High friction mechanism of ZDDP tribofilm based on in-situ AFM observation of nano-friction and adhesion properties

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Abstract

Zinc dialkyl dithiophosphate (ZDDP) is a typical anti-wear additive that forms tribofilm on sliding surfaces and prevents adhesion wear but increases the friction force. In this study, the nano-friction and adhesion properties of ZDDP tribofilms were investigated by performing in-situ observations by atomic force microscopy to explore the relationship between the formation process and physical properties of ZDDP tribofilm. The results showed that the nano-friction force increased with the formation of the ZDDP tribofilm. In addition, the adhesion force on the ZDDP tribofilm increased with the friction force. It was confirmed that the Young's modulus and nanoindentation hardness of the ZDDP tribofilms were lower than those of steel. However, the contact areas calculated using the Hertz contact theory were similar. In addition, the shear strengths, calculated with the contact areas of the Hertz model, of the ZDDP tribofilm were substantially higher than those of steel. From the above, it was hypothesized that the high friction force of the ZDDP tribofilm was derived from the high adhesion layer at the surface.

1. Introduction

Recent environmental issues have emphasized the importance of improving automobile fuel efficiency [1–3]. The use of lower viscosity oils is one way to improve fuel efficiency, which reduces friction in the form of fluid resistance in automotive engines under hydrodynamic lubrication [2]. However, a lower viscosity results in seizure birth and increased wear under boundary and mixed lubrication conditions. Therefore, lubricants need to be optimized to improve the lubrication performance of sliding elements [3].

Anti-wear additives play essential roles in improving and expanding the lifespans of engine components. A typical anti-wear additive, zinc dialkyl dithiophosphate (ZDDP), is a multifunctional additive essential for lubricants owing to its anti-oxidation, anti-seizure, and anti-wear properties, has been utilized for approximately 80 years [4–6]. ZDDP forms a tribofilm during rubbing to protect the surface by preventing direct metal/metal contact [7]. ZDDP generally forms a rough and patchy film, a so-called pad-like structure, with a thickness of approximately 50–150 nm [4–6]. ZDDP tribofilms consist of a bottom layer of iron/zinc sulfide, middle layer of iron/zinc phosphates and polyphosphate, and top layer of mixed oxide and zinc sulfide [4, 7]. The anti-wear action of phosphates/polyphosphate is to wear self-sacrificingly instead of substrates and to protect adhesive wear [8].

On the other hand, ZDDP tribofilms also have the disadvantage of increasing friction, although tribofilms have high anti-wear properties [4, 9–11]. Miklozic et al. reported that the friction coefficient increases when ZDDP forms a tribofilm [11]. In addition, they considered that the formation of a rough ZDDP tribofilm resulted in the inhibition of fluid entrainment into the contact area and increased friction [11]. Meanwhile, the friction mechanism was not described in terms of the effects of the adhesion property on the friction at each contact junction. The friction force is known to be influenced by the real area of contact comprising the sum of each junction of the nanoscale [12, 13]. Hence, to explain the high friction mechanism of ZDDP, it is necessary to investigate the friction mechanism with a focus on the effects of

the adhesion and mechanical properties of ZDDP tribofilms on a single asperity. Therefore, we attempted to observe nanoscale phenomena using atomic force microscopy (AFM).

The in-situ AFM methods is considered to be one of the most useful techniques for exploring the friction mechanism of the tribofilm formed in lubricants [6, 8, 14–16]. Gosvami et al. succeeded in observing the formation process of ZDDP-derived reaction films in lubricating oil using AFM [6]. They reported that the rate of reaction film formation increased exponentially with increasing temperature and contact pressure [6, 8]. They also made it possible to observe the friction force in the ZDDP solution [15, 16]. In addition, AFM can be used to investigate the physical properties of nanomaterials, such as the adhesion property [17, 18]. Therefore, using AFM, the effects of the adhesion and nano-friction properties of ZDDP tribofilms on a single asperity can be explored and the high friction phenomena of ZDDP on the nanoscale can be explained.

In this study, we investigated the physical properties of ZDDP tribofilm during in-situ AFM observation to reveal the friction mechanism of the ZDDP tribofilm. We used the in-situ AFM method to measure the physical properties such as the frictional and mechanical properties, as well as the adhesion force between the AFM tip and sliding surface, to analyze the friction mechanism of the ZDDP tribofilm. In addition, we conducted scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS) and nanoindentation measurements to investigate the chemical composition, Young's modulus, and hardness of the ZDDP tribofilm.

2. Experimental

2.1 Lubricants and materials

Poly- α -olefin 4 (PAO4) and a ZDDP, which has an alkyl structure of secondary C3/C6 mixed, were used as the base oil and lubricant additive, respectively. The lubricants were formulated so that the phosphorus content was 0.08 mass%. Bearing steel (AISI 52100 with a hardness of 700 HV) was used for in-situ AFM as the sliding substrate.

2.2 In-situ AFM sliding tests

Figure 1 shows a schematic of the in-situ AFM sliding tests. In-situ AFM sliding tests were performed using a commercial AFM system (Nano Navi, Hitachi High-Tech, JP) with a silicon tip (SI-DF20, Hitachi High-Tech, JP).

We calculated the normal and torsional spring constants, k_n and k_t using dimensional methods from the following formulas [19, 20]:

$$k_n = \frac{E_c w t^3}{4l^3} \quad (1)$$

$$k_t = \frac{G_c w t^3}{3l(h + t/2)^2} \quad (2)$$

where E_c and G_c are the elastic and shear moduli of the cantilever, respectively; w is the width of the cantilever; h is the height of the cantilever tip; t is the thickness of the cantilever; and l is the length of the cantilever. The cantilever had a tip radius of 140 nm (Fig. S1). Additionally, the elastic modulus was that of Si (100), and the shear modulus was calculated using the following equation [12, 21, 22]:

$$G_c = \frac{E_c}{2(1 + \nu_c)} \quad (3)$$

where ν_c is Poisson's ratio of the cantilever. In addition, we set the normal and lateral forces by detecting the normal deflection of the position-sensitive photodetector (PSPD). Therefore, it was necessary to determine the sensitivities of the AFM optical system for normal and lateral deflection, S_n and S_l , respectively [20, 23, 24]. The sensitivity of the AFM optical system for the normal deflection was calculated from the gradient of the force-displacement curve (FD curve), and that for lateral deflection was calculated using the following formula:

$$S_l = \alpha \frac{h + \frac{t}{2}}{l} S_n \quad (4)$$

where α is a unique correction constant used to correct the output ratio between the normal and lateral voltage signals. In this experiment, we calculated the normal and lateral forces, F_n and F_l , as follows:

$$F_n = k_n S_n V_n \quad (5)$$

$$F_l = k_t S_l V_l \quad (6)$$

where V_n and V_l are the photo potentials of the PSPD in the normal and lateral directions, respectively [23–25].

Using Eqs. (2) and (4), Eq. (6) can then be rewritten as

$$F_l = \alpha \frac{G_c w t^3}{3l^2 \left(h + \frac{t}{2}\right)} S_n V_l \quad (7)$$

Table 1 shows the normal and torsional spring constants, normal and lateral sensitivity, unique correction constant (α), elastic and shear modulus, Poisson's ratio, and each measurement parameter of the cantilever [8, 9]. To measure the shape of each cantilever, we used 3D laser scanning microscopy (VK-X150, KEYENCE, Japan) and SEM (TM4000, Hitachi High-Tech, Japan).

In-situ AFM sliding tests were conducted by imaging of the contact mode until 600 cycles with a normal force of 2000 nN, sliding velocity of 20 Hz, temperature of 120 °C, and an AFM image range of 2.0 $\mu\text{m} \times$

2.0 μm . After that, we acquired an image at a range of $4.0 \mu\text{m} \times 4.0 \mu\text{m}$ to confirm the tribofilm growth on a sliding area with a normal force of 800 nN and sliding velocity of 2.0 Hz. In addition, FD curves were obtained every 50 cycles with an indentation depth of approximately 60 nm and indentation frequency of 10 Hz.

Table 1
Each parameter using the AFM measurement

Parameter	Value	
Length, l	232.1	μm
Width, w	31.1	μm
Thickness, t	4.5	μm
Hight of the tip, h	12.5	μm
Elastic modulus, E_c	130	GPa
Shear modulus, G_c	50	GPa
Poisson's ratio, ν	0.28	
Normal spring constant, k_n	7.4	N/m
Torsional spring constant, k_t	942.5	N/m
Sensitivity of AFM optical system (normal), S_n	82.7	nm/V
Sensitivity of AFM optical system (lateral), S_l	2.10	nm/V
Unique correction constant of AFM, α	0.4	

2.3 Surface analysis

An analysis of the surface was conducted on the AFM sliding area using an SEM/EDS (SUPRA40, ZEISS, DE) and nanoindentation system (iMicro, Nanomechanics, US). After performing the in-situ AFM sliding tests, each test specimen was cleaned by slowly shaking it in 30 ml of n-hexane for 30 s.

2.3.1 SEM/EDS

SEM/EDS was conducted to investigate the chemical composition of the rubbed surface at 0 (outside), 200, 400, and 600 cycles by in-situ AFM sliding tests under an accelerating voltage of 5 keV.

2.3.2 Nanoindentation measurement

Continuous stiffness measurements (CSMs) were performed to measure the Young's modulus and nanoindentation hardness of the tribofilm at an indentation depth of 100 nm [26]. The CSM method has the advantage of continuously determining the Young's modulus and hardness to the indentation depth.

The principle of the CSM method is to determine the stiffness from the oscillatory component of the displacement and the phase difference between the load and displacement, which is done by applying a small AC load to the DC component of the indentation load change [26]. The Young's modulus was calculated assuming that the mechanical properties on the surface were uniform, and the Poisson's ratio of the sample was 0.3. A diamond Berkovich tip (Young's modulus: 1140 GPa, Poisson's ratio: 0.07, tip radius: less than 20 nm) was used for the nanoindentation measurements.

3. Results And Discussion

3.1 In-situ AFM sliding test

Figure 2 shows the friction behavior acquired using the in-situ AFM sliding tests. As shown in Fig. 2(a), the base oil exhibited a constant friction force up to 600 cycles, and the friction force was 55 nN at 600 cycles. In Fig. 2(b), however, the friction force in the ZDDP solution gradually increased with sliding until 300 cycles. After 300 cycles, the friction force became stable with a high friction force. The friction force was measured to be 116 nN at 600 cycles. From these results, we found that ZDDP also increased the friction force on single asperity contacts.

Figure 3 shows AFM images at 0 and 600 cycles of the tribofilm area rubbed in PAO4. These results show that there was no wear on the sliding steel surface. Figure 4 shows AFM images from 0 to 600 cycles in ZDDP solution. These images reveal that tribofilm was formed on the sliding area. Furthermore, we confirmed that the shape of the tribofilm was rough. ZDDP is known to form a rough tribofilm called a pad-like structure on a macroscale sliding test [4, 6, 8]. Figure 5 shows the thickness of the tribofilm formed in ZDDP solution as the number of sliding cycles increased. These results show that the thickness of the tribofilm increased linearly until 600 cycles when the thickness was approximately 100 nm. Furthermore, according to Fig. 2, the friction force of the initial sliding cycle was lower than that at 600 cycles (Fig. 2 (b)). Therefore, it is considered that the formation of the ZDDP tribofilm causes an increase in the friction force.

3.2 Measurement of adhesion property

Figure 6 shows FD curves on steel (0 cycles) and tribofilm (after 600 cycles) in ZDDP solution. These results confirm the detection of the adhesion force on steel and tribofilm. Therefore, it is possible to evaluate the adhesion properties on steel and tribofilm in ZDDP solution. The FD curves showed that the adhesion forces on the steel and tribofilm were 1.7 nN and 14.0 nN, respectively. The adhesion property difference between the steel and tribofilm indicated that the adhesion property of ZDDP was approximately eight times higher than that of steel. Figure 7 shows the adhesion force on the sliding area in the ZDDP solution as a function of the number of sliding cycles. These results showed that the adhesion force increased with the number of sliding cycles. Hence, we found that the adhesion force increased with the growth of the ZDDP tribofilm.

3.3 SEM/EDS analysis

To analyze the chemical composition of the tribofilm formed by ZDDP, we conducted SEM/EDS analysis on each sample surface rubbed after 0 (outside), 200, 400, and 600 cycles. Figure 8 shows the SEM images and EDS profiles obtained after 0, 200, and 600 cycles. The SEM images show that a tribofilm was formed on each sliding area at 200 and 600 cycles and that the amount of the tribofilm increased with the number of sliding cycles, similar to the AFM results. Additionally, from the EDS profile, we confirmed the peaks of Zn, P, and S at 200 and 600 cycles. These findings demonstrate that the tribofilm was composed of ZDDP-derived elements. Therefore, we assumed that ZDDP reacted on the steel surface and formed a tribofilm on the single asperities. In contrast, the peaks of Zn, P, and S at 0 cycles were quite low because the tribofilm was not formed outside the sliding area.

Figure 9 shows the atomic concentrations of Zn, P, and S at 0–600 cycles. These results indicate that the atomic concentrations of Zn, P, and S increased up to 600 cycles. ZDDP is known to form Fe/Zn sulfide and phosphates during sliding [4, 27]. Therefore, we assumed that ZDDP formed a tribofilm composed of sulfide and phosphates with sliding cycles on a single asperity.

3.4 Nanoindentation measurement

Nanoindentation tests were conducted to examine the Young's modulus and hardness of the ZDDP tribofilm formed by performing in-situ AFM sliding tests. Figure 10 shows the results of the nanoindentation tests on the steel and ZDDP tribofilm. The results show that the Young's modulus and nanoindentation hardness of the ZDDP tribofilm were lower than those of the steel surface, regardless of the indentation depth. The Young's modulus of steel and the ZDDP tribofilm were measured to be 183 GPa and 159 GPa, respectively. The nanoindentation hardnesses of the steel and ZDDP tribofilm were 8.11 GPa and 6.46 GPa, respectively, at an indentation depth of 10 nm. Many studies have reported that the nanoindentation hardnesses of ZDDP tribofilms range from 1 to 10 GPa, with significant variations observed [28–39]. In addition, Nehme et al. measured the nanoindentation hardnesses of tribofilms formed at higher and lower contact loads and showed that a higher contact pressure causes the formation of harder and thicker tribofilms in fully formulated oil containing ZDDP [32]. Therefore, we assumed that the variation in the ZDDP tribofilm hardness in previous studies was caused by the differences in contact pressure during the sliding test. However, most of these studies showed that the Young's modulus and nanoindentation hardnesses of ZDDP tribofilms are much softer than those of steel surfaces [28, 30]. Accordingly, we assumed that the differences in Young's modulus and nanoindentation hardness between the steel and ZDDP tribofilm were low compared to previous research because the high contact load at a single asperity resulted in the formation of a hard ZDDP tribofilm.

3.5 Assumption of contact area on ZDDP tribofilm

We focused on the contact area during the in-situ AFM sliding test to examine the friction mechanism. We calculated the maximum contact pressure from the nanoindentation results at an indentation depth of 10 nm using the Hertz model. The maximum contact pressure p_{max} was calculated using the following formulas [17]:

$$p_{max} = \frac{3W}{2\pi a^2} \quad (8)$$

$$a = \left(\frac{3WR'}{4E'} \right)^{\frac{1}{3}} \quad (9)$$

$$\frac{1}{E'} = \frac{1-\nu^2}{E} + \frac{1-\nu_c^2}{E_c} \quad (10)$$

$$\frac{1}{R'} = \frac{1}{R} + \frac{1}{R_c} \quad (11)$$

where a is the contact radius; W is the normal load (2000 nN); E' and R' are the reduced Young's modulus and reduced radius of curvature, respectively; and R_c is the radius of the cantilever. The Poisson's ratio of the steel and ZDDP tribofilm ν was assumed to be 0.3 [28].

The calculated maximum contact pressures on the steel and ZDDP tribofilm with the AFM tip were 5.14 GPa and 4.94 GPa, respectively. These values are lower than the measured nanoindentation hardnesses, which were 8.11 GPa and 6.46 GPa for the steel and ZDDP tribofilm, respectively. Therefore, the deformation is considered to be the range of the elastic deformation between the AFM tip and sliding surface. For this reason, we calculated the contact area πa^2 from the Hertz model.

Figure 11(a) shows the contact areas of the steel and ZDDP tribofilm. From these results, we confirmed that the values of the contact area were quite similar between the steel and ZDDP tribofilms. Therefore, we assumed that the main cause of high friction of the ZDDP tribofilm was not the increase in the contact area.

3.6 Assumption of shear strength on ZDDP tribofilm

The friction force F_l is generally given by the product of the shear strength and contact area as follows:

$$F_l = \tau A_r \quad (12)$$

where τ and A_r are the shear strength and contact area, respectively. Therefore, to identify the effects of high friction by the ZDDP tribofilm, we examined the shear strength of steel and the ZDDP tribofilm using friction forces at 600 cycles (F_l) and the contact areas from Hertz model (A_r).

Figure 11(b) shows the shear strength of the steel and ZDDP tribofilm after 600 cycles. We confirmed that there was a significant difference in shear strength between the steel and ZDDP tribofilms. Therefore, we assumed that the increase in friction force by the ZDDP tribofilm was caused by the increase in shear strength on a single asperity.

3.7 Relationship between adhesion and nano-friction property

From the FD curve results, it was confirmed that the adhesion force increased with the formation of the ZDDP tribofilm. In addition, Section 3.6 showed that the increase in friction force was due not to the contact area, but rather to the shear stress. Figure 12 confirms the correlation between the adhesion force and nano-friction force. Oblak and Kalin investigated the macroscopic friction and adhesion properties of tribofilms formed on steel and diamond-like carbon coatings and suggested that the adhesion property was directly correlated with the macroscopic friction on each tribofilm [19]. Therefore, we assumed that the increase in the nano-friction force on the ZDDP tribofilm was also due to the increase in the adhesion of the ZDDP tribofilm.

4. Conclusions

We conducted an in-situ AFM sliding test, SEM/EDS analysis, and nanoindentation measurements to explain the friction mechanism of ZDDP. The following conclusions were drawn:

- (1) From the in-situ AFM sliding test, we confirmed that the friction in the ZDDP solution increased with increasing tribofilm growth. The SEM/EDS analysis confirmed that the chemical composition of the tribofilm formed by in-situ AFM sliding tests included Zn, P, and S. These results indicate that the formation of the ZDDP tribofilm caused high friction in the ZDDP solution on single asperities.
- (2) We confirmed that the adhesion force increased with the ZDDP tribofilm growth from the FD curves in the ZDDP solution. This result indicates that the ZDDP tribofilm has a high adhesion property.
- (3) We confirmed from the nanoindentation results that the Young's modulus and nanoindentation hardness of the ZDDP tribofilm were lower than those of the steel surface. However, the contact areas calculated using the Hertz contact theory were quite similar. We therefore assumed that the influence of the contact area on the friction property was low in our experiments.
- (4) We confirmed the relationship between the adhesion and nano-friction force and found a correlation. In addition, the shear strength of the ZDDP tribofilm calculated using the Hertz model was substantially higher than that of steel. These results suggest that the high adhesion force of ZDDP tribofilm contributes to the high friction.

Declarations

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Competing interest

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

Author Contributions

Kaisei Sato: Conceptualization, performing and interpreting all measurements, writing – original draft, methodology, and applying analysis

Seiya Watanabe: Interpreting AFM measurements, Reviewing

Shinya Sasaki: Supervision, Reviewing, Writing, Interpreting all measurements, and Editing

References

1. Holmberg, K., Erdemir, A.: The impact of tribology on energy use and CO₂ emission globally and in combustion engine and electric cars. *Tribol Int.* **135**, 389–369 (2019). <https://doi.org/10.1016/j.triboint.2019.03.024>
2. Maroto-Centeno, J.A., Pérez-Gutiérrez, T., Fernández-Ruiz-Morón, L., Quesada-Pérez, M.: Prediction of fuel economy performance of engine lubricants based on laboratory bench tests. *Tribol Int.* **94**, 67–70 (2016). <https://doi.org/10.1016/j.triboint.2015.07.041>
3. Cui, J., Oberoi, S., Briggs, S., Goldmints, I.: A viscosity modifier solution to reconcile fuel economy and durability in diesel engines. *Tribol Int.* **101**, 43–48 (2016). <https://doi.org/10.1016/j.triboint.2016.03.038>
4. Spikes, H.: The history and mechanisms of ZDDP. *Tribol Lett.* **17**, 469–489 (2004). <https://doi.org/10.1023/B:TRIL.0000044495.26882.b5>
5. Zhang, J., Spikes, H.: On the mechanism of ZDDP antiwear film formation. *Tribol Lett.* **63** (2016). <https://doi.org/10.1007/s11249-016-0706-7>
6. Gosvami, N.N., Bares, J.A., Mangolini, F., Konicek, A.R., Yablon, D.G., Carpick, R.W.: Tribology. Mechanisms of antiwear tribofilm growth revealed in situ by single-asperity sliding contacts. *Science*. **348**, 102–106 (2015). <https://doi.org/10.1126/science.1258788>
7. Kontou, A., Taylor, R.I., Spikes, H.A.: Effects of dispersant and ZDDP additives on fretting Wear. *Tribol Lett.* **69** (2021). <https://doi.org/10.1007/s11249-020-01379-6>
8. Dorgham, A., Parsaeian, P., Azam, A., Wang, C., Morina, A., Neville, A.: Single-asperity study of the reaction kinetics of P-based triboreactive films. *Tribol Int.* **133**, 288–296 (2019). <https://doi.org/10.1016/j.triboint.2018.11.029>
9. Dawczyk, J., Morgan, N., Russo, J., Spikes, H.: Film thickness and friction of ZDDP tribofilms. *Tribol Lett.* **67** (2019). <https://doi.org/10.1007/s11249-019-1148-9>
10. Zhang, J., Ueda, M., Campen, S., Spikes, H.: Boundary friction of ZDDP tribofilms. *Tribol Lett.* **69**, 8 (2021). <https://doi.org/10.1007/s11249-020-01389-4>
11. Miklozic, K.T., Forbus, T.R., Spikes, H.A.: Performance of friction modifiers on ZDDP-generated surfaces. *Tribol Trans.* **50**, 328–335 (2007). <https://doi.org/10.1080/10402000701413505>

12. Bhushan, B.: Springer Handbook of Nanotechnology, 3rd edn. Springer, Berlin (2010).
<https://doi.org/10.1007/978-3-642-02525-9>
13. Bowden, F.P., Taber, D.: The Friction and Lubrication of Solids. Oxford University Press, Oxford (2001)
14. Israelachvili, J.N., Chen, Y.L., Yoshizawa, H.: Relationship between adhesion and friction forces. *J. Adhes. Sci. Technol.* **8**, 1231–1249 (1994). <https://doi.org/10.1163/156856194X00582>
15. Khare, H.S., Gosvami, N.N., Lahouij, I., Milne, Z.B., McClimon, J.B., Carpick, R.W.: Nanotribological printing: A nanoscale additive manufacturing method. *Nano Lett.* **18**, 6756–6763 (2018).
<https://doi.org/10.1021/acs.nanolett.8b02505>
16. Gosvami, N.N., Ma, J., Carpick, R.W.: An in situ method for simultaneous friction measurements and imaging of interfacial tribochemical film growth in lubricated contacts. *Tribol Lett.* **66** (2018).
<https://doi.org/10.1007/s11249-018-1112-0>
17. Gosvami, N.N., Lahouij, I., Ma, J., Carpick, R.W.: Nanoscale in situ study of ZDDP tribofilm growth at aluminum-based interfaces using atomic force microscopy. *Tribol Int.* **143** (2020).
<https://doi.org/10.1016/j.triboint.2019.106075>
18. Butt, H.J., Cappella, B., Kappl, M.: Force measurements with the atomic force microscope: Technique, interpretation and applications. *Surf. Sci. Rep.* **59**, 1–152 (2005).
<https://doi.org/10.1016/j.surfrep.2005.08.003>
19. Oblak, E., Kalin, M.: Relationship between the nanoscale topographical and mechanical properties of tribochemical films on DLC coatings and their macroscopic friction behavior. *Tribol Lett.* **59** (2015).
<https://doi.org/10.1007/s11249-015-0575-5>
20. Meyer, G., Amer, N.M.: Simultaneous measurement of lateral and normal forces with an optical-beam-deflection atomic force microscope. *Appl. Phys. Lett.* **57**, 2089–2091 (1990).
<https://doi.org/10.1063/1.103950>
21. Wang, C., Gojzewski, H., Schipper, D.J.: A multi-technique characterization of the tribofilm formed by a fully formulated CVT fluid. *Tribol Int.* **146** (2020). <https://doi.org/10.1016/j.triboint.2020.106201>
22. Gan, L., Ben-Nissan, B., Ben-David, A.: Modelling and finite element analysis of ultra-microhardness indentation of thin films. *Thin Solid Films.* **290–291**, 362–366 (1996).
[https://doi.org/10.1016/S0040-6090\(96\)08972-9](https://doi.org/10.1016/S0040-6090(96)08972-9)
23. Sarid, D., Elings, V.: Review of scanning force microscopy. *J. Vac Sci. Technol. B.* **9**, 431–437 (1991).
<https://doi.org/10.1116/1.585585>
24. Liu, W., Bonin, K., Guthold, M.: Easy and direct method for calibrating atomic force microscopy lateral force measurements. *Rev. Sci. Instrum.* **78**, 063707 (2007). <https://doi.org/10.1063/1.2745733>
25. Tocha, E., Schönherr, H., Vancso, G.J.: Quantitative nanotribology by AFM: A novel universal calibration platform. *Langmuir.* **22**, 2340–2350 (2006). <https://doi.org/10.1021/la052969c>
26. Pharr, G.M., Strader, J.H., Oliver, W.C.: Critical issues in making small-depth mechanical property measurements by nanoindentation with continuous stiffness measurement. *J. Mater. Res.* **24**, 653–666 (2009). <https://doi.org/10.1557/jmr.2009.0096>

27. Miklozic, K.T., Graham, J., Spikes, H.: Chemical and physical analysis of reaction films formed by molybdenum dialkyl-dithiocarbamate friction modifier additive using Raman and atomic force microscopy. *Tribol Lett.* **11**, 71–81 (2001). <https://doi.org/10.1023/A:1016655316322>
28. Martin, J.M., Grossiord, C., Mogne, T.L., Bec, S., Tonck, A.: The two-layer structure of Zndtp tribofilms Part 1: AES, XPS and XANES analyses. *Tribol Int.* **34**, 523–530 (2001). [https://doi.org/10.1016/S0301-679X\(01\)00029-9](https://doi.org/10.1016/S0301-679X(01)00029-9)
29. Aktary, M., McDermott, M.T., McAlpine, G.A.: Morphology and nanomechanical properties of ZDDP antiwear films as a function of tribological contact time. *Tribol Lett.* **12**, 155–162 (2002). <https://doi.org/10.1023/A:1014755123184>
30. Ye, J.P., Kano, M., Yasuda, Y.: Evaluation of local mechanical properties in depth in MoDTC/ZDDP and ZDDP tribochemical reacted films using nanoindentation. *Tribol Lett.* **13**, 41–47 (2002). <https://doi.org/10.1023/A:1016559807453>
31. Graham, J.F., McCague, C., Norton, P.R.: Topography and nanomechanical properties of tribochemical films derived from zinc dialkyl and diaryl dithiophosphates. *Tribol Lett.* **6**, 179–157 (1999). <https://doi.org/10.1023/A:1019124026402>
32. Nehme, G., Mourhatch, R., Aswath, P.B.: 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**, 1129–1147 (2010). <https://doi.org/10.1016/j.wear.2010.01.001>
33. Nicholls, M.A., Do, T., Norton, P.R., Bancroft, G.M., Kasrai, M., Capehart, T.W., Cheng, Y.T., Perry, T.: Chemical and mechanical properties of ZDDP antiwear films on steel and thermal spray coatings studied by XANES spectroscopy and nanoindentation techniques. *Tribol Lett.* **15**, 241–248 (2003). <https://doi.org/10.1023/A:1024813203442>
34. Nicholls, M.A., Norton, P.R., Bancroft, G.M., Kasrai, M., De Stasio, G.D., Wiese, L.M.: Spatially resolved nanoscale chemical and mechanical characterization of ZDDP antiwear films on aluminum–silicon alloys under cylinder/bore wear conditions. *Tribol Lett.* **18**, 261–278 (2005). <https://doi.org/10.1007/s11249-004-2752-9>
35. Nicholls, M.A., Bancroft, G.M., Norton, P.R., Kasrai, M., De Stasio, G., Frazer, B.H., Wiese, L.M.: Chemomechanical properties of antiwear films using X-ray absorption microscopy and nanoindentation techniques. *Tribol Lett.* **17**, 245–259 (2004). <https://doi.org/10.1023/B:TRIL.0000032451.97552.3d>
36. Kalin, M., Oblak, E., Akbari, S.: Evolution of the nano-scale mechanical properties of tribofilms formed from low- and high-SAPS oils and ZDDP on DLC coatings and steel. *Tribol Int.* **96**, 43–56 (2016). <https://doi.org/10.1016/j.triboint.2015.12.013>
37. Nicholls, M.A., Norton, P.R., Bancroft, G.M., Kasrai, M., Do, T., Frazer, B.H., De Stasio, G.: Nanometer scale chemomechanical characterization of antiwear films. *Tribol Lett.* **17**, 205–216 (2004). <https://doi.org/10.1023/B:TRIL.0000032447.32442.6a>
38. Pereira, G., Munoz-Paniagua, D., Lachenwitzer, A., Kasrai, M., Norton, P.R., Capehart, T.W., Perry, T.A., Cheng, Y.T.: A variable temperature mechanical analysis of ZDDP-derived antiwear films formed on

52100 steel. Wear. **262**, 461–470 (2007). <https://doi.org/10.1016/j.wear.2006.06.016>

39. Warren, O.L., Graham, J.F., Norton, P.R., Houston, J.E., Michalske, T.A.: Nanomechanical properties of films derived from zinc dialkyldithiophosphate. Tribol Lett. **4**, 189–198 (1998). <https://doi.org/10.1023/A:1019194903262>

Figures

Figure 1

Schematic of in-situ AFM sliding tests

Figure 2

0 cycles

600 cycles

Figure 3

AFM image of 0 and 600 cycles in base oil

Figure 4

AFM image until 600 cycles in ZDDP solution

Figure 5

Tribofilm thickness by lubricated in ZDDP solution with sliding cycle number

Figure 6

FD curves of 0 and 600 cycles in ZDDP solution

Figure 7

Adhesion property of ZDDP tribofilm with sliding cycle number

Figure 8

SEM-EDS analysis for sliding areas of 0 (outside), 200, and 600 cycles

Figure 9

Atomic concentration of P, S, and Zn element until 600 cycles

Figure 10

Young's modulus and nano indentation hardness of steel and sliding surface lubricated in ZDDP solution

Figure 11

Calculated contact area and shear strength by Hertz model

Figure 12

Correlation relationship between adhesion force and Friction force obtained by in-situ AFM sliding tests in ZDDP solution

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