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Article

N-Oleoyl Sarcosine as an Engine Oil Friction Modifier, Part 1: Tribological Performance of NOS+ZDDP Mixture at 100°C

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Abstract

The friction coefficient when a Fe surface was lubricated with an additive mixture of N-Oleoyl sarcosine (NOS), a commercial organic friction modifier, and zinc dialkyldithiophosphate (ZDDP) was measured at 100°C using a ball-on-disk tribometer under boundary lubrication conditions. The sliding surface was observed with a 3D laser microscope to investigate the tribo-film morphology and to evaluate the anti-wear performance. The findings indicate that this additive mixture enhanced tribological lubrication behavior in terms of friction-reducing and anti-wear properties under extended sliding cycle conditions. Scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDX) studies were conducted to analyze the elemental composition of sliding surfaces after tribo-tests and to estimate the friction reduction mechanism of the additive mixture. The EDX results revealed a noticeable decrease in S, suggesting that the NOS suppresses ZDDP decomposition and reduces the adsorption of the decomposition products.

Keywords

ZDDP, organic friction modifiers, boundary lubrication, EDX, ball on disk

1 Introduction

Low-viscosity engine oil has been put in use with the need to reduce friction loss and improve fuel consumption [1–4]. Theoretically, low-viscosity engine oil should reduce friction loss under mixed-hydrodynamic lubrication conditions. However, the usage of low-viscosity oil can greatly increase the risk of wear and friction for engine components operating in a boundary/mixed lubrication regime [2, 5, 6]. Maintaining low-friction and anti-wear performance has thus become an urgent task. This has resulted in investigations of the synergistic effects of anti-wear additives such as zinc dialkyldithiophosphate (ZDDP) and friction modifiers (FMs) [7–29]. ZDDP is a widely used additive with extremely good anti-wear properties [30]. It forms a glassy tribo-film on surfaces that rub together, which prevents direct surface contact [25, 30–36]. Although these pad-like tribo-films show excellent wear resistance, they can cause undesirable high friction due to insufficient lubricant in the contact interface [25, 37–39]. Friction modifiers such as molybdenum dialkyldithiocarbamate (MoDTC) [7–9], glycerol monooleate (GMO) [17–22], and amines/amides [17, 23–27] are mixed with ZDDP aiming to obtain enhanced tribological performance, but there are still limits for these friction modifiers.

MoDTC forms low-friction MoS_2 layers under rubbing conditions [40–44]. Studies have demonstrated that ZDDP promotes the formation of MoS_2 in a tribo-chemistry reaction, resulting in a lower friction coefficient, while MoDTC interaction with ZDDP produces S [10–14]. However, MoDTC reduces the anti-wear properties of ZDDP tribo-films, which results in greater wear when the sliding surfaces are lubricated with a MoDTC+ZDDP mixture compared with ZDDP lubrication alone [15, 16]. Nevertheless, the tribo-chemical reaction is essential to forming MoS_2, and the tribological performance depends on temperature [45].

GMO and amine/amides can be sorted as the organic friction modifiers (OFMs), which comprise molecules consisting of an adsorption group and a hydrocarbon tail. OFMs adsorb on sliding surfaces, forming single- or multi-layer surface films that reduce wear and friction by preventing direct contact [39, 46, 47]. GMO consists of an oleoyl tail, a carboxyl group, and two hydroxyl groups, is believed to be hydrolyzed to oleic acid and glycerol in steel-steel contact during sliding [48, 49]. The hydrolysis products form aggregations and micelles, which process better with metal and reduce the friction coefficient [50–52]. However, the synergistic effects on friction and wear reduction have not been clarified for the GMO+ZDDP mixture. Studies have shown that adding GMO to ZDDP-containing oils leads to thinner reaction films, but the friction-reducing effect has not been determined [17, 22]. The GMO+ZDDP mixture can reduce friction to the same level as GMO alone for DLC/DLC pairs but no additional friction reduction or anti-wear tribo-film formation has been reported [17, 20, 21]. In addition to those of GMO, the tribological effects of amine/amide+ZDDP mixtures have been investigated. The addition of saturated amines, especially monoamine, to ZDDP resulted in synergistic effects on friction reduction and anti-wear performance, but the effect depends on the molar ratio of the additives [25, 26]. The addition of oleylamine to ZDDP resulted in limited friction reduction and slightly negative anti-wear performance [23, 27], whereas the addition of oleamide to ZDDP resulted in a synergistic effect on friction reduction for steel surfaces, but the synergistic effect in anti-wear performance was limited [24]. The mechanism of the synergistic effects of amine/amide+ZDDP may originate from the difference in the complex formation of the lubricating oils. Studies have shown that the addition of GMO along with basic fatty acids results in neutral ZDDP complex formation, whereas the addition of amines results in base ZDDP complex formation [53].

This study focused on the lubricity of N-oleoyl sarcosine (NOS) and its performance when mixed with ZDDP. The chemical structure of the NOS is given in Fig. 1, which is an oleic acid derivative with a sarcosine head, consisting of an oleoyl tail, a carboxyl group, and an amide group. NOS was first used as a rust inhibitor [54, 55], and its ability to improve friction and wear performance was recently reported [56]. NOS can function as an OFM in engine oil, suppressing boundary friction and improving oil retention, due to its strong adsorption to the metal surface. The sarcosine head forms chelate-like structures [55] on metal surfaces and the C=C double bond in the oleoyl tail strengthens the adsorption [57, 58].

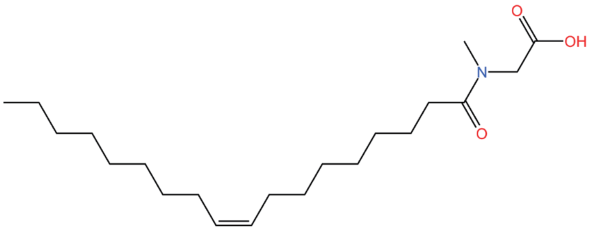


Fig. 1 Chemical structure of N-Oleoyl sarcosine

Above all, as NOS is one of the OFMs that are expected to have a synergistic effect on tribological behavior when mixed with ZDDP, the main aim of this study is to clarify the tribological performance of the NOS and its performance when mixed with ZDDP. Experiments using a ball-on-disk tribometer were conducted to investigate the tribological performance of NOS and the NOS+ZDDP additive mixture. The focus was on the tribo-film formed by each lubricating oil instead of the lubricating film, which was the tribo-film plus the oil film. Therefore, boundary tribo-films after tribo-tests were imaged to investigate the tribo-film formation and morphology of different lubricating oils. The tribo-tests were conducted at 100°C, a representative engine operating temperature, which typically ranges from 80 to 140°C. Energy dispersive X-ray spectroscopy (EDX) studies were conducted on the sliding areas of the tribometer balls to investigate the chemical compositions of the tribo-film.

2 Experimental materials and methods

2.1 Tribo-tests

SUJ2 disks (15×15×t4 mm) and balls (3/16-in. diameter) were used. The disks (Ra ~0.04 µm, HRC 58–60) were purchased from the Standard Test Piece Co., Ltd. (Japan) and machined to the size above by wire-cut electrical discharge machining. The balls (Ra ~0.05 µm, HRC 62–67) were made by TSUBAKI NAKASHIMA Co., Ltd. (Japan). The balls and disks were ultrasonically cleaned with acetone for 10 minutes before the tribo-tests. Poly-α-olefin was used as the base oil. Secondary-type ZDDP [R=C_4H_9] was used as the anti-wear additive. The details of the lubricating oils tested are given in Table 1.

The tribo-tests were carried out using a reciprocating ball-on-disk machine (FPR-2100, RHESCA Co. Ltd., Japan) while heated at 100°C. A schematic diagram of the ball-on-disk setup including the heating unit is shown in Fig. 2. The heating unit was activated before the tests to heat the disk and lubricating oils to 100°C. Tribo-tests were conducted after the temperature stabilized. The normal load was set at 1, 3, 5, or 8 N. The lambda ratio was calculated to confirm that the tests were conducted under boundary lubrication conditions. The test conditions are summarized in Table 2.

Table 1 Lubricating oils

Base oil: Poly-α-olefin (PAO), $C_{10}H_{21}(C_{10}H_{20})_nH$	
Dynamic viscosity (m²/s)	4×10^{-4}
Pressure-viscosity coefficient (m²/N)	1.06×10^{-8}
Oil mixtures	
PAO+ZDDP	ZDDP (700 ppm P)
PAO+NOS	NOS (0.3 mass%)
PAO+ZDDP+NOS	NOS (0.3 mass%) and ZDDP (700 ppm P)

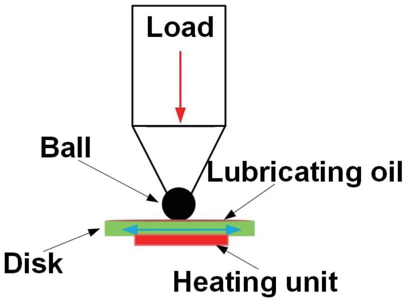


Fig. 2 Schematic diagram of ball-on-disk setup including heating unit

Table 2 Tribo-test conditions

Parameter	*Values*	
Frequency (Hz)	1	
Sliding speed (mm/s)	10	
Stroke length (mm)	5	
Normal load (N)	1, 3, 5, 8	
Test duration (s)	1800	5400

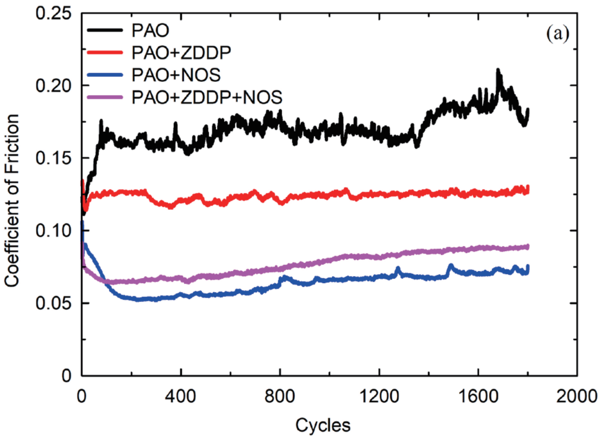
2.2 Surface analyses (Microscopy, SEM–EDX studies)

A 3D measuring laser microscope (OLS4000-SAT, Olympus Co., Japan) was used to image the ball contact areas after the tribo-tests to determine the size of the wear marks. The balls were ultra-sonic bathed for 10 minutes with hexadecane and blew with N_2 gas to dry. Scanning electron microscopy (SEM, SU6600, HITACHI Co. Ltd., Japan) with EDX (E-MAX20, Oxford Instruments plc) was performed on the contact areas to obtain clear images of the tribo-films formed by each lubricating oil. EDX mapping was performed to obtain chemical analyses of the tribo-films formed on the contact areas. Each ball was scanned for 45 scans, accumulated, and normalized automatically to obtain the mapping results.

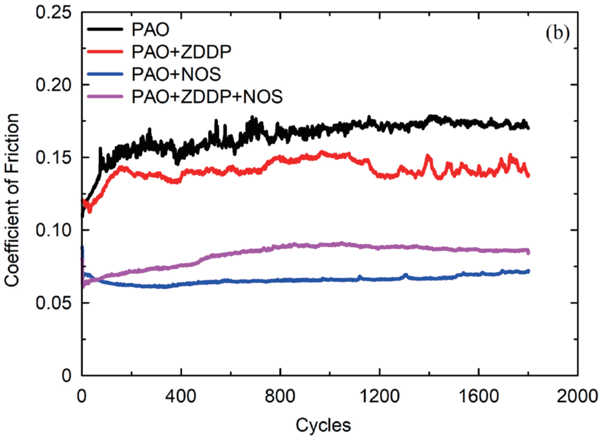
3 Results and discussion

3.1 Tribological behavior within 1800 sliding cycles

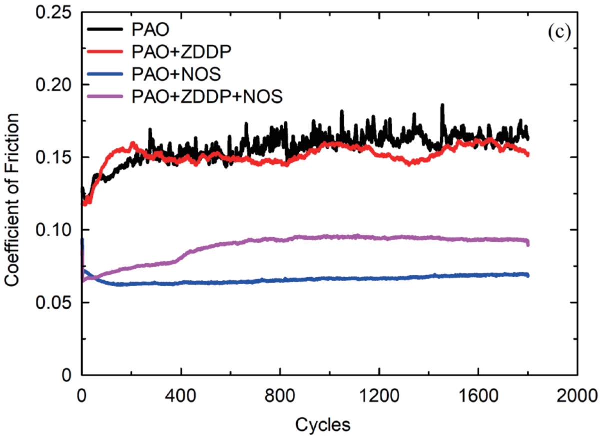
The friction coefficients at loads of 1, 3, and 5 N are shown in Figs. 3a, b, and c, respectively. In general, PAO+ZDDP+NOS exhibited the lowest friction coefficient at these loads over the first several cycles. Its friction coefficient then exceeded that of PAO+NOS over the remaining cycles. The friction coefficient of PAO+ZDDP was lower than that of PAO (0.16) at 1 N (around 0.12) and 3 N (0.13–0.15), whereas it was close to that of PAO at 5 N (0.14–0.16). Moreover, it fluctuated more noticeably than that of the other lubricating oils as the applied load was increased. This fluctuation may be due to the formation and destruction of the glassy tribo-film during the sliding cycles.



(a) 1 N load



(b) 3 N load



(c) 5 N load

Fig. 3 Friction coefficient curves over 1800 cycles at 100°C

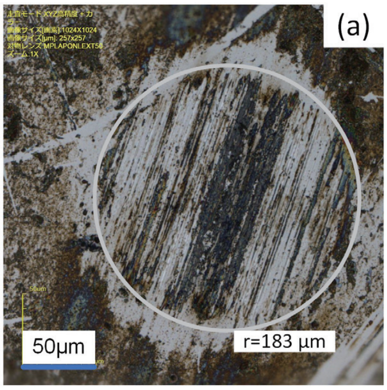
Increasing the applied load also altered the friction curve. PAO+NOS exhibited a stable friction coefficient within fewer sliding cycles as the applied load was increased from 1 to 5 N. Moreover, fluctuation of the friction coefficient decreased, which indicates that NOS is more effective in improving friction performance under severe contact conditions. The friction coefficient of PAO+NOS after 1800 cycles under all three loads was the smallest of the four lubricating oils, about 0.06. PAO+ZDDP+NOS exhibited different behaviors under different loads, which differed from PAO+NOS: the friction coefficient first decreased and then stabilized. Under a 1 N load, as shown in Fig. 3a, it exhibited similar decrease-to-stable behavior as

PAO+NOS, suggesting that the NOS contributes more to the friction behavior in the additive mixture. However, under heavier loads, it exhibited increase-to-stable behaviors, the same tendency as that of PAO+ZDDP. Increasing the applied load may accelerate the decomposition of ZDDP and the ZDDP tribo-film formation, which could induce an increase in the friction coefficient. However, the NOS in the mixture contributed to the friction behavior, so that the friction curve was as smooth as that of PAO+NOS, with fewer fluctuations than that of PAO+ZDDP. This suggests that the presence of NOS in the lubricating oil prevents the thickening of the high-friction ZDDP tribo-film so that the friction coefficient of PAO+ZDDP+NOS eventually stabilized between those of PAO+ZDDP and PAO+NOS.

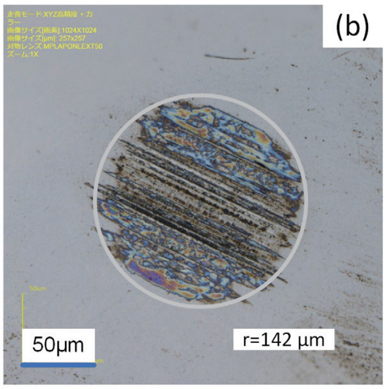
Microscope images of the ball contact areas after 5 N load tribo-tests are shown in Fig. 4, which were balls lubricated with PAO, PAO+ZDDP, PAO+NOS, and PAO+ZDDP+NOS referred to Fig. 4a, b, c, and d. Ravine-like scars are evident on all the balls. As the kinematic viscosity of the base oil was only 4 mm^2/s, the oil film would have been very thin, so the balls would tend to wear. The additives improved the anti-wear performance noticeably. After 1800 cycles, the wear diameter with PAO (Fig. 3a) was the largest while that with PAO+ZDDP+NOS (Fig. 3d) was the smallest.

The results of the SEM–EDX studies are shown in Figs. 5 to 8. Linear wear scars are evident in the SEM images shown in Fig. 5, which suggests that abrasive wear occurred with the PAO lubrication. Element mapping revealed the presence of O, especially in the middle of the contact area, where the contact pressure was higher. Both O and C are evident around the wear area, which could have resulted from deposits of PAO and iron oxide wear debris. A clear view of tribo-films was present on the contact area with PAO+ZDDP lubrication as shown in Fig. 6. Linear wear scars were present along the sliding direction of the contact area, where severe contact may have occurred. EDX mapping shows that Zn, P, and S were detected as well as O and C. This suggests that Zn, P, S, and O accounted for most of the tribo-film composition. Considerable distributions of C and S were detected both inside and outside the contact area. These findings suggest adsorption of the ZDDP decomposition products, which could be the alkyl chains or the thiophosphates, or both. A dark grey area which is supposed to be the contact area with PAO+NOS lubrication can be seen in Fig. 7. Linear wear scars along with sliding direction and spotted structures were evidenced on the contact area. According to the EDX mapping, the lines were rich in O and the spotted structures are rich in C. As shown in Fig. 8, the ZDDP+NOS tribo-film structure was mostly a mixture of tribo-films formed by ZDDP and NOS. Tribo-film fragments similar to those of ZDDP tribo-film are evident on both sides of the contact area, but the film was incomplete and piecemeal. The EDX mapping results support the assertion that Zn- and P-rich areas overlapped in the area where ZDDP tribo-films are assumed to have been present. Furthermore, C-rich spots overlapped the spotted structures formed by the NOS because the ZDDP tribo-films lacked C; similar C-rich spots are evident in Fig. 7. Moreover, the tribo-film area lacked S compared with the results shown in Fig. 6.

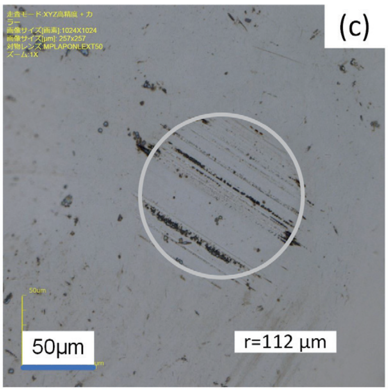
The above results roughly suggest a mechanism different from those of all known OFM+ZDDP mixtures. According to the literature, the origin of friction reduction with GMO+ZDDP is the interaction between the hydrolysis product from the GMO and ZDDP. However, previous research has shown that the interaction products of oleic acid and ZDDP exhibit



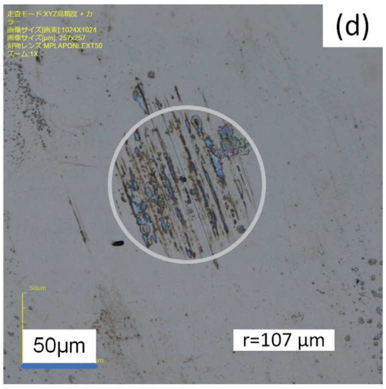
(a) PAO



(b) PAO+ZDDP



(c) PAO+NOS



(d) PAO+ZDDP+NOS

Fig. 4 Worn areas on ball surface after 5 N load tribo-tests corrosive properties to metal, which could be the reason for the limited anti-wear performance of the GMO+ZDDP mixture [59]. Moreover, the addition of GMO to ZDDP results in tribo-films with more S content [18, 19]; the addition of saturated amines results in tribo-films with less phosphate [25]; the addition of oleyl amine/oleamide has limited effect on the tribo-film composition except for N [23, 24]. One study reported that the formation of S is activated by the severity of the wear conditions [60], which suggests that the presence of NOS in this study lessened the wear condition. The distribution of C as well as that of S was lower outside the contact area. The NOS may have suppressed the decomposition of ZDDP and oleamide was reported to exhibit an effect similar to that of ZDDP [24]. Moreover, the adsorption of NOS on the metal surface may have prevented the adsorption of the ZDDP decomposition products rich in C and S.

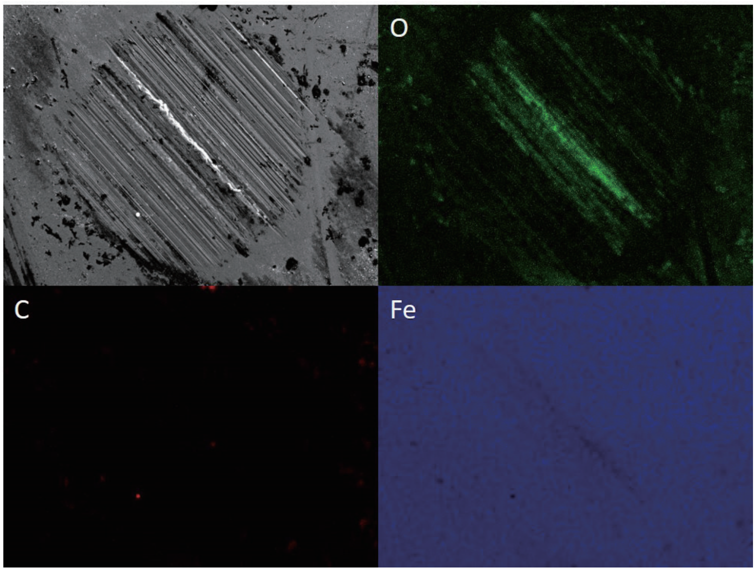


Fig. 5 SEM–EDX results with PAO lubrication

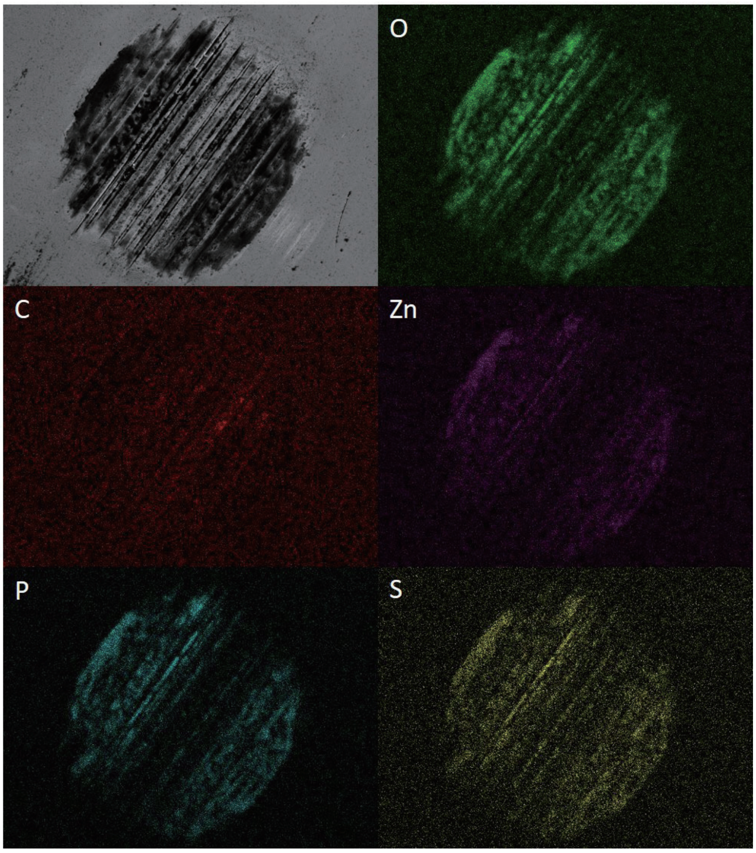


Fig. 6 SEM–EDX results with PAO+ZDDP lubrication

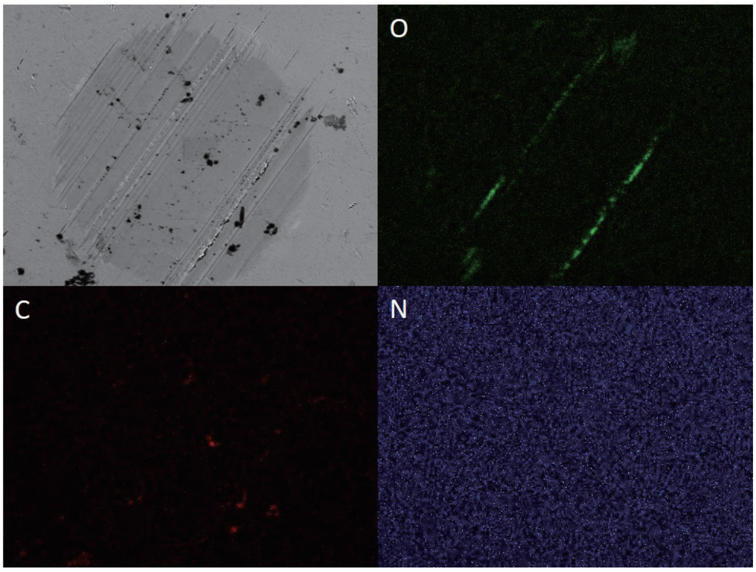


Fig. 7 SEM–EDX results with PAO+NOS lubrication

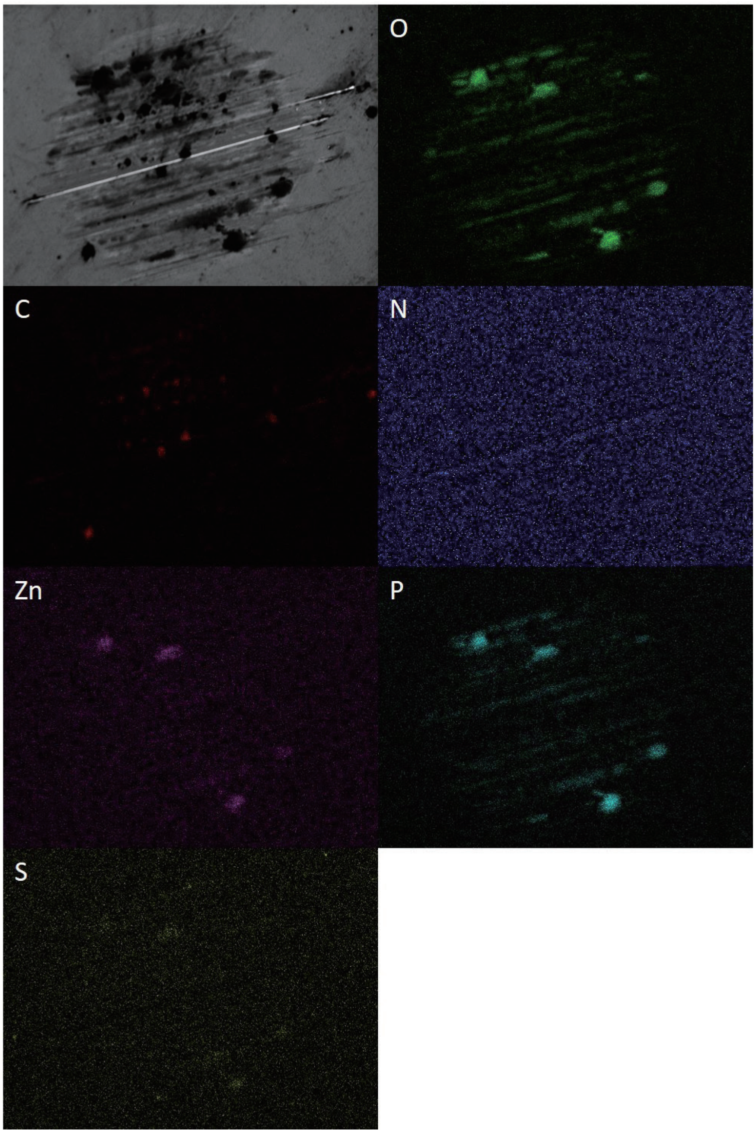


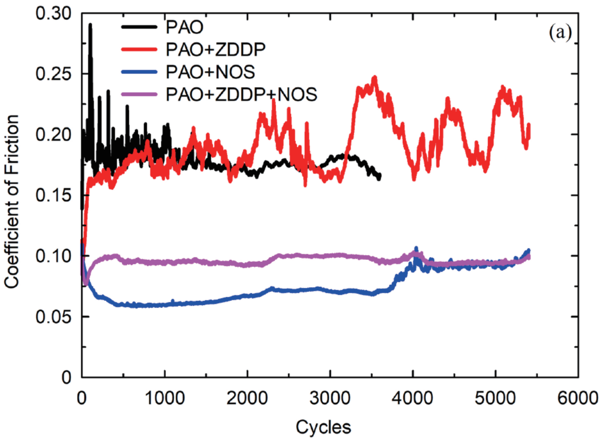
Fig. 8 SEM–EDX results with PAO+ZDDP+NOS lubrication

3.2 Tribological behavior within 5400 sliding cycles under heavier load

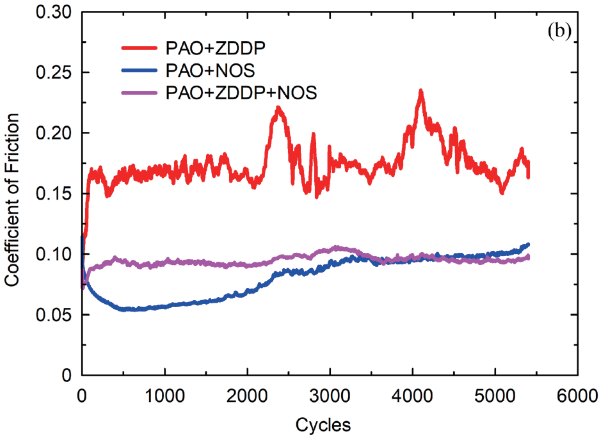
Extended tribo-tests were conducted to investigate the durability of the tribo-film formed by each lubricating oil. With a 5 N load (Fig. 9a), the friction coefficient of PAO+NOS started to increase at around 3500 cycles and stabilized at around 4000 cycles. The friction coefficient of PAO+ZDDP+NOS was close to that of PAO+NOS; it increased at around 2000 and 4000 cycles, possibly due to the coupling process of NOS adsorbed film destruction, the ZDDP film formation, and the wear effect.

With an 8 N load (Fig. 9b), the friction coefficient behavior of PAO+NOS was similar: the coefficient started to increase gradually after about 2000 cycles and exceeded that of PAO+ZDDP+NOS after about 3500 cycles and continued to rise. This may be because of the oxidization of the additive. The iron oxide formation and NOS degradants worsen the friction-reducing performance. In contrast, that of PAO+ZDDP+NOS remained stable despite the increasing-decreasing pattern similar to that under the 5 N load.

Microscope images of ball surfaces lubricated with the base oil PAO and the additive mixtures are shown in Fig. 10. The microscope images of balls lubricated with PAO (Fig. 10a) and PAO+ZDDP (Fig. 10b) were similar: the contact area was covered with linear wear scars. Dark areas with black spots are observed within the contact area of the ball lubricated with PAO+NOS

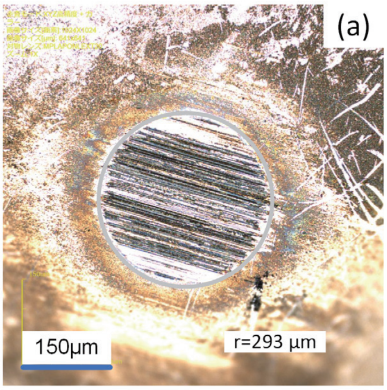


(a) 5 N load

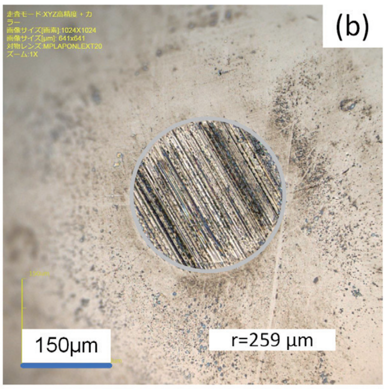


(b) 8 N load

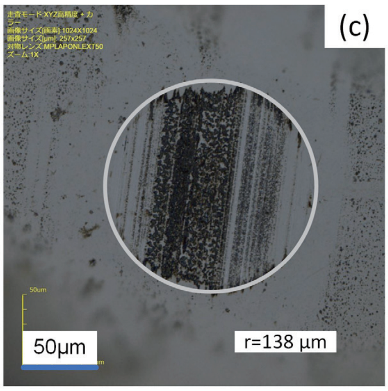
Fig. 9 Friction coefficient curves over 5400 cycles at 100°C



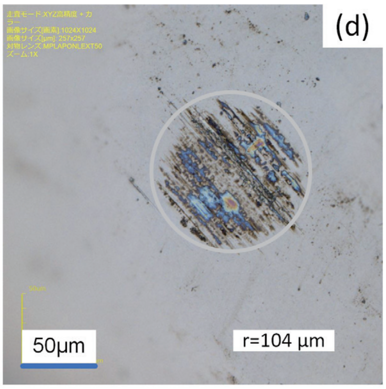
(a) PAO



(b) PAO+ZDDP



(c) PAO+NOS



(d) PAO+ZDDP+NOS

Fig. 10 Worn areas on ball surface after 5 N load tribo-tests

(Fig. 10c). When lubricated with PAO+ZDDP+NOS, as shown in Fig. 10d, film formation is also observed. The SEM images in Fig. 11 show the detailed surface structures of the same areas as Fig. 10. As shown in Fig. 11a, with PAO lubrication, the wear scars were filled with dark deposits, which may have been iron oxide, as mentioned in section 3.1. Dark deposits are also evident at the edge of the contact area; they may have been the byproducts of hydrocarbon from the PAO. In contrast, with PAO+ZDDP lubrication, although wear scars are evident in the SEM images, deposits are not evident in the scars. Instead, tribo-film fragments were trapped in the scars, as shown by the red arrow in Fig. 11b. Dark spots, possibly due to adhesive wear [61], were also found in the tribo-film. In the PAO+NOS tribo-film (Fig. 11c), irregular fragments were found in the contact area. The tribo-film, which might have been O-rich decompositions of the NOS, was a developed reaction film shown in Figs. 3 and 6. This suggests that the formation of the reaction film in the contact area is related to the increase in the friction coefficient over the cycles. The PAO+ZDDP+NOS tribo-film inherited the features of both the PAO+ZDDP tribo-film and the PAO+NOS tribo-film, as shown in Fig. 11d. Moreover, both films seem to have been thinner with fine wear debris trapped in the wear scars as shown by the red arrow in Fig. 11d.

3.3 Steady-stage tribological behavior

The steady friction coefficients at different loads for each lubricating oil are shown in Fig. 12. The friction coefficients over the last 200 cycles were averaged to obtain a steady friction

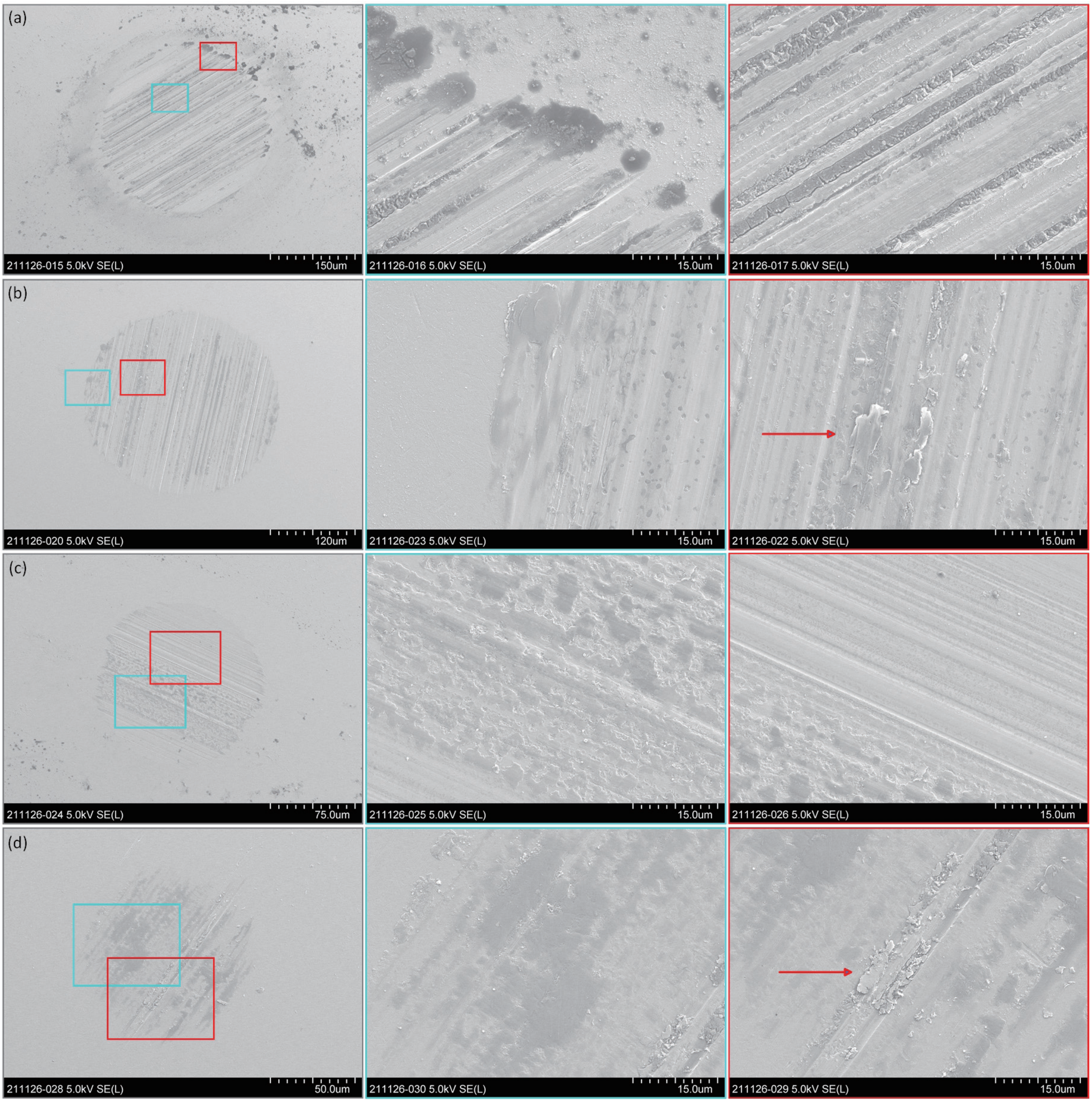


Fig. 11 SEM images of worn surfaces after 5 N load 5400-cycle tribo-tests
(a) PAO, (b) PAO+ZDDP, (c) PAO+NOS, (d) PAO+ZDDP+NOS

coefficient. The black dotted–dashed line represents the steady friction coefficient of PAO+ZDDP+NOS at 8 N after 5400 cycles at 100°C as a reference. When the test duration was 1800 s, PAO+NOS exhibited the lowest friction coefficient for the three applied loads. However, it increased noticeably when the duration was increased to 5400 s for both loads. This suggests that NOS adsorption film has poor durability under severe contact conditions. Although PAO+ZDDP+NOS exhibited higher friction coefficients than PAO+NOS after 1800 cycles, the increase in the coefficient over the longer time scale was smaller for PAO+ZDDP+NOS than for the other oils. The results suggest that ZDDP in the mixture improves tribo-film durability by suppressing NOS reaction, which could be the main reason for friction increase when NOS was used alone; and a similar effect of ZDDP on oleyl amine has been reported [23]. This also illustrates the enhanced friction reduction effect of the ZDDP+NOS mixture.

The relative wear diameters with each lubricating oil are shown in Fig. 13 with the wear diameter of PAO at 8 N and 5400 s as 1.0. The diameters with PAO+NOS and PAO+ZDDP+NOS after 1800 cycles were close for each load. After 5400 cycles at 5 N, the diameter of PAO+NOS was substantially larger, whereas that of PAO+ZDDP+NOS remained the same as after 1800 sliding cycles. The wear diameter with PAO+ZDDP+NOS was the smallest for both 5 N and 8 N, suggesting that ZDDP improves the durability and enhances the anti-wear property of tribo-films.

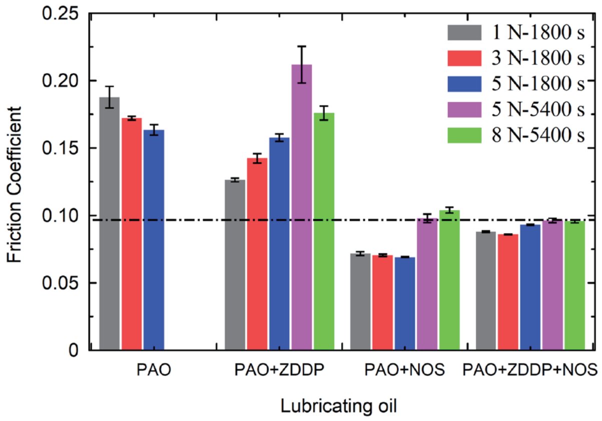


Fig. 12 Stable friction coefficients with different lubricating oils

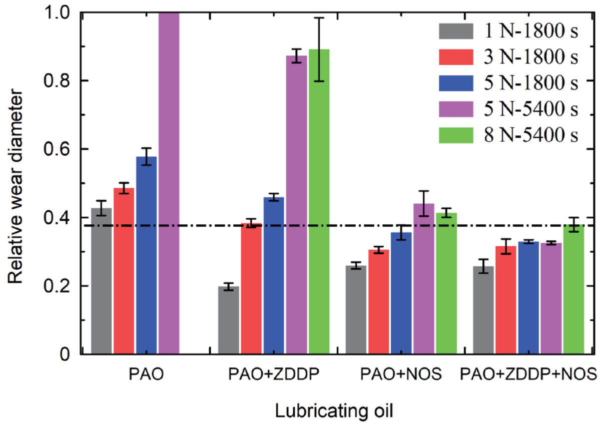


Fig. 13 Relative wear diameter with different lubricating oils

4 Conclusion

This study investigated tribological behavior when an organic friction modifier, N-oleoyl sarcosine, and its mixture with zinc dialkyldithiophosphate were added to a base lubricating oil (poly-α-olefin). Friction tests were carried out with a ball-on-disk tribometer. The effects on the tribo-film formation of each lubricating oil were observed with a 3D laser microscope, and the element composition was measured using scanning electron microscopy and energy dispersive X-ray spectroscopy.

- The NOS additive alone had a considerable friction-reducing property as it exhibited the lowest friction coefficient after the first 1800 sliding cycles. However, the coefficient increased noticeably in extended testing and eventually exceeded that of the NOS+ZDDP additive. The EDX mapping results suggest that the formation of an O-rich reaction layer is the reason for the friction coefficient increase.
- The NOS+ZDDP additive exhibited a lower friction coefficient than the other additives after 5400 sliding cycles, and the size of the wear area was the smallest after both 1800 and 5400 sliding cycles.

The friction behavior at room temperature was also investigated and is discussed in a companion paper. The mechanism of the friction-reducing property of the ZDDP-NOS mixture is furtherly discussed in the companion paper.

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