other well, confirming that E08Z02 possesses a more homogeneous Zn distribution than Z02, although SEM mapping probes a thicker layer than ToF-SIMS. The reason for the evenly distributed film for E08Z02 can be plausibly given from the aspect of the film formation process. At the beginning of the tribological process, there exist both ZDDP and ester molecules on the iron substrate. As discussed above, the ester molecules decrease the shear force, providing a mild condition for ZDDP, especially within high contact pressure zones, so that the whole contact surface shares a similar environment, leading to a uniform and gradual growth of zinc polyphosphate film all over the wear track. Therefore, lubricant with the additive combination generates a homogeneous tribo-film. As support for this explanation, the friction curve against time was plotted in Fig. 13. During the first 600 s of the whole tribological process, the friction for E08Z02 goes down gradually clearly indicating a low friction film was produced in a progressive way. This friction development implies ester molecules shifted the reaction between 0.2 wt% ZDDP to iron surface from a fast reaction to a gradual process, so that ZDDP molecules can undergo almost identical tribochemical reaction, consequently forming a uniform tribo-film containing more elements of zinc, and phosphorus from the ZDDP.

To illustrate the key contribution of the bio-based ester, a schematic view of the formed tribo-films formation is shown in Fig. 14. From 0.2 wt% ZDDP oil, a 200 nm thick tribo-film is formed, consisting of short-chain iron phosphate located in a stripe pattern with embedded

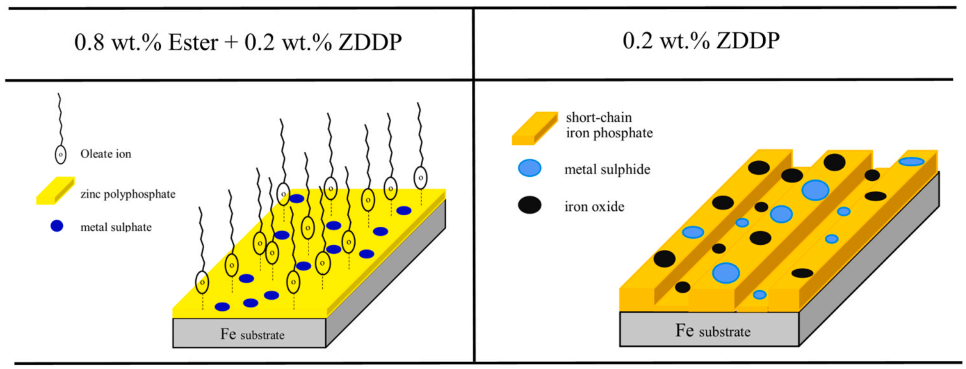


Fig. 14. Schematic images for the tribo-films generated from additive combination E08Z02 (0.8 wt% ethyl oleate and 0.2 wt% ZDDP) in the left part and only 0.2 wt % ZDDP as an additive in the right part.

metal sulphide and iron oxide clusters, seen from right part of Fig. 14. When the additive combination is used (E08Z02 containing 0.8 wt% ethyl oleate and 0.2 wt% ZDDP), the tribo-film consists of a uniformly distributed zinc polyphosphate layer, containing metal sulphates. Oleate ions are deposited on top of the tribo-film.

Based on the features of the tribo-film, a synergistic performance can be explained as bio-based ester reduces the shear forces on the contact promoting the formation of a uniform polyphosphate tribo-film that greatly reduces the wear loss. Furthermore, the tribo-film promotes the adsorption of ester fragments, which further decreases the friction, outperforming both 1 wt% ester or 1 wt% ZDDP in base lubricant.

5. Conclusions

As an endeavour to reduce the impact of lubricant additives on environment while retaining or modifying tribological performance, ethyl oleate, readily obtained from bio-based resources was investigated in terms of tribological performance under severe reciprocating contacts together with low-concentration ZDDP. Various surface analysing techniques have been conducted on the wear tracks from the additive mixture and low concentration ZDDP to have a deeper understanding of the tribological response. The main conclusions are:

- Strong synergism between bio-based ester, ethyl oleate, and ZDDP has been reported for the first time. This lubricant combination showed a 15% friction reduction and 80% wear reduction benchmarked to base oil under severe reciprocation movement.
- One function of 0.2 wt% ZDDP in the additive combination is to provide essential resource, namely Zn and P, to form a protecting tribo-film to significantly reduce wear loss. More importantly, the zinc polyphosphate tribo-film promotes the adsorption of ester fragments.
- The bio-based ester in the combination decreases the shear in contacts, providing a mild environment so that even very low concentration ZDDP can form a uniform glassy zinc polyphosphate tribo-film which is not witnessed for only 0.2 wt% ZDDP as additive. Another role of ester is to provide the molecular fragment, oleate anion on the ZDDP film, further improving the tribological performance, compared to 1 wt% ZDDP or 1 wt% ester.
- A thicker tribo-film composed of short-chain iron phosphate does not guarantee better tribological performance than a thinner film with zinc polyphosphate generated from the additive combination, indicating the specific composition of tribo-film shares a more critical role in protecting the surface.

The obtained results underline the significant potential for a simple bio-based ester, ethyl oleate, to partially replace ZDDP as a boundary lubrication additive, with the benefit of both synergistic phenomenon in tribology and lower SAPS content. It also exhibits prospects of being further investigated in a fully formulated lubricant due to its relatively inert property, towards the development of greener lubricants.

Statement of originality

12) The paper has not been published previously, that it is not under consideration for publication elsewhere. If this work is accepted, it will not be published elsewhere in the same form, in English or in any other language, without the written consent of the publisher.
13) The paper does not contain material which has been published previously, by the current authors or by others, of which the source is not explicitly cited in the paper.

CRediT authorship contribution statement

Shu Ju: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Espejo Cayetano:** Writing – review & editing, Validation, Supervision, Methodology, Conceptualization. **Kalin Mitjan:** Writing – review & editing, Validation, Supervision, Funding acquisition, Formal analysis, Conceptualization. **Morina Ardian:** Writing – review & editing, Validation, Supervision, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.triboint.2024.109252.

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