The Tribological Property of a-C:H Coating with Tribolayer by Additive Having Glycerol and Phosphate Oxide Structure

T. Tokoroyama · K. Tanaka · T. Kani · M. Murashima · W.-Y. Lee · N. Umehara · T. Oshio · K. Yagishita

Received: 9 July 2022 / Accepted: 26 September 2022 / Published online: 19 October 2022
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Abstract
The tribological properties of a-C:H coating sliding against a SUJ2 ball, a SUJ2 roller, and an a-C:H coated roller were investigated under temperatures ranging from 20 to 80 °C in PAO with different additives. The additives had a glycerol and hydroxyl functional group in one molecule to enhance additive adsorption for mating with the a-C:H coating disk material and to build a phosphorus oxide tribolayer. Additives with different numbers of hydroxyl groups and primary or secondary-type C6H13O structures were also prepared. The tribolayer derived from each additive was analyzed via EDS, XPS, and ToF-SIMS. XPS depth analysis for the tribolayers revealed that additives were dissociated by friction and suggested C–O bond cleavage occurred.
1 Introduction

Direct contact between two surfaces under lubrication can shorten the lifetime of a surface. Thus, lubricant viscosity is important to the design of machine components. Lubricant additives have been developed for a long time to provide superior tribological properties through the formation of a surface tribolayer. Recently, the viscosity of base oil has been found to decrease energy-saving decreases requirements such that mating surfaces are subjected to severe lubrication conditions. Using a metal morphing surface to control lubricant thickness between mating surfaces so that friction force is reduced [1, 2], and using a carbonaceous hard coating (for example, tetrahedral amorphous carbon (ta-C) [3–6], hydrogenated amorphous carbon (a-C:H) [7–9], amorphous carbon (a-C), or other dopant types [10, 11]) are methods for overcoming this situation. However, some additives cause high coating wear [12–25]. Diamond-Like Carbon (DLC) wear acceleration is assumed to be due to its structural change [26–30]. For example, nitrogenated amorphous carbon (a-CNx) was affected by friction or ultraviolet irradiation such that it released nitrogen atoms from the coating [31, 32], and experienced oxygen atom desorption from the coating [33, 34] or carbon diffusion to the mating material [35–37]. These changes caused graphitization of the topmost surface, which was assumed to be lower in hardness than the original surface. It is complicated to achieve low friction and high wear proof using multiple additives; therefore, it is desirable to achieve both low friction and high wear proof with as few additives as possible. Ultralow friction using ta-C and glycerol mono-oleate (GMO) was reported by Kano et al. and because of the hydroxyl functional group, GMO adsorbed to the ta-C surface [36]. Nevertheless, GMO was found to cause severe wear [9, 38]. For achieving low friction, hydroxyl adsorption on a carbonaceous coating has potential; therefore, the authors believe providing a hydroxyl (–OH) group to an additive structure like GMO would yield positive results. Another important
aspect for the improvement of tribological properties is realizing low wear of the mating surface. If we use conventional bearing steel as the mating material, a phosphate structure is assumed to be a good candidate to protect the surface via tribolayer, as observed for zinc dialkyldithiophosphate (ZnDTP).

The abovementioned hydroxyl group and phosphate combination in one structure is considered to be an optimal additive for DLC. We have already investigated the tribological properties of candidate additives, such as primary-type dialkyl dihydroxypropyl phosphonate (Pri-DDHP), which has straight C₆H₁₃O structure with a phosphate and two hydroxyls, secondary-type dialkyl dihydroxypropyl phosphate (Sec-DDHP), which has branch C₆H₁₃O structure with a phosphate and two hydroxyls, and secondary-type dialkyl monohydroxypropyl phosphonate (Sec-DMHP), which has branch C₆H₁₃O structure with a phosphate and one hydroxyl, under temperatures ranging from 20 to 80 °C in poly-α-olefin (PAO) [39]. Our results indicated that even if the friction pair was an a-C:H coated fixed roller and an a-C:H coated disk, a phosphate tribolayer was formed on the surfaces (as detected by energy-dispersive spectroscopy (EDS)). Nevertheless, the specific tribolayer formation mechanism remains unclear. In this study, we elucidate the effect of contact pressure, mating material, including a SUJ2 (high-carbon chromium bearing steel conforming with JIS G 4805) ball, a SUJ2 roller, and an a-C:H coated SUJ2 roller, on the tribological properties. Surface investigations using X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS) were also conducted to understand the tribolayer formation mechanism. Particularly for XPS analysis, we focused on C–P–O and C–O–P bonds because the C–P–O bond confirms a structure of C₆H₁₃O with a phosphorus side and C–P–O confirms that the bond is related to the hydroxyl bond side. These differences were detected via XPS narrow-peak measurements of O1s and P2p peaks.

2 Experimental Procedure

2.1 Friction Test Conditions and Material Properties

Friction tests were conducted using a ball or a roller-on-disk type friction equipment with an oil bath, as shown in Fig. 1. The ball is SUJ2 stainless steel with a diameter of 8.0 mm, and the roller is SUJ2 with both length and diameter of 5.0 mm. The ball/roller specimen was fixed to a specimen holder that is connected to a cantilever. The friction force was measured by a load cell and the normal load was applied by dead weights. Table 1 shows specific friction test conditions. The a-C:H coating was prepared via plasma-enhanced chemical vapor deposition with a thickness of approximately 2.0 μm [40]. No coated specimens experienced peeling off or were worn out through in this study.

The base oil was PAO (19.3 mm²/s @25 °C) with GMO (2000 ppm in base oil), Pri-DDHP, Sec-DDHP, and Sec-DMHP. Figure 2 shows the schematic images of the molecular structure of these components. GMO is used as the friction modifier and has two hydroxyl groups at the end. The other additives have the same hydroxyl group (Pri-DDHP and Sec-DDHP), except for Sec-DMHP, which has one hydroxyl group. Without GMO, these additives have the same number of carbon and hydrogens as phosphate. The differences between the additives are whether or not they have straight- or branch-type C₆H₁₃O. The additives were added in the amount of 350 ppm to the PAO. The viscosity of all lubricants with additives ranges from 18.7 to 19.6 mm²/s @25 °C.

Before the friction tests, all specimens were cleaned with benzene and acetone for 15 min. Friction tests were conducted with different normal loads to compare contact pressure. First, a 30 N normal load for the SUJ2 ball (approximately 1.9 GPa at the beginning of the friction test) and a-C:H coated disk was set in oil bath. Then, friction tests were conducted at

![Fig. 1 Schematic of ball or roller-on-disk friction test equipment](image_url)

![Table 1 Friction test conditions](table_url)
temperatures of 20, 50, and 80 °C. Each friction test was conducted three times, and the specific wear rate was calculated from the wear volume. Second, SUJ2 roller and a-C:H coated disk friction tests were performed. The contact pressure was approximately 93 MPa at the beginning of the friction test. After the friction tests, each surface was observed using a laser optical microscope, scanning electron microscope (SEM), and EDS to determine wear scar size, tribolayer thickness, and elemental composition.

Consequently, additional friction tests were conducted to determine tribolayer formation after 1, 10, and 60 min. Friction with Sec-DDHP as the representative additive at 80 °C with a SUJ2 ball and an a-C:H coated disk pair was measured. After the friction test, the ball surface and disk surface were observed using EDS.

The wear volume of the ball and roller specimens were calculated as following equation. In the case of a ball specimen, a wear scar diameter was observed by SEM, then the wear volume was calculated as following formulae (1) and (2), and the representative SEM image and schematics are shown in Fig. 3a, b.

\[ h = r - \sqrt{r^2 - \left(\frac{d}{2}\right)^2}, \]  
\[ V = \frac{\pi}{6} h(3h(2r-h) - h^2), \]

here \( V \) is the wear volume of the ball specimen, \( h \) is the wear depth from the top of the ball specimen, \( d \) is the wear diameter, and \( r \) is the ball radius. The wear volume of the roller was also in same procedure, of the ball specimen, the wear width was determined by SEM observation, and then the wear volume was calculated geometrically.

### 2.2 XPS and ToF-SIMS Analysis

Tribolayer analysis of C1s, O1s, and P2p was conducted via XPS (Ulvac phi VersaProbe III) with an Al Kα monochromatic X-ray source under vacuum lower than \(10^{-7}\) Pa. Prior to measurements of the topmost surface, Ar-ion beam sputter cleaning was performed (acceleration voltage: 4 kV) on an \( \sim 2000 \mu m^2 \) area. Afterward, XPS measurements were performed (acceleration voltage of 15 kV and power of 13 W) on an \( \sim 50 \mu m^2 \) area. Narrow-peak measurements

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**Fig. 2** Schematic images of a GMP, b Pri-DDHP, c Sec-DDHP, and d Sec-DMHP additives

**Fig. 3** a Representative wear scar on a ball specimen observed via SEM, b schematic of the wear volume of the ball specimen
for energy values ranging from 280.0 to 290.0 eV, 525.0 to 539.0 eV, and 128.0 to 138.0 eV, for C1s, O1s, and P2p, respectively, were conducted at 0.125 eV/step. The C1s peak dissociated to sp² as 284.3 eV, sp³ or aliphatic as 284.9 eV, hydroxyl as 286.1 eV, and carboxyl as 289.4 eV [41, 42]. The O1s peak was also dissociated to nonbridging oxygen (NBO) with phosphorus as 531.6 eV, bridging oxygen (BO) as 532.0 eV, C–O–P bond as 535.6 eV, and if there was another bond, such as an oxygen-containing organic species, as 535.4 eV [43]. Finally, the P2p peak was dissociated to atomic phosphorus as 122.9 eV, P2p3/2 (C–P–O) bond as 132.7 eV, and P2p1/2 (PO₄)³⁻ as 133.9 eV [44, 45]. The representative tribolayer built on the a-C:H disk slid against the a-C:H coated roller at 80 °C with Sec-DDHP was prepared to measure depth information and understand the existence of NBO and C–P–O or C–O–P bonds.

ToF-SIMS surface analysis was performed using PHI TRIFT V nanoTOF equipment. The Bi³⁺ ion with 30 kV acceleration voltage was applied to the measurement surface. The measured area was ~ 100 μm². These results reveal the existence of PO₂, PO₃, and other species.

3 Results

3.1 Friction Tests with Different Initial Contact Pressure and Contact Pairs of an a-C:H Disk vs. a SUJ2 Ball or a Roller, and an a-C:H Disk vs. an a-C:H Coated Roller

Friction tests of the SUJ2 ball and the a-C:H coated disk were conducted at temperatures of 20 °C, 50 °C, and 80 °C. Figure 4 shows the representative friction coefficient data at 80 °C for several sliding cycles. The friction coefficient for several initial cycles of the SUJ2 ball in Fig. 4a is highest under Sec-DMHP, then it decreases to the same level as Pri-DDHP. On the other hand, Sec-DDHP did not show clear friction reduction compared with the other additives. From the viewpoint of initial contact pressure, the SUJ2 roller in Fig. 4b shows a lower contact pressure situation compared with the SUJ2 ball in Fig. 4a. In this situation, all additives showed friction reduction from the very beginning of the friction test and with several cycles. This result indicates that friction coefficient reduction is related to adsorption and tribolayer
formation on the surface. Finally, for the a-C:H coated roller in Fig. 4c, the effect of only an a-C:H coated disk sliding against a-C:H roller situation is observed for each additive.

Figure 5 shows the wear scars observed on the balls. Figure 6 shows the mating surface of the a-C:H coated disks under every temperature. Under GMO [Fig. 6(a1)–(a3), 20–80 °C] and Pri-DDHP [Fig. 6(b1)–(b3), 20–80 °C], wear scar was appeared on the a-C:H coatings; however, there were no clear tribolayers. For the case of Sec-DDHP [Fig. 6(c1)–(c3), 20–80 °C] and Sec-DMHP [Fig. 6(d1)–(d3), 20–80 °C], a clear tribolayer is observed especially 80 °C for Sec-DDHP, and over 50 °C for Sec-DMHP. To compare the wear amount of each friction test temperature, a summary of ball wear is shown in Fig. 7a, and a-C:H disk results are shown in Fig. 7b. The specific wear rate of the SUJ2 ball at 20 °C with Sec-DDHP showed the lowest value; however, this value increased rapidly at 50 °C. This difference is assumed to be related to the adsorption ability of the additive because the observed surface did not have clear tribolayer. The additive GMO was assumed to be an adsorption type, and the observation results of Pri-DDHP looked similar to the GMO, and Sec-DDHP is also similar surface under 20 °C and 50 °C. Such that Pri-DDHP was also assumed to be adsorption type, and Sec-DDHP was also same type below 50 °C. On the other hand, Sec-DMHP showed almost the same value of specific wear rate from 20 to 80 °C. The surface observation results indicated that Sec-DMHP showed similar surface when it slid under 20 °C, then over 50 °C surface showed clear tribolayer formation. This implied that the additive changed.

The wear resistance of the SUJ2 ball, from adsorption to tribolayer formation, is varied with increasing temperature. Figure 7b shows the wear of the a-C:H disk. In the case of GMO and Pri-DDHP, the wear volume increased if the temperature rose over 50 °C which was assumed that desorption of the additives from the surface. Sec-DDHP and Sec-DMHP showed reduction of specific wear rate because of a tribolayer formation and it would protect the surface.

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**Fig. 5** SEM images of SUJ2 balls under a GMO, b Pri-DDHP, c Sec-DDHP, and d Sec-DMHP

**Fig. 6** Optical microscope images of a-C:H disks after experiencing friction under a GMO, b Pri-DDHP, c Sec-DDHP, and d Sec-DMHP
Compared with Sec-DDHP, Sec-DMHP had greater ability to form a tribolayer on the surface under high contact pressure (initially 1.9 GPa).

Friction tests of the a-C:H disk versus the SUJ2 roller were conducted next, and the wear surface of the rollers is shown in Fig. 8. Figure 9a, b summarizes the specific wear rate of the roller and the disk. The SUJ2 roller wear in GMO was almost the same from 20 to 80 °C. Conversely, Sec-DDHP and Sec-DMHP showed wear reduction from 20 to 80 °C. To confirm a-C:H disk wear from Fig. 9b,
there were not so much differences among additives at each temperature. From the wear amount of the a-C:H disk under high (1.9 GPa) and low (93 MPa) pressure as shown in Figs. 7b and 9b, a Pri-DDHP-derived tribolayer was assumed to be insufficiently formed on the a-C:H disk at 80 °C under high pressure, and therefore, the specific wear rate of Pri-DDHP did not decrease same value as other Sec-DDHP and Sec-DMHP. On the other hand, under the low pressure situation, Sec-DDHP and Sec-DMHP also showed same specific wear rate at 80 °C. It implies that low pressure at the contact did not efficiently act to form tribolayer.

Finally, friction tests between an a-C:H coated roller and an a-C:H disk were conducted to determine the differences in ferrous-based material existence in the contact area. Figure 10 shows the wear scar on the a-C:H coated rollers, and Fig. 11 summarizes the specific wear rate of the roller (a-C:H disk wear was not measurable). The specific wear rate of GMO from 20 to 80 °C was the same value across the entire temperature range. This implies that GMO adsorption to the a-C:H did not change at different temperatures.

A summary of the specific wear rate at 80 °C of all mated materials is provided in Fig. 12 as a function of Hertzian contact pressure. Sec-DDHP and Sec-DMHP showed lower wear rates. To compare only friction between a-C:H and SUJ2, the SUJ2 roller versus a-C:H disk experiment showed a lower specific wear rate. This result implied that the additives worked actively when in contact with ferrous material.

The friction tests of the a-C:H disk with the SUJ2 ball at 80 °C and with Sec-DDHP and Sec-DMHP were confirmed via EDS analysis, as shown in Fig. 13. The SEM images indicated several indentation marks and both surfaces showed carbon, oxygen, and phosphorus. The detailed tribolayer formation mechanism is explored in the next section.
3.2 Tribolayer Formation Mechanism of Sec-DMHP as a Representative Additive of Hydroxyl with Phosphate

The tribolayer formation mechanism was investigated through different friction cycles of 1, 10, and 60-min during friction tests, as shown in Fig. 14. The friction coefficient at the beginning of each test was also same value. It decreased when the number of sliding cycles exceeded ~100 cycles. The tribolayer formation process on the SUJ2 ball and the a-C:H disk was thoroughly analyzed via EDS as shown in Fig. 15. It includes an SEM image of the a-C:H disk surface, measurement specifications, and carbon, oxygen, phosphorus, and ferrous content, which show the same results for the SUJ2 ball across the cycle series. From the EDS analysis, Fig. 15(a)–(i4), (i5), and (i6) shows typical adhesion elements from the SUJ2 ball. The wear scar on the SUJ2 ball exhibited some carbon and phosphorus adhesion, as well as oxygen. After 10 min from the beginning of the friction application, the a-C:H surface was covered by oxygen and phosphorus. Nevertheless, a tribolayer on the SUJ2 ball was difficult to detect via EDS. After 60 min of the friction test, the a-C:H coating disk was covered by phosphorus and oxygen. The mating SUJ2 ball surface was slightly covered by oxygen and phosphorus. These results indicated that the initial presence of friction from 0 to 1 min exhibited phosphorus and oxygen, which were generated from the additive and ferrous element acting as an adsorbed material on the a-C:H surface. The friction test from 0 to 10 min showed enhanced tribolayer formation on the a-C:H disk, wherein the contact width of the SUJ2 ball and the a-C:H disk was thoroughly covered by tribolayer. After tribolayer formation, the friction coefficient decreased.

3.3 XPS and ToF-SIMS Analysis of the Topmost Tribolayer Surface

According to the friction test results of each additive of the primary and secondary series, it was of interest to determine the molecular bonds included in the tribolayer. The topmost surface of each tribolayer was analyzed via XPS, as shown in Fig. 16. The surface was prepared from the friction of the a-C:H disk against the a-C:H roller at 80 °C. Figure 16 includes C1s, O1s, and P2p data. The C1s data were assumed to be related to the additive because of the XPS detection depth (~2 nm). All C1s data showed a very small amount of carboxyl group and mainly consisted of sp2 hybridization. The sp3 or aliphatic structure and hydroxyl group existed; however, there were no clear differences between them. Based on the O1s data, Pri-DDHP in Fig. 16a–(ii) indicated NBO as the main tribolayer structure. The second highest peak was the C–O–P bond, which was followed by BO and the C–O–P bond. The P2p data in Fig. 16a–(iii) indicated that the main bond could be assumed to be P2p(3d) (C–P–O). The next additive data in Fig. 16b–(ii) show O1s of Sec-DDHP. The BO and the C–P–O peak consisted main peak
of O1s [Fig. 16b–(iii)]. Finally, the Sec-DMHP tribolayer exhibited primarily BO [Fig. 16c–(ii)] and C–P–O bonds [Fig. 16c–(iii)]. The main differences between the primary and secondary-type additives were revealed from the O1s peak such that the primary type showed an NBO-type tribolayer at the topmost surface.
The topmost surface of the tribolayer on the a-C:H rollers was measured using ToF-SIMS, as shown in Fig. 17. Each figure includes mass information, a surface observation optical image, and CH, O, C₂H, PO₂, and PO₃ spectra. All ToF-SIMS data indicated that every tribolayer included PO₂ and PO₃ at the contact area.

### 3.4 XPS Depth Analysis for Sec-DMHP

As discussed in previous sections, the friction coefficient decreased after a tribolayer formed on the a-C:H disk surface. The depth information of the tribolayer is of interest because the tribolayer was assumed to form by additive molecule adsorption and a chemical reaction changed the additive structure to other material, like phosphorus oxide. Thus, XPS depth analysis was conducted for both the a-C:H coated roller and disk. Figure 18 summarizes the results of O1s and P2p. Figure 18a shows the O1s spectra of the a-C:H disk surface. The topmost surface mainly consisted of the NBO structure. It was assumed that the additive itself adsorbed on the tribolayer. Underneath the NBO structure, the O1s peak center moved toward the BO structure. This result indicated that the inside of the tribolayer was affected by friction and the additive molecular structure changed to BO type. Figure 18b shows the P2p spectra, which clearly indicates that the topmost surface is mainly a C–P–O bond structure. However, the inside of the tribolayer consisted of (PO₄)³⁻ structure and atomic phosphorus. The counter material of the a-C:H coated roller was covered by NBO, BO, and C–O–P bonds at the topmost surface, as shown in Fig. 18c. The main structure of the tribolayer also consisted of C–P–O and (PO₄)³⁻. It was assumed that the tribolayer on the a-C:H coated roller was thinner than that of the a-C:H disk because after only a small amount of Ar-ion beam sputtering peeled the topmost adsorbed additive.

![Fig. 16 XPS analysis results of the a-C:H disk surface at 80 °C in a Pri-DDHP, b Sec-DDHP, and c Sec-DMHP. (i) C1s, (ii) O1s, and (iii) P2p spectra](image-url)
4 Discussion

The differences between primary- and secondary-type C$_6$H$_{13}$O structures were assumed to influence the adsorption ability. The specific wear rate of the a-C:H disk under different friction conditions, as shown in Figs. 7b, 9b, and 11, indicated that the primary-type additive showed high wear tendency in comparison with the secondary type. This was assumed to be affected by the dissociation temperature of the additive. The authors have already reported thermogravimetric and differential thermal analysis of the additives, which indicated that only Pri-DDHP showed two dissociation temperatures (~ 80 °C and 180 °C) [40]. This result implied that the Pri-DDHP had a possibility of two dissociation process, and it was true the first dissociation temperature was less than others. Therefore, Pri-DDHP may lost adsorption ability rather than others due to structural change of the additive itself. To compare with Sec-DDHP (two hydroxyl group) and Sec-DMHP (one hydroxyl group), friction coefficient decreased with number of hydroxyl group when it slid under a-C:H roller against a-C:H disk. It implied that hydroxyl group acted as a function of adsorbate acceleration. On the other aspects, in the case of friction between SUJ2 and a-C:H, Sec-DDHP showed higher friction coefficient tendency rather than Sec-DMHP, although the number of hydroxyl group was twice. In the case of friction pair includes ferrite alloy, the order of friction coefficient was not same as the number of OH functional group in the additive.
structure. Therefore, the frictional property is assumed to be determined by other factor rather than adsorption ability.

From the viewpoint of additive structure, contact pressure, and existence of ferrous material as the counter material, the friction results of Fig. 7b indicated that secondary-type additives effectively acted to form a tribolayer on the a-C:H disk when it slid against the SUJ2 ball at temperatures over 50 °C. Conversely, primary-type additives did not show protection of the a-C:H disk. Under high contact pressure, such as 1.9 GPa, at the initial and ~ 400 MPa at the end of the presence of friction, the pressure was assumed to exceed the hardness of the tribolayer formed by the primary type. To compare high contact pressure, such as that in the SUJ2 roller against the a-C:H disk friction, the specific wear rate of both secondary-type did not decrease less than GMO and primary type as shown in Fig. 9b, and it indicated that wear protect tribofilm insufficiently existed. If we changed the ferrous material to the a-C:H coating as the counter material, it clearly indicated that all additives were not subjected to a chemical reaction to form a tribolayer, causing high wear (as shown in Fig. 12). Although there were regions without ferrous material in the contact area under the a-C:H roller against the a-C:H disk, primary- and secondary-type additives adsorbed and/or formed a tribolayer on the a-C:H roller, as shown in Fig. 17. Specific XPS depth analysis (Fig. 18a) revealed that the O1s peak showed a small amount of C–O–P, BO, and NBO existed from the dissociation of Sec-DMHP when the a-C:H disk slid against SUJ2. The peak center of O1s moved toward NBO within the tribolayer thickness, which indicated that intact Sec-DMHP adsorbed on the tribolayer. P2p, as shown in Fig. 18b, also indicated that dissociated (PO₄)³⁻, C–P–O, and atomic phosphorus existed close to the a-C:H disk surface and that the peak center of P2p moved toward C–P–O within the tribolayer thickness. This C–P–O indicated the intact Sec-DMHP molecule. The abovementioned tribolayer formed on the surface is summarized in Fig. 19(a1) and (a2). XPS analysis indicated cleavage between the carbon and oxygen bond, which is related to C₆H₁₃O. This
was assumed to have occurred due to the catalytic effect of the ferrous material to dissociate the additives at the C–O bond. If ferrous material existed close to phosphorus oxide ester, C–O cleavage was taken place easier than P–O cleavage [46].

In the case of the a-C:H roller against the a-C:H disk, dissociation of the additives was suppressed because there was no catalytic effect. In this situation, the additives were assumed to act as a friction modifier, as shown in Fig. 19(b1) and (b2). The secondary-type additives have a different number of hydroxyl groups, which was assumed to affect the friction and wear of mating materials. Figure 12 indicates that secondary-type additives showed almost the same tribological properties. From the viewpoint of environmental impairment by poisonous emission control catalysts and by blocking filters in car exhaust systems, fully dissociable additives are considered most beneficial to the environment. Of the additives investigated in this paper, Sec-DMHP can be fully dissociated under approximately 259 °C without a catalyst [40]. Thus, the Sec-DMHP additive has proved to be most beneficial in this paper.

5 Conclusion

In this paper, to determine a beneficial additive for a-C:H coating with/without SUJ2 or against a-C:H, we conducted friction tests under PAO with different additives. The additives were GMO, Pri-DDHP, Sec-DDHP, and Sec-DMHP, which were chosen to elucidate the effect of differences between primary- and secondary-type of C₆H₁₃O structures and the differences between the number of hydroxyl groups (one or two). After the friction tests, the wear scar on the a-C:H disk and the roller was analyzed using XPS and ToF-SISM.

The specific wear rate as a function of Hertzian contact pressure revealed that Sec-DDHP and Sec-DMHP showed a lower wear rate tendency compared to GMO and Pri-DDHP. To compare friction between a-C:H and SUJ2, SUJ2 roller
versus a-C:H disk conditions showed a lower specific wear rate. This result implied that additives worked actively when in contact with ferrous material.

From XPS depth analysis of the tribolayer formed by the a-C:H disk against the SUJ2 ball, the O1s peak showed that a small amount of C–O–P, BO, and NBO was present due to dissociated Sec-DMHP at the bottom of the tribolayer. The peak center of O1s moved toward NBO at the topmost surface, which indicated that intact Sec-DMHP adsorbed on the tribolayer. P2p also indicated that dissociated (PO₄)³⁻, C–P–O, and atomic phosphorus existed close to the a-C:H disk surface. The peak center of P2p moved toward C–P–O close to the topmost surface. This C–P–O indicated the presence of intact Sec-DMHP molecules. XPS analysis indicated cleavage between carbon and oxygen bond, which is related to C₆H₁₃O. This was assumed to occur due to the catalytic effect of a ferrous material such that it dissociated Sec-DMHP to C₆H₁₃O, (PO₄)³⁻, and C–P–O, BO, and NBO was present due to catalytic dissociation at the C–O bond.

In the case of the a-C:H roller against the a-C:H disk, dissociation of the additives was suppressed because there was no catalytic effect. The additives were assumed to act as friction modifiers in this condition. The secondary-type additive no catalytic effect of a ferrous material such that it dissociated the additives at the C–O bond.

The peak center of O1s moved toward NBO at the topmost surface, which indicated that intact Sec-DMHP adsorbed on the tribolayer. P2p also indicated that dissociated (PO₄)³⁻, C–P–O, and atomic phosphorus existed close to the a-C:H disk surface. The peak center of P2p moved toward C–P–O close to the topmost surface. This C–P–O indicated the presence of intact Sec-DMHP molecules. XPS analysis indicated cleavage between carbon and oxygen bond, which is related to C₆H₁₃O. This was assumed to occur due to the catalytic effect of a ferrous material such that it dissociated the additives at the C–O bond.

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Declarations

Competing interest The authors have no relevant financial or nonfinancial interests to disclose.

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