



Article

## Interfacial Structure and Tribological Property of Adsorbed Layer Formed by Dibasic Acid Ester Derivative

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### Abstract

An investigation was conducted of the low-friction and low-wear mechanism of the adsorbed layer formed by dibasic acid ester derivative. First, the film thickness and film density of the adsorbed layer on an iron surface was evaluated by neutron reflectometry. The density of the adsorbed layer formed at 25°C was twice that at 100°C. The macroscale tribological properties of an adsorbed layer formed by dibasic acid ester derivative and its constituent additives (succinic acid and amine) were evaluated using a ball-on-disk tribometer at 25°C and 150°C. The derivative exhibited low friction and wear properties even at high temperature. To clarify the mechanism of the excellent low friction property, nanoscale tribological testing was conducted using an atomic force microscope. The precise measurement indicated that the dibasic acid ester derivative initially exhibits low friction due to generation of metal soap from the amine, and then subsequent friction generates metal soap from the succinic acid that has superior friction reduction performance, which promotes lower friction, especially under low-contact-pressure sliding conditions.

### Keywords

friction modifier, boundary lubrication, dibasic acid ester derivative, neutron reflectometry, atomic force microscopy

## 1 Introduction

To curb the progression of global warming, emissions of carbon dioxide, a greenhouse gas, need to be reduced. Lowering the viscosity of automobile engine oils can improve fuel efficiency by reducing friction due to fluid resistance, mainly in the piston and bearing, and thus reduce emissions of greenhouse gases. However, low-viscosity engine oils are prone to oil film breakage, which increases the risk of seizure as well as increase friction and wear of sliding parts. Molybdenum dithiocarbamate and zinc dialkyldithiophosphates (ZnDTP) prevent friction and wear by forming a reactive film on metal surfaces at high temperatures and pressures [1–4], but they also cause problems such as the formation of metal sludge, the clogging of oil filters, and catalytic poisoning of exhaust gas treatment by phosphorus and sulphur. Therefore, the development of ashless lubricating additives that do not contain

metal, phosphorus, or sulphur has been promoted [5, 6].

Common ashless lubricating additives are effective in reducing wear as well as friction by forming an adsorbed layer on the metal surface. For example, ball-on-disk friction tests using a lubricant containing palmitic acid resulted in a 30% reduction in the coefficient of friction (CoF) and a 90% reduction in the amount of wear on the surface of the ball compared with the same tests using only the base oil [7]. In testing with stearic acid, a saturated fatty acid, low friction and low wear were maintained at a high temperature (150°C), whereas an unsaturated fatty acid containing double bonds in the alkyl chain was not effective above 100°C [8]. Glycerol monooleate (GMO) has been shown to be effective on steel and diamond-like carbon surfaces even when added to a fully formulated engine oil, demonstrating excellent suppression of friction and wear even at a high temperature (110°C) [9]. A study of additives with amino groups found that, the higher the

number of amino groups in the additive molecule, the greater the stability at high temperatures, resulting in lower friction and wear [6]. In addition, polymeric friction modifiers were shown to form a thick adsorbed layer on a metal surface through the multiple functional groups contained in a molecule and thus were resistant to desorption even at high temperature; they exhibited not only low-friction but also high-surface-protection performance [10–12].

This study focused on the use of a dibasic acid ester derivative as an ashless lubricating additive. This derivative had an excellent friction-reducing effect equivalent to that of GMO under room temperature conditions and exhibited a wear-inhibiting effect equivalent to that of ZnDTP and phosphate ester amine salt at high temperature in a high-speed reciprocating friction and wear test [13, 14]. However, the interfacial structure of the adsorbed layer formed on the metal surface by this additive and the mechanism of improvement in friction and wear properties have not been fully investigated. In this study, the interfacial structure of the adsorbed layer on an Fe surface was evaluated using neutron reflectometry, and the macro- and nano-tribological properties of each additive constituting the derivative (i.e., succinate and amine) were evaluated. The relationship between the interfacial structure and the tribological properties of the adsorbed layer was investigated.

## 2 Additives

This study focuses on dibasic acid ester derivative [13, 14], which is an organic lubricant additive reported to have friction-reducing and wear-inhibiting effects, and evaluates the structure of the adsorbed layer it forms on the Fe surface. The tribological properties of the dibasic acid ester derivative and its constituent acid and amine are also evaluated to investigate how the two

components of the derivative act on the sliding surface. The dibasic acid ester derivative used in this study was monooleyl succinate-dimethyl lauryl amine salt (SA-DA), the acid was monooleyl succinate (C18:1SA), and the amine was dimethyl lauryl amine (C12DA). The SA-DA was prepared by mixing C18:1SA and C12DA in equal proportions and neutralizing the carboxy group in the succinate with a tertiary amine. A common organic friction modifier, palmitic acid (C16FA), was used for comparison. The structural formulae of these additives are shown in Figs. 1 (a)–(d); those in Figs. 1 (e)–(g) are the additives used in the neutron reflectometry. They are described in detail in Sec. 4.1. Each additive was added to the base oil, poly alpha olefin (PAO), one by one and tested. The lubricants used in this study are summarized in Table 1. Since the mass ratio of C18:1SA and C12DA in SA-DA is approximately 1:1, the mass concentration of the SA-DA was set to twice in those additives. The concentrations of the additives in each lubricant were sufficiently low so that the viscosity was not noticeably different from that of the base oil (30 cSt at 40°C).

## 3 Transmission infrared (IR) spectroscopy

### 3.1 Experimental methods

IR transmission spectra were obtained to evaluate the morphology of the additives in the PAO. The transmission spectra of the lubricants were measured between two potassium bromide windows 0.05 mm apart using an IR spectrometer (VERTEX70; Bruker). The wavenumber resolution of the measurements was  $2\text{ cm}^{-1}$ ; the integration time was set to 256. Background measurements were first carried out using the PAO without any additives and then using lubricants containing SA-DA, C18:1SA, or C12DA. Measurements under the same conditions were conducted to evaluate the IR absorbance of the additives.

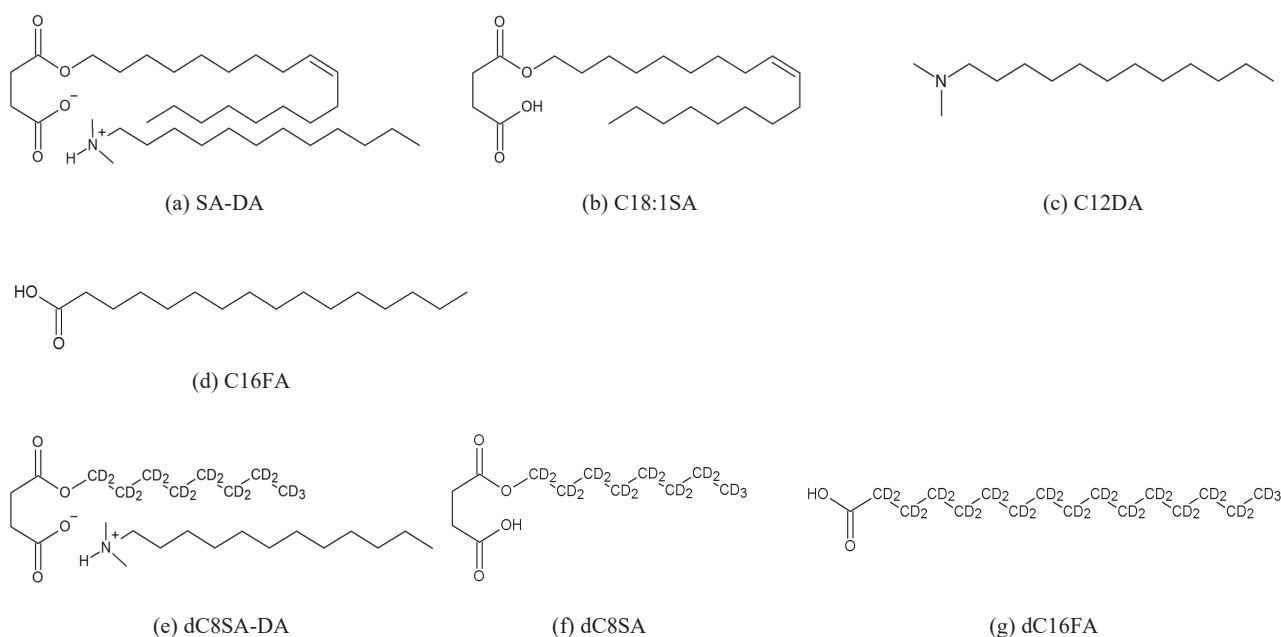


Fig. 1 Structure of additives tested, (a) monooleyl succinate-dimethyl lauryl amine salt (SA-DA), (b) monooleyl succinate (C18:1SA), (c) dimethyl lauryl amine (C12DA), (d) palmitic acid (C16FA), (e) deuterated monooleyl succinate-dimethyl lauryl amine salt (dC8SA-DA), (f) deuterated monooleyl succinate (dC8SA), (g) deuterated palmitic acid (dC16FA); reproduced with permission from [37] Copyright (2022) Japanese Society of Tribologists

Table 1 Lubricant used in this research; reproduced with permission from [37] Copyright (2022) Japanese Society of Tribologists

No.	Base oil	Additive	Concentration	Experiment
1	PAO	SA-DA	0.1 mass%	Friction test and IR measurement
2		C18:1SA	0.05 mass%	
3		C12DA	0.05 mass%	
4		C16FA	0.1 mass%	Friction test
5		dC8SA-DA	0.1 mass%	Neutron reflectometry
6		dC8SA	0.05 mass%	
7		dC16FA	0.1 mass%	

### 3.2 Results

The results for each lubricant are shown in Fig. 2. Generally, two molecules with carboxy groups form a dimeric structure in a non-polar solvent due to hydrogen bonding between the carbonyl group ( $>C=O$ ) and the hydroxyl group ( $-OH$ ) [15–18]. Two carbonyl group absorption peaks usually appear between  $1660$  and  $1780\text{ cm}^{-1}$ ; the peak at the larger wavenumber corresponds to a monomer and that at the smaller one corresponds to a dimer bound by hydrogen bonds. In the present measurement, the peak from the monomer structure was observed at  $1742\text{ cm}^{-1}$ , and that from the dimer structure was observed at  $1718\text{ cm}^{-1}$ . The ratio of the maximum value of the monomer absorption peak to that of the dimer absorption peak was  $0.9$  for C18:1SA. Because succinate has two carbonyl groups in a molecule, C18:1SA forms a dimer by hydrogen bonding with a terminal carboxy group, and the carboxy groups on the alkyl chain side (ester carbonyl group) exist in an unbound state. In contrast, the monomer to dimer ratio for SA-DA was  $2.3$  in PAO, higher than that for C18:1SA. A study by Fry et al. revealed that lubricants containing a mixture of oleic acid and amine-based additives have a higher monomer to dimer ratio for oleic acid, which enhance adsorption performance on metal surfaces [15]. Their study also revealed that amine-based additives adsorb on a metal surface, forming a dense molecular film, which improves friction and wear properties compared

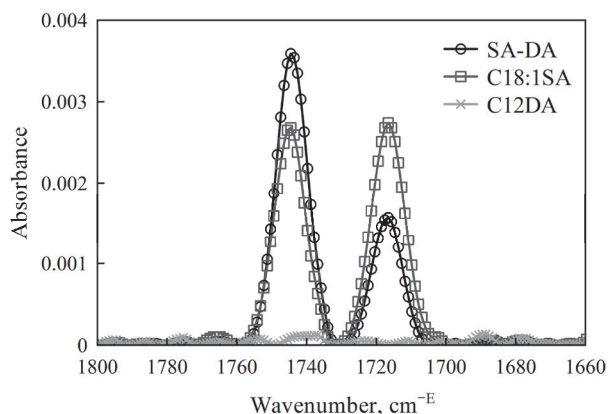


Fig. 2 IR absorbance of carboxyl peaks of additives in PAO; reproduced with permission from [37] Copyright (2022) Japanese Society of Tribologists

with lubricants containing each additive alone. Similarly, for SA-DA, it is possible that the presence of C12DA in the vicinity of the hydroxyl group of C18:1SA prevented the formation of a dimer by the terminal carboxy group in the PAO, thereby improving its adsorption performance. Moreover, since C12DA should also adsorb on metal surfaces, the frictional properties of the SA-DA should be substantially improved.

## 4 Neutron reflectometry

### 4.1 Sample preparation

To evaluate the interfacial structure of the adsorbed layer formed by the additives on an Fe surface, neutron reflectometry, which enables analysis of the thickness and surface roughness of a thin layer and compositional distribution in the film thickness direction [19–21], was performed. Mirror-polished silicon blocks ( $50 \times 50 \times 10\text{ mm}$ ) were prepared, and an Fe film with a thickness of  $30\text{ nm}$  was formed on them using an Fe beam sputtering system (KUR-IBS [22]). In neutron reflectometry, the layer structures at a solid-liquid interface can be clearly distinguished by converting hydrogen atoms in either the base oil or the additive to deuterium. In this experiment, the additives were deuterated because it was difficult to obtain deuterated PAO. SA-DA in which all hydrogen atoms are deuterated should be used ideally, but it was also difficult to obtain both deuterated C18:1SA and C12DA. A deuterated monooleyl succinate (dC8SA, Fig. 1(f)) in which the oleyl chain ( $-\text{CH}_2(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}$ ) of C18:1SA was replaced with a deuterated octane chain ( $-\text{C}_7\text{D}_{14}\text{CD}_3$ , 98% deuteration) was prepared alternatively, and its derivative (dC8SA-DA, Fig. 1(e)) was formed by mixing the dC8SA with non-deuterated C12DA. The dC8SA-DA was added to PAO at a concentration of  $0.1\text{ mass\%}$ , and the dC8SA was added at a concentration of  $0.05\text{ mass\%}$ . For comparison, a lubricant containing  $0.1\text{ mass\%}$  deuterated palmitic acid (dC16FA, 98% deuteration, Fig. 1(g)) added to PAO was also prepared.

### 4.2 Experimental procedure

A time-of-flight neutron reflectometer (BL16 SOFIA [23, 24]) installed at the Materials and Life Science Experimental Facility of the Japan Proton Accelerator Research Complex (J-PARC MLF) was used for the experiments. A schematic illustration of the measurement principle and theoretical values of the scattering length density (SLD), which is a material-specific parameter, are shown in Fig. 3. The SLD was obtained

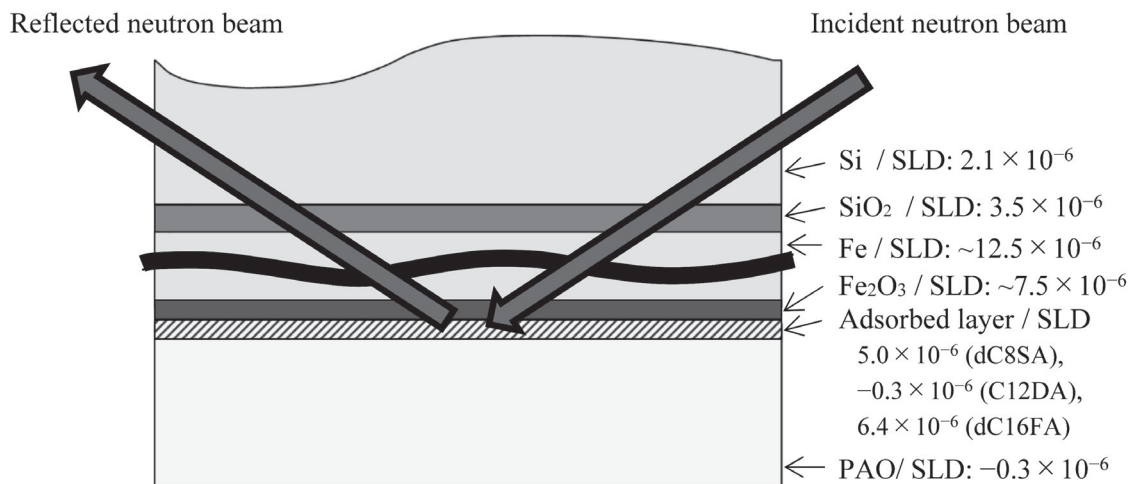


Fig. 3 Schematic illustration of neutron reflectometry and SLD values used in fitting analysis; reproduced with permission from [37] Copyright (2022) Japanese Society of Tribologists

by multiplying the number density of the constituent atoms by the coherent scattering length, which quantifies the degree of neutron scattering.

A silicon block with an Fe coating was placed in a holder, and the reflectance was measured while the Fe surface was immersed in base oil. The base oil was then replaced with lubricants containing each additive and left at room temperature for 2 hours, after which the reflectivity was measured again. The changes in the state of the adsorbed layer on the Fe surface at high temperatures were evaluated by additional measurement after heating at 50°C for 30 min and then again after heating at 100°C for 30 min.

Fitting analysis of the reflectivity profiles obtained for each measurement was performed using Motofit analysis software [25] to estimate the thickness of the Fe film and the thickness and density of the adsorbed layer formed by the additive.

#### 4.3 Results

The reflectivity profiles and the best fitting results are shown in Figs. 4 (a)–(c). Scattering vector  $Q_z$  on the horizontal axis is given by

$$Q_z = 4\pi / \lambda \sin\theta \quad (1)$$

where the wavelength of the neutron beam is  $\lambda$ , and the incident angle is  $\theta$ . Although the surface roughness was set to zero in the fitting analysis, the  $\chi^2$  parameter, which is the error between the experimental and analyzed values, was small (less than  $1 \times 10^{-4}$ ) in all cases, indicating that the analysis was sufficiently accurate. This result suggests that the Fe and adsorbed layers formed homogeneously on the silicon block.

Figures 5 (a)–(c) show the SLD profiles obtained from the fitting analysis results shown in Figs. 4 (a)–(c). The profiles show the change in the SLD in the vertical direction from the silicon surface. From these figures, the film thickness and density of the thin metal film on the silicon block and the adsorbed layer formed by the additives can be estimated. The SLD values for the materials used in this measurement are  $2.1 \times 10^{-6} \text{ \AA}^{-1}$  for silicon,  $3.5 \times 10^{-6} \text{ \AA}^{-1}$  for silicon oxide,  $5.0 \times 10^{-6} \text{ \AA}^{-1}$  for dC8SA,  $6.4 \times 10^{-6} \text{ \AA}^{-1}$  for dC16FA and  $-0.3 \times 10^{-6} \text{ \AA}^{-1}$  for C12DA and PAO. The SLD values of Fe film vary depending on the deposition conditions, but the SLD values for Fe and Fe oxide in this fitting analysis were  $12\text{--}13 \times 10^{-6} \text{ \AA}^{-1}$  and  $7\text{--}8 \times 10^{-6}$

$\text{\AA}^{-1}$  respectively, which were close to the theoretical values. As shown in the figures, the thickness of the Fe film including the oxide layer was 32 nm, which is close to the target thickness.

For the lubricant measurements, the film thickness and density of the adsorbed layer were estimated on the assumption that the state of the Fe coating did not change and that a single homogeneous adsorbed layer formed on the Fe oxide surface. Since the C12DA in the dC8SA-DA was not deuterated and thus not detected in the neutron reflectometry, the film thickness and density of the dC8SA-DA were estimated from the thickness and density of the dC8SA molecules adsorbed in the film. The film density of the adsorbed layer was calculated from the ratio of the bulk SLD of the deuterated additive to that of the PAO and C12DA; e.g., if the SLD of the adsorbed layer is  $2.35 \times 10^{-6} \text{ \AA}^{-1}$ , the density of the adsorbed layer formed by the dC8SA is 50%.

The thicknesses and densities of the adsorbed layer formed by each additive as determined by neutron reflectometry are summarized in Table 2. The thickness of the adsorbed layer formed by dC8SA and it in dC8SA-DA at 25°C was 1.9 nm and 2.0 nm, respectively, and the film density was 30% and 26%, respectively. The thickness and density of the adsorbed layer formed by dC16FA were 1.5 nm and 40%, respectively. The length of alkyl chains with 16 carbon atoms is approximately 2 nm, indicating that the dC16FA formed a monolayer on the Fe surface. On the other hand, the length of alkyl chains with eight carbon atoms is about 1 nm. Therefore, the dC8SA possibly formed a multilayered structure on the Fe surface. The density of the adsorbed film formed by the dC8SA was lower than that of the dC16FA, possibly due to the larger molecular size of the part involved in the adsorption on the Fe surface since dC8SA has one hydroxyl group and two carbonyl groups in its molecules.

The change in the state of the adsorbed layer formed by each additive at 50°C was small and did not differ significantly from that measured under 25°C. Lubricant containing dC16FA formed an adsorbed layer at 100°C with a high SLD corresponding to a film density of 98%. However, it is unlikely that the film density formed by self-organization in the lubricant would be high enough to be comparable to that of the bulk state [19]. In general, a decrease in the degree of the amplitude of the fringes in the reflectivity profile indicates an increase in surface roughness. The decrease in the amplitude was most pronounced for dC16FA at 100°C compared with the



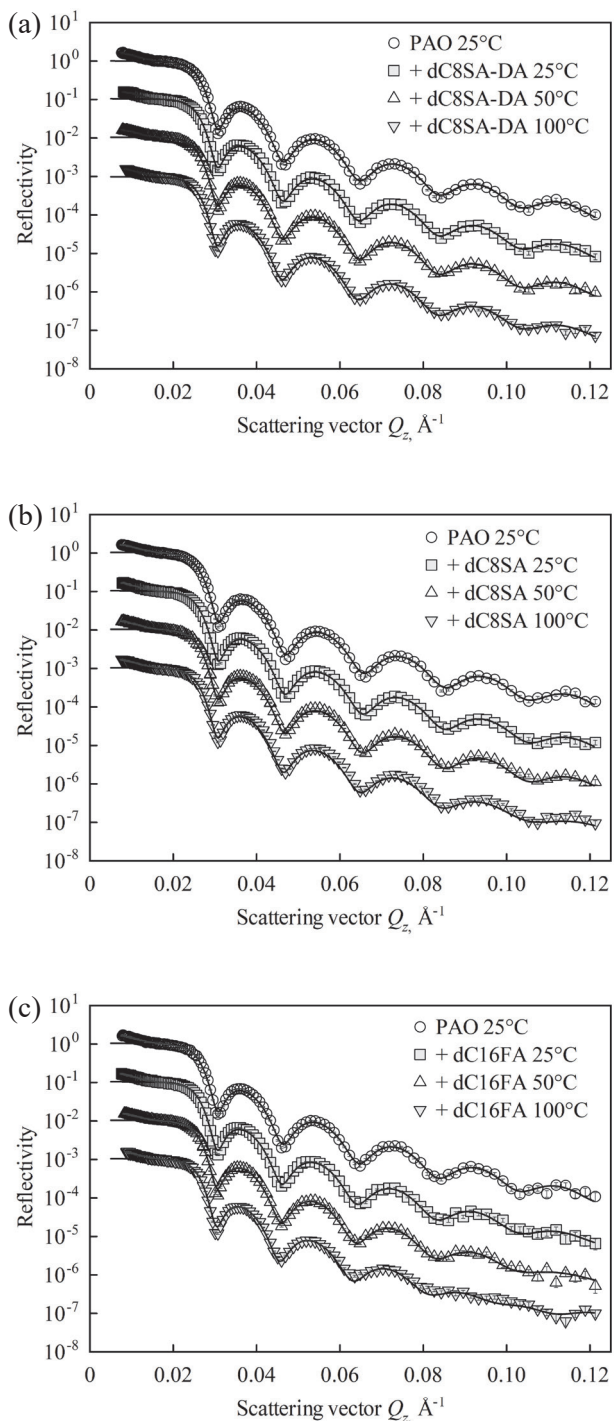


Fig. 4 Neutron reflectivities measured for evaluating temperature dependence of (a) dC8SA-DA, (b) dC8SA and (c) dC16FA adsorbed layer formation. Solid lines are optimized fitting results; reproduced with permission from [37] Copyright (2022) Japanese Society of Tribologists

other additives, indicating the possibility of Fe film corrosion. The SLDs of the Fe and Fe oxide used in these tests were  $12\text{--}13 \times 10^{-6} \text{\AA}^{-2}$  and  $7.1 \times 10^{-6} \text{\AA}^{-2}$ , respectively, which are higher than that of dC16FA in the bulk state ( $6.4 \times 10^{-6} \text{\AA}^{-2}$ ). The adsorbed dC16FA molecular film measured in this study was not in the state of a simple monolayer because the lubricating additives

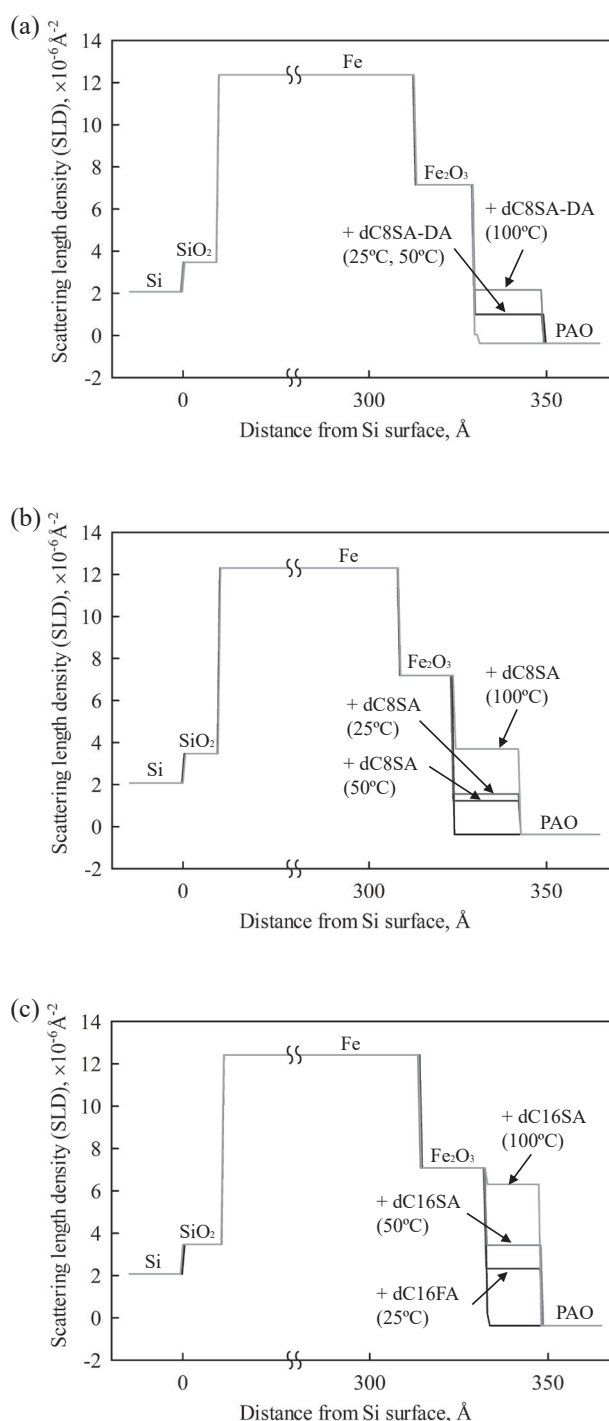


Fig. 5 SLD profiles obtained from optimum fitting analysis for (a) dC8SA-DA, (b) dC8SA and (c) dC16FA adsorbed layer formation; reproduced with permission from [37] Copyright (2022) Japanese Society of Tribologists

corroded the Fe surface at high temperature, and the dC16FA metal salts that desorbed at high temperature were deposited on the surface. Therefore, the presence of Fe in the adsorbed layer is likely to have increased the SLD. In contrast, when dC8SA and dC8SA-DA were used at 100°C, the density of the adsorbent film formed by dC8SA increased to 76% while that of dC8SA-DA was only 47%. The mechanism of the increase in the density of the adsorbed layer at high temperature is expected

Table 2 Thickness and film density of adsorbed layer estimated by neutron reflectometry (The film density of dC8SA-DA is represented by that of deuterated part (dC8SA) composing dC8SA-DA.); reproduced with permission from [37] Copyright (2022) Japanese Society of Tribologists

	dC8SA-DA		dC8SA		dC16FA	
	Thickness [nm]	Film density [%]	Thickness [nm]	Film density [%]	Thickness [nm]	Film density [%]
25°C	2.0	26	1.9	30	1.5	40
50°C	1.9	25	1.9	36	1.6	56
100°C	1.9	47	1.9	76	1.5	98

to be that the diffusivity of the additive molecules in the PAO increases, making them more accessible to the surface [8]. In addition, the fluctuation of additives already adsorbed on an Fe surface is more pronounced, which should facilitate exposure of the Fe surface areas, where additives can newly adsorb [26]. The apparent film density of dC8SA-DA was lower than that of dC8SA, while the IR measurements described in Sec. 3.2 indicate that derivatization would increase the adsorption of succinate on the Fe surface. If not only the dC8SA but also the C12DA was adsorbed on the Fe surface, it prevents the increase in the density of neutron-detectable dC8SA in adsorbed layer. As in the model presented by Kondo [27], both dC8SA and C12DA adsorbed on the Fe surface, and the derivative may have had a higher overall film density than that of succinate alone.

As mentioned in Sec. 4.1, the dibasic acid ester derivative used in the neutron reflectometry was composed of succinate with an alkyl chain with eight carbon atoms, which has a strictly different molecular structure from that of SA-DA. However, they both are composed of succinate and amines. Therefore, the difference in the density of the adsorbed molecular films formed by dC8SA and dC8SA-DA suggests that the adsorbed SA-DA layer was formed by the co-adsorption of succinate and amine. In fact, the friction test results presented in the next section indicate that both molecules were adsorbed.

## 5 Macro-tribology tests

### 5.1 Lubricants and experimental conditions

To evaluate the macro-tribological properties of the adsorbed layer formed by each additive, friction tests were carried out with disks and balls made of bearing steel (AISI 52100). The surface roughness of the disks was about Ra 0.01, and the balls were 3/16 inch in diameter and grade G28 (Ra less than 0.05). The specimens were ultrasonically cleaned with hexane and acetone for ten minutes each, followed by a ten-minute cleaning with a UV ozone cleaner (UV253E; Filgen). The specimens were immersed in lubricant for 12 hours at room temperature before friction measurements were started using a ball-on-disk friction tester (FPR-2100; Rhesca). Linear reciprocating friction testing (1000 cycles) was performed at a load of 0.49 N (maximum Hertzian contact pressure 600 MPa), a speed of 20 mm/s, and a period of 1 Hz at 25°C. The same testing was then performed again after heating the balls and disks in lubricant at 150°C for more than 30 min, and completed so that the heating time was within 2 hours. This series of tests was performed six times for each lubricant.

A stylus profilometer (Dektak XT-S; Bruker) was used to measure disk surface wear after reciprocating friction

and ultrasonic cleaning with hexane and acetone for 5 min. Cross-sectional profiles were obtained by scanning the probe perpendicular to the wear scar. The scanning conditions were a load of 29.4 mN and a speed of 100  $\mu\text{m/s}$ . Although the tip radius of the stylus probe is 12.5  $\mu\text{m}$ , the outlines of the wear scars were correctly measured since the widths of the scars were about 50  $\mu\text{m}$  and the depths were less than 300 nm. The profiles were measured at five points from each scar, and the maximum wear depth was taken as the average.

### 5.2 Results

Figures 6 (a) and (b) show typical results for each test. When SA-DA, C18:1SA, and C16FA were used, the fluctuation of the CoF with the friction cycle was smaller; when C12DA and

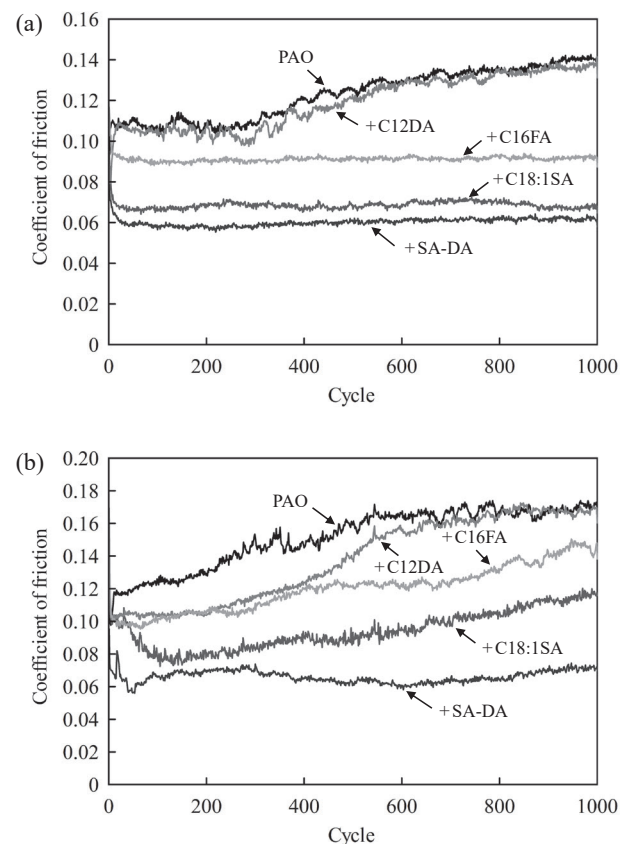


Fig. 6 Typical result of macro-scale friction test conducted at (a) 25°C and (b) 150°C; reproduced with permission from [37] Copyright (2022) Japanese Society of Tribologists

PAO (without additives) were used, the CoF tended to increase in the latter half of the test. The average CoFs for 1–100 ( $\mu_{1-100}$ ), 901–1000 ( $\mu_{901-1000}$ ), and 1–1000 ( $\mu_{Total}$ ) cycles of the six friction tests for each lubricant are shown in Figs. 7 (a) and (b). For SA-DA and C18:1SA, the differences between  $\mu_{1-100}$ ,  $\mu_{901-1000}$ , and  $\mu_{Total}$  were small, which indicates stable friction, and the values were smaller than for the other additives. The average values of the maximum wear depth are shown in Fig. 8. The wear of the lubricant with SA-DA and C18:1SA was less than with PAO without additives. When C12DA was used, the wear depth was

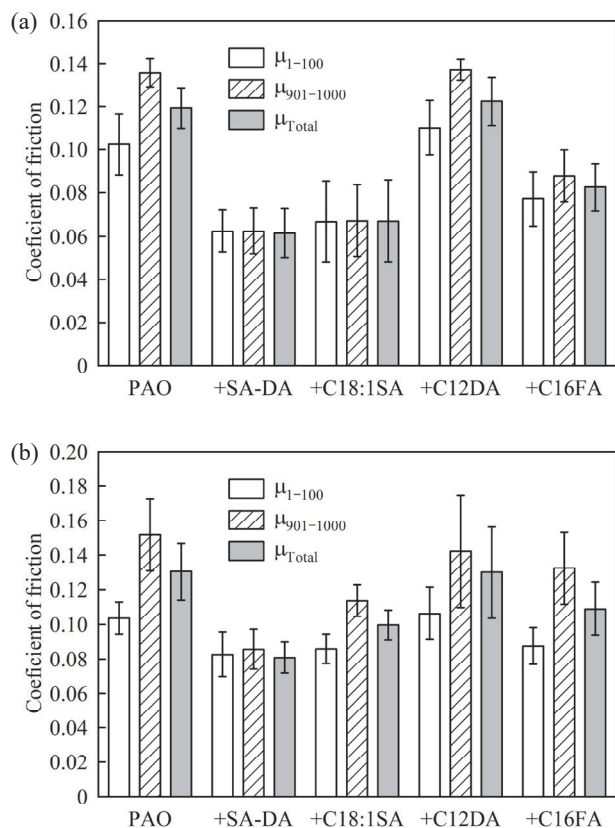


Fig. 7 Average coefficient of frictions for each lubricant measured at (a) 25°C and (b) 150°C; reproduced with permission from [37] Copyright (2022) Japanese Society of Tribologists

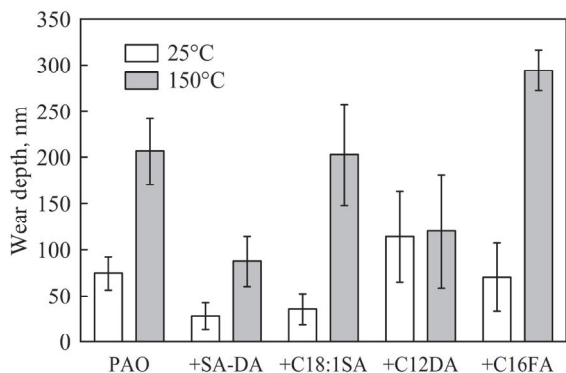


Fig. 8 Wear depth measured after macro-scale frictional test; reproduced with permission from [37] Copyright (2022) Japanese Society of Tribologists

almost the same as that without additives, indicating that it has poor wear reduction performance.

Since the terminal carboxy groups of C16FA, C18:1SA, and SA-DA were chemically adsorbed on the steel surface, both the ball and disk specimens had an adsorbed layer with a high load capacity, resulting in low friction. C18:1SA has one more carbonyl group, which can create a hydrogen bond between the additive and a steel surface, than C16FA [8]. In general, additives with more functional groups can adsorb more tightly to steel surfaces [28]. Therefore, C18:1SA and SA-DA strongly adsorbed on the steel surface and showed better wear reduction performance than C16FA. The results of neutron reflectometry suggested that C18:1SA and SA-DA form multilayer on the ball and disc surfaces. Therefore, not only slip between opposing adsorbed layers at the contact point, but also slip within the multilayer structures, which contributed to the further reduction of friction and wear. Amine-based additives have been reported to form a weak adsorbed layer and to have poor friction reduction performance [6, 15]. Similarly, the C12DA was not able to maintain its adsorbed layer under friction at a contact pressure of 600 MPa and was not effective in reducing friction and wear.

At 150°C, SA-DA showed a smaller amount of wear compared to the other additives. Generally, under high-temperature conditions, fatty acids more easily desorb from a steel surface, and the desorption is faster under applied friction conditions than under ambient conditions. Since fatty acids desorb with Fe atoms chemically bonded with a carboxyl group and other fatty acids are newly adsorbed on the steel surface, corrosive wear is caused by the continuous adsorption and desorption of fatty acids during continuous friction. Therefore, even though C16FA was effective in reducing wear at 25°C, the wear increased significantly at 150°C. For C18:1SA, because it has two carbonyl groups in the molecules and is more strongly adsorbed on a steel surface, its desorption is more difficult, and the increase in wear at 150°C seems to be less than that with C16FA. It is generally known that unsaturated fatty acids with double bonds in the alkyl chain, such as oleic acid, are less effective in reducing friction and wear in high-temperature environments. This is because, although molecular motion is more intense in high-temperature environments, the bending structure at the cis-type double bond prevents the formation of a densely packed layer due to steric hindrance, and the adsorbed layer cannot be maintained sufficiently stable against friction [8, 29]. On the other hand, when the density of an adsorbed layer is high, the interaction between the alkyl chains increases the film strength and improves the friction and wear properties [30, 31]. The results of the neutron reflectometry indicate that the adsorbed layer formed by SA-DA may have been densified by C12DA filling the spaces where C18:1SA was not adsorbed. Therefore, the adsorbed SA-DA layer not only had excellent friction properties due to the high film density but also maintained high wear resistance under high-temperature conditions because the interaction between the alkyl chains inhibited the desorption of C18:1SA, thus preventing excessive corrosive wear.

## 6 Nano-tribology tests

### 6.1 Sample preparation

The neutron reflectometry results indicate that not only C18:1SA but also C12DA was adsorbed on the steel surface when lubricant containing SA-DA was used. However, in the

macro-tribological tests, the CoF did not decrease when C12DA was used alone, and the CoF for SA-DA was similar to that for C18:1SA alone. To elucidate the low-friction mechanism of SA-DA, friction tests using atomic force microscopy (AFM) were carried out. In AFM friction measurements, additives such as fatty acids, which form relatively dense adsorbed layers, have been reported to provide results that correspond to friction measurements under macro-scale conditions [7]. In addition, since the friction area is small (such as micrometer scale), the effect of contamination on the CoF can be eliminated. Then, by suppressing the increase in the localized contact pressure, the frictional properties of the additives can be correctly evaluated.

Silicon wafers cut into  $10 \times 10$  mm chips were used as substrates in the AFM friction measurements. After ultrasonic cleaning of the chips with acetone, isopropyl alcohol, and ultrapure water for ten min, the remaining organic matter on the surface was removed by oxygen plasma treatment (50 W, 10 Pa) for ten min using a dry etching system (FA-1; Samco). The chips were then coated with a 100-nm-thick Fe film using a sputtering system (SVC-700ESS; Sanyo Electronics).

## 6.2 Experimental procedure

The Fe-coated silicon chips were covered with each lubricant and left for more than 12 hours at room temperature before starting the friction tests using an AFM (SPM-9700; Shimadzu). A round probe cantilever (SD-R150-NCL; NanoWorld) made of silicon with a tip radius of about 150 nm was used. In general, additives such as those used in this study do not adsorb on silicon surfaces, and therefore, it can be assumed that there is no effect for the friction measurements by adsorbing to the probe. In the AFM friction measurement, a load is applied by pressing the cantilever against the substrate, so the range of load applied is determined by the spring constant of the cantilever, and the contact pressure with the substrate can be calculated from the tip radius of the probe. The experimental procedure is described below.

- (1) A  $2 \times 2$   $\mu\text{m}$  area was continuously scanned 100 times with a load of 7000 nN and a speed of 20  $\mu\text{m/s}$  at a resolution of 256 lines/image (7.8 nm/pixel). The CoFs were calculated from friction images measured simultaneously during successive image observations, and the relationship between the scanning cycle and the CoF was evaluated.
- (2) A  $10 \times 10$   $\mu\text{m}$  area, including the  $2 \times 2$   $\mu\text{m}$  area in step (1), was observed at a low load of 700 nN and a speed of 20  $\mu\text{m/s}$  to evaluate the amount of wear in the area applied continuous friction.
- (3) A  $5 \times 5$   $\mu\text{m}$  area, including the  $2 \times 2$   $\mu\text{m}$  area in step (1), was scanned at a speed of 10  $\mu\text{m/s}$ . The CoFs inside and outside the area subjected to continuous friction were simultaneously obtained under various loads (700–7000 nN).

The cantilever has a larger tip radius than a typical point probe cantilever and is less likely to be damaged, but the tip will mildly wear under continuous friction. Therefore, the contact pressure may have varied between tests, but the behavior of the CoF measured for each lubricant was highly reproducible.

## 6.3 Results

Figures 9 (a) and (b) show the change in CoF during continuous friction over 100 cycles. Tests for each lubricant were carried out more than three times, but since the behavior of the CoF for each additive was highly reproducible, the CoFs measured at the 1st, 5th, 10th, 15th, 95th, and 100th cycle

were averaged. In all tests, the CoF was initially relatively high and then subsequently decreased.

The average depth of wear caused by continuous friction is shown in Fig. 10. The depth was determined by estimating the difference in height between inside and outside the area with continuous friction, as shown in the AFM images. The average wear depth was 4.6 nm when PAO without additives

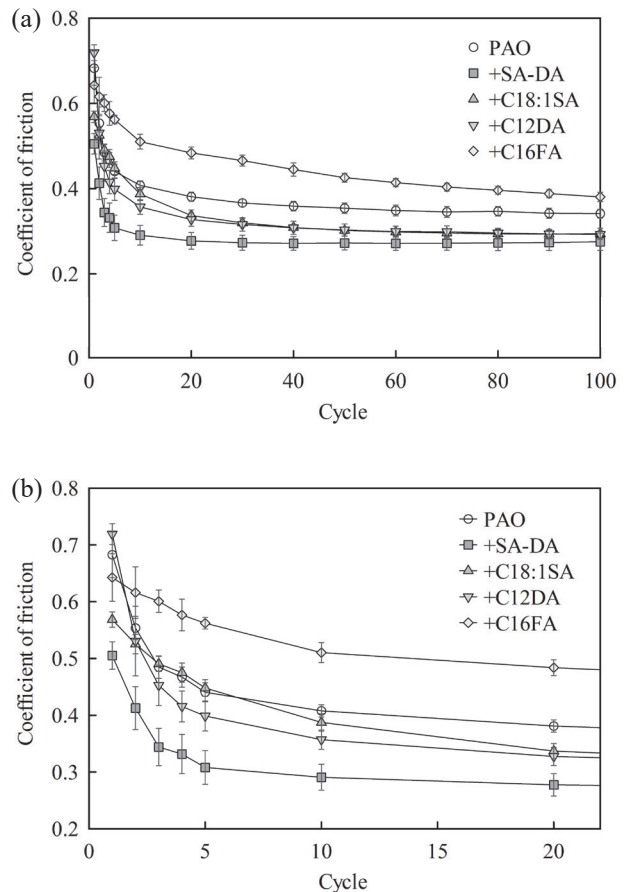


Fig. 9 Coefficient of frictions measured in nano-scale frictional test showing (a) 1-100 cycle and (b) 1-20 cycle range; reproduced with permission from [37] Copyright (2022) Japanese Society of Tribologists

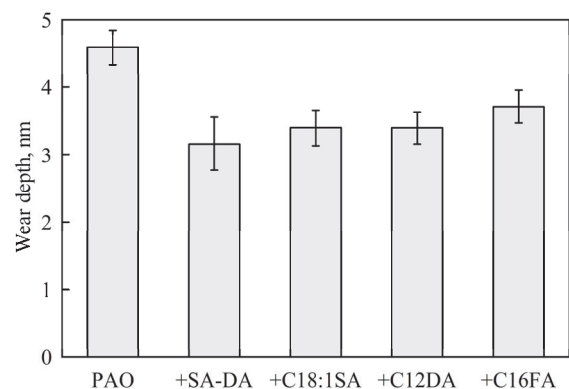


Fig. 10 Wear depth measured after 100 cycle repeated friction by AFM; reproduced with permission from [37] Copyright (2022) Japanese Society of Tribologists



was used. For SA-DA, C18:1SA, C12DA, and C16FA, it was 3.2, 3.4, 3.4, and 3.7 nm, respectively. Although the differences in wear depth among the additives was small, the difference of about 1 nm compared with PAO alone indicates that the use of additives suppressed wear on the Fe surface.

Figures 11 (a) and (b) show the CoFs measured respectively inside and outside the area where continuous friction was applied over 100 cycles. The CoFs measured outside the area (Fig. 11 (b)) show that the load dependence of the CoF was small. In contrast, inside the area (Fig. 11 (a)), a clear load dependence of CoF was observed for the lubricants with an additive. The finding that the load dependence of the CoF for PAO in the continuous friction area remained small clearly shows that the use of an additive has an effect on the frictional properties other than the running-in effect of the Fe surface.

#### 6.4 Low-friction mechanism of dibasic acid ester derivatives

The results obtained for PAO without any additives show that the CoF was initially 0.68 and then decreased with subsequent continuous friction, approaching a final value of 0.34 (Fig. 9 (a)). The initial decrease in the CoF for PAO, a non-polar hydrocarbon with low adsorption of Fe, is attributed to the running-in effect of the Fe surface caused by continuous friction.

Next, the results of friction measurements with lubricants containing additives are discussed. Generally, additives form an adsorbed layer on a metal surface and reduce friction,

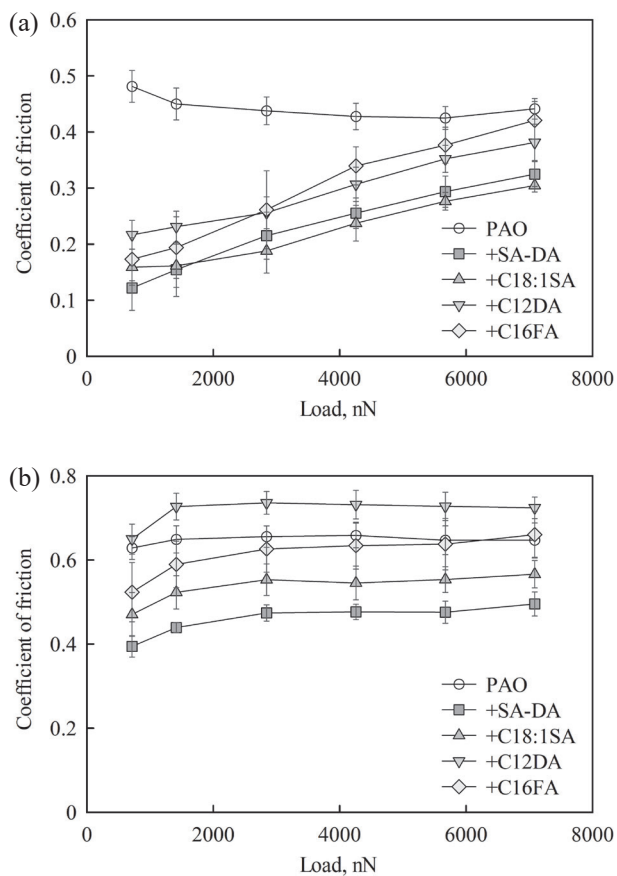


Fig. 11 Nano-scale friction measurement for evaluating load dependence in (a) pre-friction area and (b) non-friction area; reproduced with permission from [37] Copyright (2022) Japanese Society of Tribologists

but it is difficult to maintain its function effectively under high load conditions. In this friction measurement, the exact contact pressure cannot be calculated due to wear of the tip of the AFM cantilever probe, but without considering tip wear, maximum Herzian contact pressure is calculated to be about 10 GPa. The CoF for C16FA was smaller than that for PAO immediately after the start of continuous friction, but it did not decrease smoothly in response to continuous friction, and was larger than that of PAO at the 100th cycle. As described above, the CoF is greatly reduced by the running-in effect of the Fe surface, but the adsorbed layer of C16FA seems to protect the Fe surface and prevent progression of the effect. Fatty acids such as C16FA have been reported to exhibit low friction due to forming a metallic soap layer under macroscopic frictional conditions [32]. In addition, recent studies using AFM have shown that a thick metallic soap layer (~20 nm) forms in a region subjected to mechanical stimulation by a cantilever tip in a lubricant containing fatty acids [33] and that the CoF is lower in a region where a metallic soap layer is formed by applying continuous friction beforehand [34]. These results indicate that the formation of metallic soap plays an important role in the reduction of friction. Although it is assumed that a metallic soap layer of C16FA was formed in this work, more friction cycles appear to be necessary before a sufficient amount of metallic soap is formed to produce an excellent low-friction state.

In the measurement results using C12DA, the initial CoF was greater than that of PAO. It has been reported that the CoF tends to increase when the alkyl chain of the additive molecule is short or when the film density of the adsorbed layer is low [35, 36]. Since C12DA has a relatively short alkyl chain with 12 carbon atoms and two methyl groups at the end, which may have prevented its dense adsorption on the Fe surface, the disordered adsorbed layer may have caused the larger initial CoF. However, when continuous friction was applied, the CoF decreased more rapidly than that of PAO and stabilized at a smaller value, indicating that the molecular film state may change and contribute to the low friction in addition to the running-in effect. Amines around Fe atoms, forming complexes, which seem to play a role similar to that of the metallic soap formed by an acid-based additive. It has been reported that when amine additives are used alone, the density of the adsorbed molecular film tends to be low and the film lies flat against the substrate, resulting in a thin film [35, 36]. However, since the roughness of the Fe surface used in this work was at the sub-nanometer level, it may be possible that even a layer of metal complexes formed by a thin adsorbed molecular film with a small amount of C12DA is effective in reducing friction and wear.

Comparison of the results for the three additives (SA-DA, C18:1SA, and C12DA) shows that the CoF with C12DA was initially 0.72 and then rapidly decreased and that the CoF at the 5th cycle was 0.39. This rapid decrease may have been due to the weak adsorption of C12DA on the Fe surface, as shown in the macro-tribological tests, and to the ease of desorption and formation of metal complexes with wear on the Fe surface. The CoFs for SA-DA and C18:1SA were initially 0.51 and 0.57, respectively, while at the 5th cycle they were 0.31 and 0.45, respectively, indicating that there was a difference in the decrease behavior of the CoFs with the number of cycles. When C18:1SA was used, the CoF did not decrease quickly, similar to the behavior with C16FA, and a large number of cycles were necessary before reaching a constant low value. This suggests that the number of friction cycles required for an acid-type

additive to form a metallic soap layer with a noticeable low-friction effect may be greater than for an amine-type additive to form a metal complex layer. The CoFs for SA-DA and C18:SA were similar at the 100th cycle (Fig. 11 (a)) and lower than that for C12DA, indicating that the metallic soap layer formed by C18:1SA had a stronger low-friction effect than that formed by C12DA.

According to the initial CoFs (Fig. 9 (b)) and those measured outside the friction area (Fig. 11 (b)) shows that the lowest CoF was obtained for SA-DA. The neutron reflectometry results indicate that the high-density film layer formed by co-adsorption of C18:1SA and C12DA seems to have prevented direct contact between the Fe surface and the AFM cantilever tip. The reason the number of cycles required to reduce the CoF for SA-DA was less than that for C18:1SA alone (Fig. 9 (b)) is that the C12DA in the SA-DA adsorbed layer may have quickly formed metal complexes due to the applied friction, resulting in a low CoF until the C18:1SA in the SA-DA adsorbed layer formed a metal soap.

In summary, SA-DA prevents direct contact of sliding parts by forming a high-density adsorbed layer on an Fe surface, and the CoF decreases immediately after the start of friction application due to the rapid formation of the metal complexes by C12DA. Further friction results in the formation of a metallic soap by C18:1SA, which has superior friction-reducing performance, resulting in excellent low friction performance, especially under low-load conditions. Thus, when lubricants containing SA-DA are used, a synergistic effect is produced by the coexistence of C18:1SA and C12DA on the Fe surface, which is effective in reducing friction and wear.

## 7 Conclusions

This study evaluated the relationship between the composition of the adsorbed layer formed on Fe surfaces by a dibasic acid ester derivative, an organic lubricating additive reported to have friction and wear reduction effects, and the derivative's tribological properties.

- The results of transmission IR spectroscopic analysis showed that the derivative was resistant to the formation of a dimeric structure with opposing carboxy groups in the base oil, indicating that it may improve its adsorption performance.
- Neutron reflectometry showed that the dibasic ester derivative formed an adsorbed layer on the Fe surface consisting of both succinate and amine additives and that the film density tended to increase, especially at higher temperatures.
- Macro- and nano-tribological tests showed that the derivative effectively reduced the CoF by forming a high-density adsorbed layer. They also showed that the CoF rapidly decreased as the number of friction cycles increased due to the properties of the amine additives and that the formation of metallic soap derived from succinate with further friction produced a sustained low-friction effect.

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## References

- [1] Taylor, L. J. and Spikes, H. A., "Friction-Enhancing Properties of ZDDP Antiwear Additive: Part I—Friction and Morphology of ZDDP Reaction Films," *Tribology Transactions*, 46, 3, 2003, 303-309.
- [2] Taylor, L. J. and Spikes, H. A., "Friction-Enhancing Properties of ZDDP Antiwear Additive: Part II—Influence of ZDDP Reaction Films on EHD Lubrication," *Tribology Transactions*, 46, 3, 2003, 310-314.
- [3] Miklozic, K. T., Forbus, T. R. and Spikes, H. A., "Film Thickness and Roughness of ZDDP Antiwear Films," *Tribology Letters*, 26, 2, 2007, 161-171.
- [4] Zhang, J. and Spikes, H. A., "On the Mechanism of ZDDP Antiwear Film Formation," *Tribology Letters*, 63, 2, 2016, 1-15.
- [5] Hu, Z., Zhang, L. and Li, Y., "Investigation of Tall Oil Fatty Acid as Antiwear Agent to Improve the Lubricity of Ultra-Low Sulfur Diesels," *Tribology International*, 114, 2017, 57-64.
- [6] Desanker, M., He, X., Lu, J. and Liu, P., "Alkyl-Cyclens as Effective Sulfur-and Phosphorus-Free Friction Modifiers for Boundary Lubrication," *ACS Applied Materials & Interfaces*, 9, 10, 2017, 9118-9125.
- [7] Simic, R. and Kalin, M., "Comparison of Alcohol and Fatty Acid Adsorption on Hydrogenated DLC Coatings Studied by AFM and Tribological Tests," *Strojnicki Vestnik-Journal of Mechanical Engineering*, 59, 12, 2013, 707-718.
- [8] Loehle, S., Matta, C., Minfray, C., Mogné, T. L., Martin, J. M., Iovine, R., Obara, Y., Miura, R. and Miyamoto, A., "Mixed Lubrication with C18 Fatty Acids: Effect of Unsaturation," *Tribology Letters*, 53, 1, 2014, 319-328.
- [9] Kim, D. W. and Kim, K. W., "Effects of Sliding Velocity and Ambient Temperature on the Friction and Wear of a Boundary-Lubricated Multi-Layered DLC Coating," *Wear*, 315, 1-2, 2014, 95-102.
- [10] Fan, J., Müller, M., Stöhr, T. and Spikes, H. A., "Reduction of Friction by Functionalised Viscosity Index Improvers," *Tribology Letters*, 28, 3, 2007, 287-298.
- [11] Müller, M., Miklozic, K. T., Dardin, A. and Spikes, H. A., "The Design of Boundary Film-Forming PMA Viscosity Modifiers," *Tribology Transactions*, 49, 2, 2006, 225-232.
- [12] Aoki, S., Yamada, Y., Fukada, D., Suzuki, A. and Masuko, M., "Verification of the Advantages in Friction-Reducing Performance of Organic Polymers Having Multiple Adsorption Sites," *Tribology International*, 59, 2013, 57-66.
- [13] Shimizu, Y., "Technical Trend in Ashless Type Anti-Wear Agent," *Tribology*, 400, 2020, 22-24 (in Japanese).
- [14] Shimizu, Y., "Development of a New Ashless Type Anti-Wear Agent," *Journal of Economic Maintenance Tribology*, 671, 2021, 36-40 (in Japanese).
- [15] Fry, B. M., Chui, M. Y., Moody, G. and Wong, J. S. S., "Interactions between Organic Friction Modifier Additives," *Tribology International*, 151, 2020, 106438.
- [16] Takiwatari, K., Nanao, H. and Mori, S., "Effect of High Pressure on Molecular Interaction between Oleic Acid and Base Oils at Elasto-hydrodynamic Lubrication Contact," *Lubrication Science*, 22, 3, 2010, 89-101.
- [17] Lu, R., Mori, S., Tani, H., Tagawa, N. and Koganezawa, S., "Low Friction Properties of Associated Carboxylic Acids Induced by Molecular Orientation," *Tribology International*, 113, 2017, 36-42.
- [18] Campen, S., Green, J., Lamb, G., Atkinson, D. and Spikes, H., "On the Increase in Boundary Friction with Sliding Speed," *Tribology Letters*, 48, 2, 2012, 237-248.

- [19] Hirayama, T., Torii, T., Konishi, Y., Maeda, M., Matsuoka, T., Inoue, K., Hino, M., Yamazaki, D. and Takeda, M., "Thickness and Density of Adsorbed Additive Layer on Metal Surface in Lubricant by Neutron Reflectometry," *Tribology International*, 54, 2012, 100-105.
- [20] Hirayama, T. and Yamashita, N., "Combined Use of Neutron Reflectometry and Frequency-Modulation Atomic Force Microscopy for Deeper Understanding of Tribology," *Japanese Journal of Applied Physics*, 59, 2020, SN0803.
- [21] Čoga, L., Simič, R., Geue, T. and Kalin, M., "Additive Adsorption on DLC Coatings in Static and Tribological Conditions Using Neutron Reflectometry," *Frontiers in Mechanical Engineering*, 5, 2019, 10.
- [22] Hino, M., Oda, T., Kitaguchi, M., Yamada, N. L., Tasaki, S. and Kawabata, Y., "The Ion Beam Sputtering Facility at KURRI: Coatings for Advanced Neutron Optical Devices," *Nuclear Instruments and Methods in Physics Research A*, 797, 2015, 265-270.
- [23] Yamada, N. L., Torikai, N., Mitamura, K., Sagehashi, H., Sato, S., Seto, H., Sugita, T., Goko, S., Furusaka, M., Oda, T., Hino, M., Fujiwara, T., Takahashi, H. and Takahara, A., "Design and Performance of Horizontal-Type Neutron Reflectometer SOFIA at J-PARC/MLF," *The European Physical Journal Plus*, 126, 2011, 1-13.
- [24] Mitamura, K., Yamada, N. L., Sagehashi, H., Torikai, N., Arita, H., Terada, M., Kobayashi, M., Sato, S., Seto, H., Gokou, S., Furusaka, M., Oda, T., Hino, M., Jinnai, H. and Takahara, A., "Novel Neutron Reflectometer SOFIA at J-PARC/MLF for In-Situ Soft-Interface Characterization," *Polymer Journal*, 45, 2013, 100-108.
- [25] Nelson, A., "Co-Refinement of Multiple-Contrast Neutron/X-Ray Reflectivity Data Using MOTOFIT," *Journal of Applied Crystallography*, 39, 2, 2006, 273-276.
- [26] Wiśniewska, M., "Temperature Effects on the Adsorption of Polyvinyl Alcohol on Silica," *Open Chemistry*, 10, 2012 1236-1244.
- [27] Kondo, H., "Tribiochemistry of Ionic Liquid Lubricant on Magnetic Media," *Advances in Tribology*, 2012, 2012, 526726.
- [28] Baek, S. Y., Kim, Y. W., Chung, K., Yoo, S. H., Kim, N. K. and Kim, Y. J., "Synthesis of Succinic Acid Alkyl Half-Ester Derivatives with Improved Lubricity Characteristics," *Industrial & Engineering Chemistry Research*, 51, 9, 2012, 3564-3568.
- [29] Levchenko, V. A., Buyanovskii, I. A. and Matveenko, V. N., "To the New Concept of Green Tribology," *Journal of Materials Science and Chemical Engineering*, 5, 1, 2017, 175-187.
- [30] Lee, S., Shon, Y. S., Colorado, R., Guenard, R. L., Lee, T. R. and Perry, S. S., "The Influence of Packing Densities and Surface Order on the Frictional Properties of Alkanethiol Self-Assembled Monolayers (SAMs) on Gold: A Comparison of SAMs Derived from Normal and Spiroalkanedithiols," *Langmuir*, 16, 5, 2000, 2220-2224.
- [31] Xiao, X., Hu, J., Charych, D. H. and Salmeron, M., "Chain Length Dependence of the Frictional Properties of Alkylsilane Molecules Self-Assembled on Mica Studied by Atomic Force Microscopy," *Langmuir*, 12, 2, 1996, 235-237.
- [32] Bowden, F. P. and Tabor, D., "The Friction and Lubrication of Solids (Chapter X)," Oxford University Press, 2001, 200-227.
- [33] Hirayama, T., Kawamura, R., Fujino, K., Matsuoka, T., Komiya, H. and Onishi, H., "Cross-Sectional Imaging of Boundary Lubrication Layer Formed by Fatty Acid by Means of Frequency-Modulation Atomic Force Microscopy," *Langmuir*, 3, 40, 2017, 10492-10500.
- [34] Hirayama, T., Maeda, M., Sasaki, Y., Matsuoka, T., Komiya, H. and Hino, M., "Growth of Adsorbed Additive Layer for Further Friction Reduction," *Lubrication Science*, 31, 5, 2019, 171-178.
- [35] Nalam, P. C., Pham, A., Castillo, R. V. and Espinosa-Marzal, R. M., "Adsorption Behavior and Nanotribology of Amine-Based Friction Modifiers on Steel Surfaces," *The Journal of Physical Chemistry C*, 123, 22, 2019, 13672-13680.
- [36] Doig, M. and Camp, P. J., "The Structures of Hexadecylamine Films Adsorbed on Iron-Oxide Surfaces in Dodecane and Hexadecane," *Physical Chemistry Chemical Physics*, 17, 7, 2015, 5248-5255.
- [37] Yamashita, N., Hirayama, T., Yamada, N. L., Shimizu, Y., Oda, K. and Kawamoto, H., "Interfacial Structure and Tribological Property of Adsorbed Layer Formed by Dibasic Acid Ester Derivative," *Journal of Japanese Society of Tribologists*, 67, 4, 2022, 284-298 (in Japanese).



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