Journal of the KSTLE Vol. 16, No. 3, June 2000, pp. 223~230
The Korean Society of Tribologists & Lubrication Engineers

Friction Reduction with Oil-Soluble Organo-Molybdenum Compound and Environmental Effect

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유용성 몰리브덴 화합물의 마찰감소 작용과 분위기효과

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요 약–Molybdenum dialkyl dithiophosphate(MoDTP) 마찰특성을 이원통 마찰시험기에 의한 마찰실험및 X-선광전자분광분석기를 이용하여 마찰표면을 분석함으로써 MoDTP의 마찰감소 작용에 대해 고찰하였다. MoDTP의 마찰감소작용은 마찰표면에 생성하는 MoS_2에 의존하였다. 몰리브덴(Mo)이 용이하게 금속내부로 확산하는 질소분위기 중에서는 MoDTP의 마찰감소 특성은 나타나지 않았으며, 금속표면에 산화피막이 존재할 때 MoDTP의 마찰감소작용이 잘 나타남을 알 수 있었다.

ABSTRACT–Factors influencing friction reduction with MoDTP(molybdenum dialkyl dithiophosphate) lubricant were investigated through a frictioning experiment using two-cylinder edge surface frictioning tester and XPS surface analysis. The friction reduction effect gained with MoDTP lubricant appeared to be largely attributable to MoS_2 formation on the frictioning interface. Under N_2 atmosphere, Mo diffused into the metal substrate, easily escaping from MoS_2 so the friction reduction effect from MoDTP was not gained. However, when an oxide surface film was preliminary prepared on frictioning surface, this Mo diffusion to metal substrate from MoS_2 was effectively inhibited. Then desired lubulication effect of MoDTP was gained even under N_2 atmosphere. As such, the existence of a surface oxide film on the frictioning surface was concluded to be of essential importance in order to gain a lubrcating effect with MoDTP.

1. INTRODUCTION

In order to reduce the viscosity resistance of a fluid lubricant, efforts have been made to develop a lubricating oil with low viscosity in automotive and other sectors of industry. One of the consequences of reduced viscosity of a lubricating oil is to increase the surface ratio of solid contact. Thus, it is desirable to add a certain solid lubricating agent to a low viscosity lubricating oil for the purpose of ensuring a sufficient lubrication effect at the solid contact part of surface area. Such an additive is called a friction modifier(FM). Sevaral FM agents have been developed. Among these, several containing Mo were proved to exert a significant friction reduction effect[1,2]. Several authors[3-7] have evaluated the effectiveness of Mo-base FM agents. Yamamoto and Gondo[1] reported that the friction reduction gained with an oil-soluble Mo-compound was attributable to the formation of a MoS_2-containing surface film. The friction reduction effect with MoDTP failed to emerge at an elevated temperature since MoO_3, instead of MoS_2, formed at frictioning interface. Zheng *et al*[2], reported that the friction reduction effect gained with MoDTP was largely due to the flattening of the frictioning surface over which the lubricating MoS_2 tended to form selectively. Since these reports[1,2], many researchers have surmised that the key factor for friction reducion with Mo-base FM agents must be the MoS_2 formation at the frictioning interfae, although the detailed mechanisms leading to the friction reduction still appear to be ambiguous. Thus, we chose MoDTP as the representative additive of this category. The factors influencing its lubrication performance were elucidated, focusing on the roles of MoS_2 through experiments conducted under variety of atmospheres.

2. EXPERIMENT

The friction experiment was done in two-cylinder edge surface frictioning tester as shown in Fig. 1. Both upper and lower test pieces were made of S45C carbon steel. The upper one was subjected to a hardening heat treatment and its hardness(H_v; micro Vickers) was raised to 600 compared with H_v=190 of the original one(lower piece).

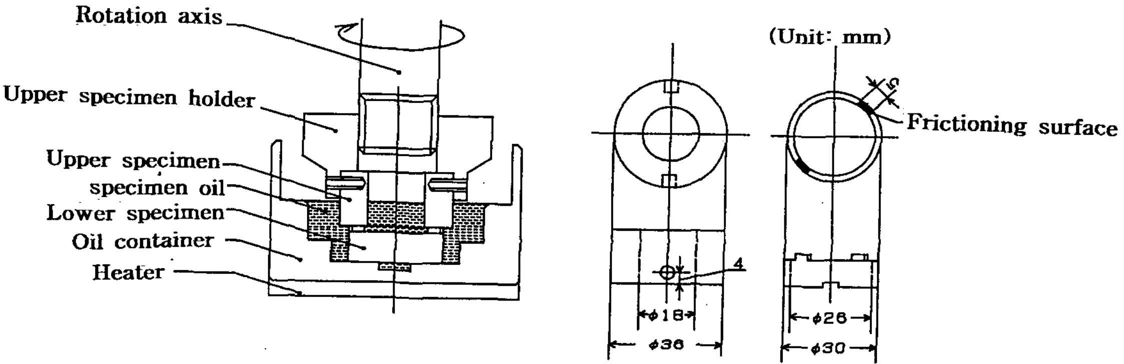
Both upper and lower specimen surfaces were machine polished to a surface roughness of R_a=0.017 m. The upper one was further polished by emery paper down to R_a=0.013 m.

Both upper and lower specimen pieces were then subjected to ultrasonic cleaning in toluene. Thereafter, thermal toluene cleaning was done using a Sockslay extracter and was subsequently dried under vacuum before serving for the test run. Standard test conditions were; load=631 N, contact surface pressure of 31.6 MPa, circumferential velocity=44 mm/s, temperature=60, 100 and 150°C. Some exprimental runs were done with a load of 2960 N or contact surface pressure of 148 MPa. The alkly-base in used MoDTP was 2-ethylhexyl. The MoDTP was dissolved into parafine-base refined mineral oil to concentrations of 1, 5 and 10 mmol/l. Table 1 lists representative properties of the oil.

3. RESULTS AND DISCUSSION

3-1. Friction reduction with MoDTP

Fig. 2 summarized the frictioning test results obtained with 1 mmol/l MoDTP -containing lubricant oil P-150. It is evident that by adding MoDTP, the friction coefficient was appreciably lowered from the value 0.14 when lubricating with a P-150 base oil without an MoDTP addition. Fig. 3 summarized similar results obtained with 10 mmol/l MoDTP-containing P-150. In this case, the friction coefficient was the lowest at 60°C, in contrast to the monotonically decrease of the friction coefficient as the temperature increased from 60°C to 150°C in the 1 mmol/l MoDTP lubricant(Fig. 2). Fig. 4 shown the friction coefficient values in form of the isotherms after 30 min. of frictioning for the MoDTP concentration in p-150. The plots in Fig. 4 clearly show the trend that friction coefficient at 60°C tends to decrease as the MoDTP concentration increased, in contrast to the opposite result exhibited at temperatures 100 and 150°C. After the frictioning experiments in oil with relatively high MoDTP concentration (5 and 10 mmol/l) at relatively high temperatures (100 or 150°C), an appreciable amount of sediment was observed in the specimen oil. This appeared to be the decomposition product of MoDTP. In an earlier work[8], We investigated the oxidation inhibiting



Frictioning test arrangement Upper specimen Lower specimen

Fig. 1. Frictioning test arrangement and specimen dimensions.

Table 1. Properties specimen oil

Specimen oil	P-150 (refined mineral oil)
Specific weight (15-14°C)	0.8621
Viscosity, cSt	40°C : 30.47 100°C : 5.323 120°C : 4.198
Viscosity Index	107
S-content, ppm	5
Average molecular weight	410

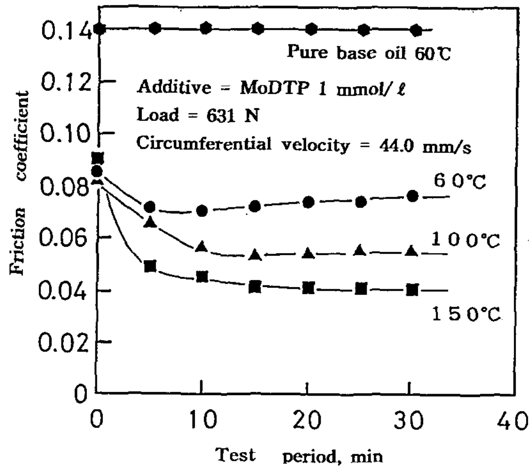


Fig. 2. Friction reduction with MoDTP (1 mmol/*l*).

power of MoDTP and clarified that MoDTP was proved to decomposition through a reaction with peroxide formed in the lubricating oil in the initial stage of oxidation. We guessed that the observed trend of an increasing MoDTP concentration must be ascribe to a certain harmful effect exerted by the decomposition product of Mo DTP. This aspect was, however, not directly related to the concern of the present work so we did not conduct further characterization of this deposit.

3-2. Friction surface characterization

The lower specimen surface was chracterized by an XPS spectroscopy under following condition:

(1) X-ray source : Mg K (8 kV~30 mA)

(2) Ar^+ etching : gas pressure 5×10^{-4}Pa, emission 5 kV~25 mA

(3) 30 repeated etching at 2 min. interval (total 60 min.)

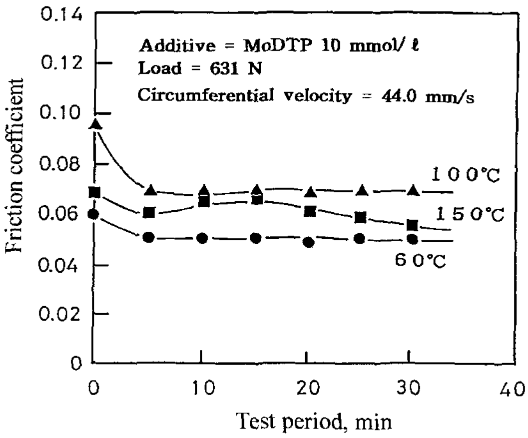


Fig. 3. Friction reduction with MoDTP (1 mmol/*l*).

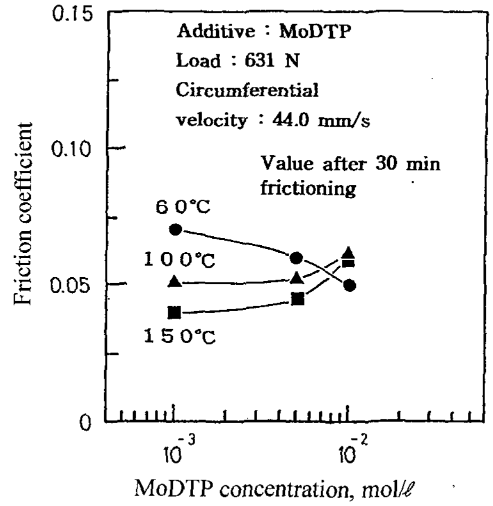


Fig. 4. Influences of temperature and MoDTP concentration on friction coefficient.

Fig. 5 compared with Mo3d spectrum obtained from the surface frictioned at 60°C with the 10 mmol/l MoDTP specimen oil with those of standard specimens MoO_3, MoS_2 and Mo. As evident from the comparison, the Mo3d spectrum of the frictioned specimen surface did not coincide with any of the spectra of the individual standards. However, as shown in Fig. 6, the spectrum obtained from mixed (MoS_2 + MoO_3 + Mo) appeared to reasonably approximate the observed spectrum of the specimen. This implied that Mo, MoS_2 and MoO_3 must co-exist on the friction surface. Fig. 7 shows the XPS spectra, along the specimen depth. Judging from Fig. 7,

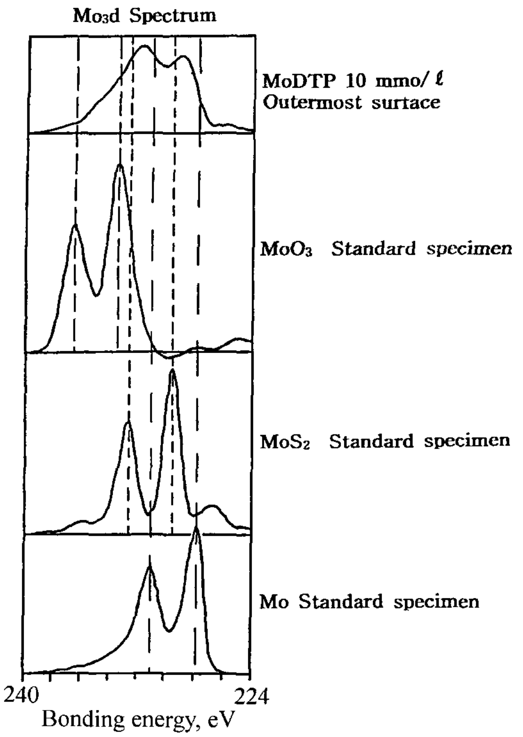


Fig. 5. Mo3d spectra I.

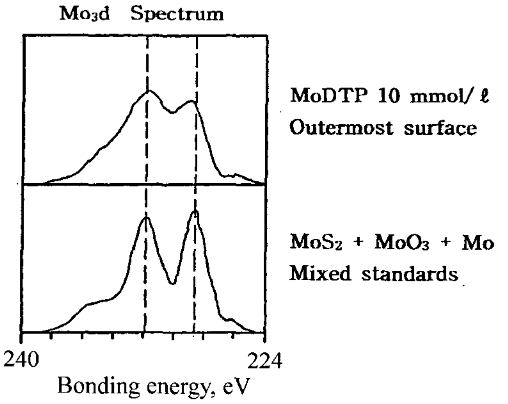


Fig. 6. Mo3d spectra II.

Mo existed only around the surface skin. Fig. 8 shows the depth profile for S2p spectra in the same specimen. Like Mo,S seemed to localize near the surface skin. It was not feasible to distinguish the MoS_2 peak (162.2 eV) and FeS (161.8 eV) from the spectra, as shown in Fig. 8. Howevr, a sufficient lubricating performance observed with this specimen and also the Mo3d spectra depth profile (Fig. 7) appeared to indicate that the surface compound was MoS_2 rather than FeS.

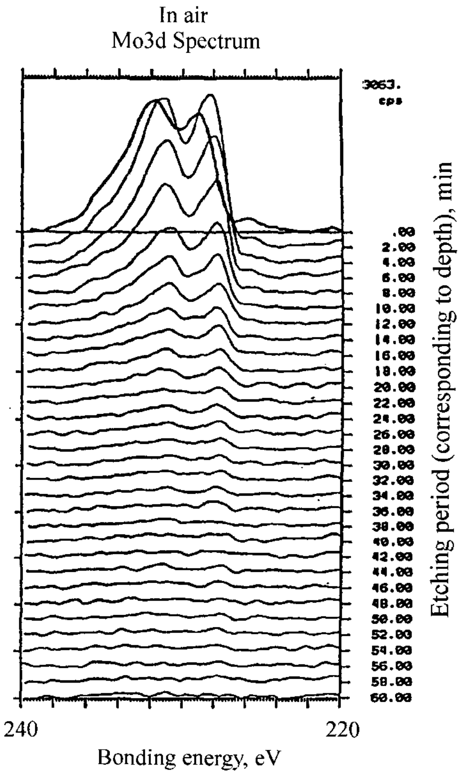


Fig. 7. XPS depth profile I (Mo3d).

3-3. Influence of environment atmosphere

As implied from the comparison shown in Fig. 6, MoO_3 coexists with MoS_2 at the specimen surface. If this MoO_3 arises from oxidation of MoS_2 deposited onto the frictioning surface from MoDTP, we might be able to further lower the friction coefficient by taking measures to suppress the oxidation of MoS_2 to MoO_3. If such an oxidation suppression is done, there would be a more eminent MoS_2 peak. We therefore conducted a frictioning experiment in N_2 atmosphere expecting to achieve MoS_2 oxidation suppression and the resultant reduction of friction coefficient.

For the frictioning experiment in N_2 atmosphere, the oil was preliminary deaerated according to following procedures. The MoDTP-added specimen oil was held in 3-mouth flask and under agitation with a stirrer, the dissolved air in the oil was removed by evacuation with oil rotary pump. Then, the N_2 gas from the cylinder was

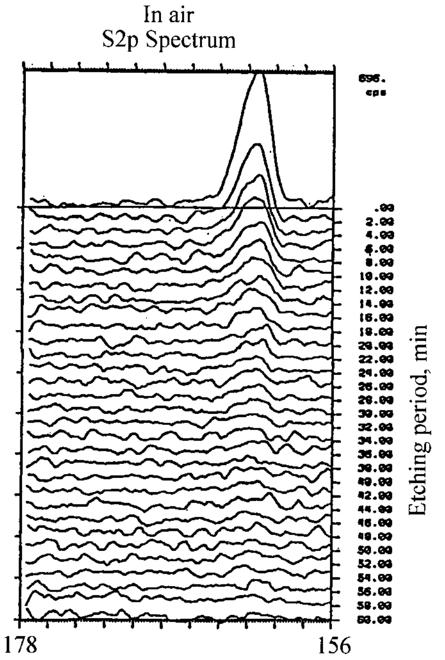


Fig. 8. XPS depth profile II (S2p).

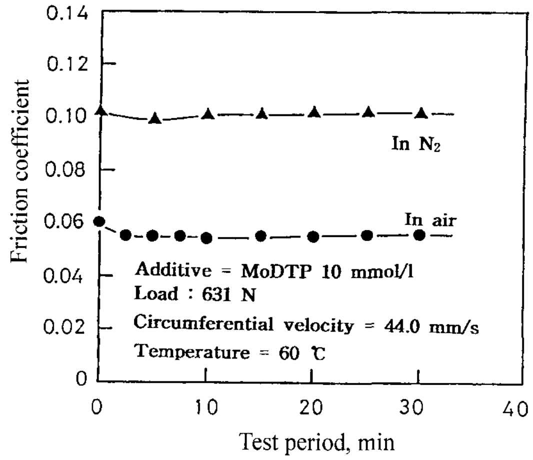


Fig. 9. Influence of N_2 atmosphere on friction coefficient.

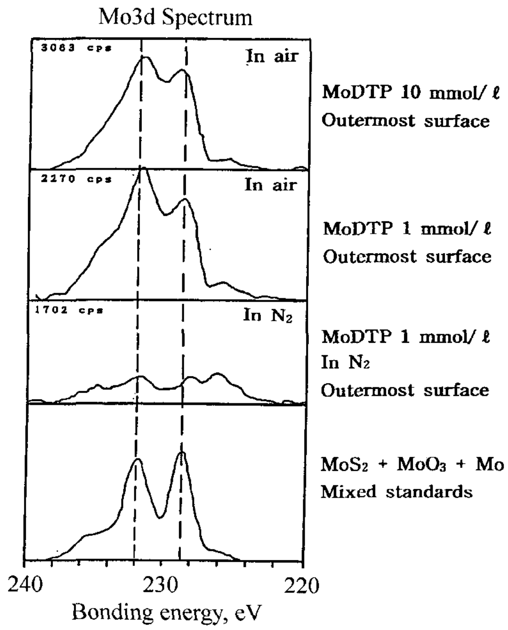


Fig. 10. Mo3d spectra III.

bubbled into the oil. These procedures were repeated 3~4 times to ensure the replacement of DO (dissolved oxygen) in the specimen oil with N_2. The frictioning test run was performed under a half-closed condition with constant bubbling of N_2 (0.9 *l*/min.).

Fig. 9 shown the experimental results obtained under N_2 atmosphere together with those obtained under air. Contrary to our anticipation, the friction coefficient under N_2 was greater than that under air, implying clearly that the friction reduction effect with MoDTP addition was possible only under air. Fig. 10 compared with the XPS Mo3d spectra between specimen friction-tested in N_2 and that in air. While the peak profile indicates a comparable compound mixing ratio with that of the specimen frictioned in air, the Mo3d peak intensity of specimen frictioned in N_2 was much lower than that of specimens frictioned in air at the outermost surface. However, the Mo3d depth profile obtained for the specimen frictioned in N_2 (Fig. 11) was clearly distinctive from that of specimen frictioned in air(Fig. 7). This indicates that the Mo penetration depth in specimen frictioned in N_2 was incomparably greater than that of the specimen frictioned in air. In Fig. 11, it is also seen that proportion of O-valent Mo among all the Mo compounds(Mo, MoS_2, MoO_3) rapidly increased with increased depth from the outermost surface. Fig. 12 plots the S2p depth profile for the specimen frictioned in N_2 atmosphere. When compared with profiles shown in Fig. 8 for a specimen frictioned in air, it is evident that S, along with Mo, penetrated deep into the specimen frictioned in N_2. As such, the sulfide

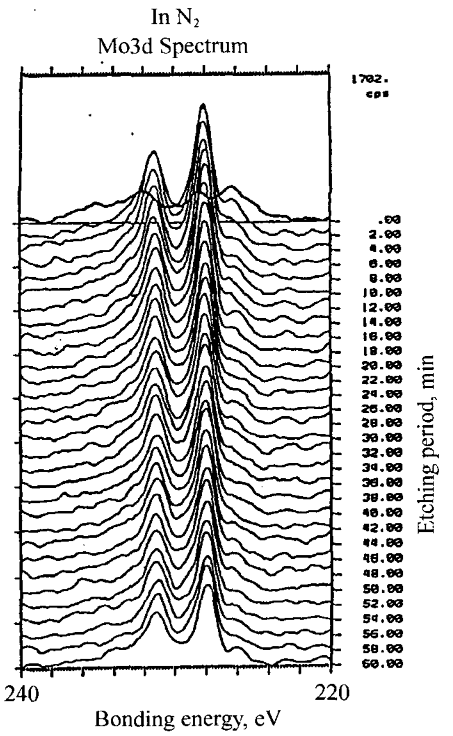


Fig. 11. XPS depth profile III.

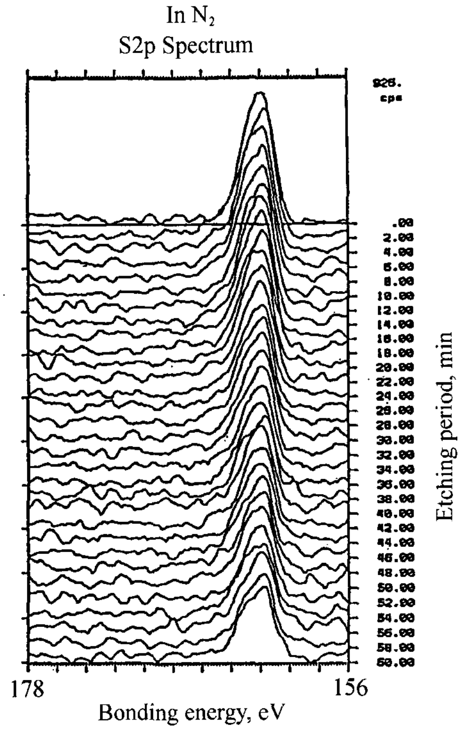


Fig. 12. XPS depth profile IV.

film with a relatively large specific volume and with a relatively high lattice deffects density[9] formed in N_2 atmosphere tended to diffuse towards specimen substrate and so it failed to contribute to the reduction of friction coefficient.

3-4. Role of oxygen

As described above, it became evident that the friction reduction with a MoDTP addition was gained only in air atomsphere under the existen of oxygen. What are the roles of oxygen in this context? The first possibility is that the oxygen is used for the oxidation of MoDTP and the oxidized product of MoDTP contributes to the friction redution. In order to study this aspect, the extent of friction reduction gained in the specimen oil mixed with model MoDTP oxide was examined. Model MoDTP oxide was prepared through a reaction of MoDTP and model peroxide, commercial CHPO (Cumen hydro-peroxide). The sediment formed in specimen oil through the reaction between them was discarded and only the solution part was used for the concered test run. As shown in Fig. 13, the contribution of oil-soluble decomposition (oxidized) producets from MoDTP for friction redution appeared to be marginal.

Next, we sought a probable correlation between Mo-penetration depth and extent of friction reduction. Experiments were designed to clarify this aspect.

The simplest guess for the cause of the observed deep penetration of Mo in the specimen frictioned in N_2 atmosphere was the enhanced diffusion rate due to increased temperature. This resulted in an increased friction coefficient when compared with the friction coefficient of the test in air. We therefore tried to evaluate the influence of the friction surface temperature on the Mo-penetration depth by conducting a frictioning test in air with an increased load. Archard's formula[10] was employed to evalute the extent of the friction surface temperature rise for this analysis. As compareed in Fig. 14, the frictionn coefficient value 0.06 that was observed under a relatively highload 2960 N in air remained appreciably lower than the 0.10 value observed under 631 N in N_2 atmosphere. This was despite the higher friction surface tem-

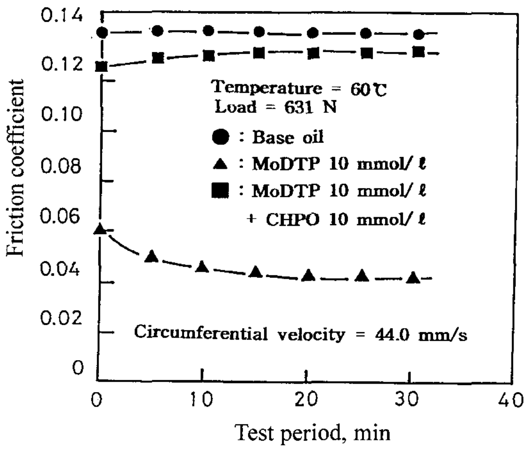


Fig. 13. Influence of perioxide (tested in N_2) on friction friction coefficient.

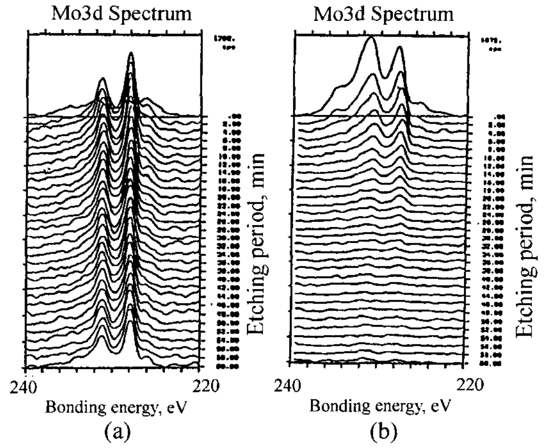


Fig. 14. High-load frictioning experimental results and frictioning surface temperature evaluated by Archard equation.

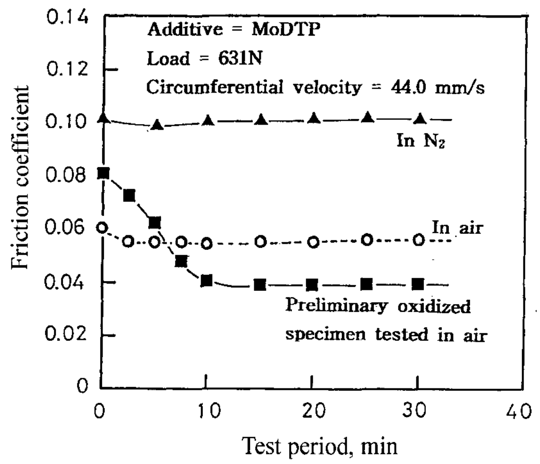


Fig. 15. Influence of preliminary formed oxide film on lubrication performance.

	In N_2 (a)	In air under high load (b)
Load	631 N	2960 N
Circumferential velocity	44.0 mm/s	44.0 mm/s
MoDTP temperature	60°C	60°C
MoDTP concentration	10 mmol/l	10 mmol/l
Friction coeffcient	0.10	0.06
Average temperature on frictioning surface	20.1°C	26.1°C

perature in the former (26.1°C) than in the latter (20.0°C). It was also confirmed in the former specimen, the Mo localized near the surface skin implying that deep Mo-penetration is origin rather than the consequence of a high friction coefficient.

Oxide film tends to form on a metal surface when frictioned in air. Therefore, the next possible cause of the problem was thought to be the surface oxide film acting as a barriier against Mo diffusion which maintained an effective friction reduction effect of MoDTP at the frictioning interface. To look into this possibility, we conducted a frictioning experiment in N_2 for a specimen on which the oxide film was preliminary formed by frictioning under low load (196 N) in pure P-150 oil in an air atmospere. As shown in Fig. 15, an even smaller friction coefficient was observed with this specimen than with the standard specimen frictioned in air. This implied that as long as the surface oxide film existed on the specimen surface, the desired lubricating effect of MoDTP was effectively derived, even in N_2. As indicated in Fig. 16, Mo was retained on the surface skin in the this specimen frictioned in N_2 similar to the results the one frictioned in air. As shown in Fig. 17, S, as well as Mo, localized on the surface skin in this specimen. As such, the existence of a surface oxide film on the frictioning surface was proved to be effective for inhibiting MoS_2 diffusion towards metal substrate and so the lubricating MoS_2 could remain at the frictioning interface to function as the lubricating medium.

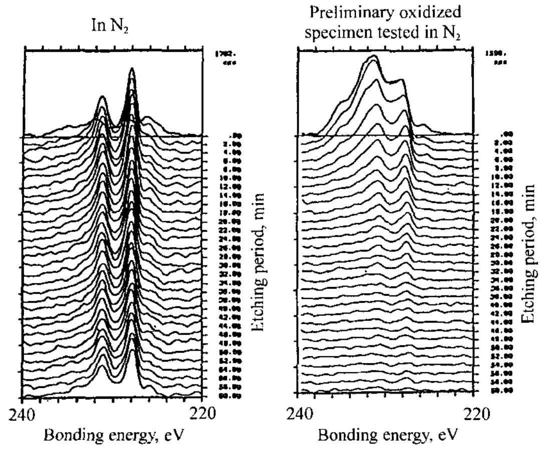


Fig. 16. XPS depth profile V.

4. CONCLUDING REMARK

The friction reduction gained with MoDTP addition was concluded to be attributable to MoS_2 formed at the frictioning interface. However, the lubrication effect of MoS_2 could be lost in a N_2 atmospere where the sulfidation of metal sustrate occurs easily, allowing Mo diffusion towards metal substrate. When an oxide film was preliminary prepared on the frictioning surface to prevent Mo diffusion from MoS_2 towards metal substrate, the desired friction reduction with MoDTP addition was gained, even in N_2. As such, the existence of an oxide film was proven to be an essential factor in retaining MoS_2 at the frictioning interface to gain its lubrication effect. With an MoDTP addition, the phosphides, as well as sulfides, formed on the frictioning surface. We are planning to publish a separate paper concerning the influences of phosphide on the lubrication performances with MoDTP. The extent of influence of phosphide is incomparably smaller than that of sulfide anyway on the lubricating performances of MoDTP additive. Therefore, this paper discussion was focused solely on the influences of sulfide.

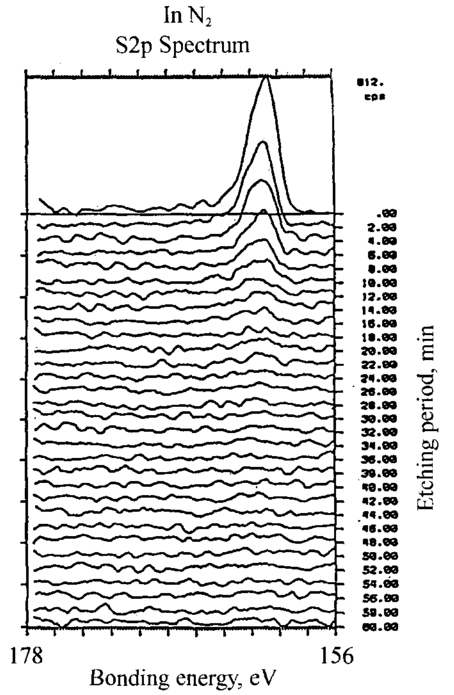


Fig. 17. XPS depth profile VI.

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