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Effects of Co-Existent Additives and the Role of Reacted Surface Film on the Friction with an Organo-Molybdenum Compound

Young-Hwan Kim

Department of Chemical Engineering, DaeHun Technical College

Abstract—In order to elucidate the effects of co-existing additives (S_8, TBP : Tri butyl phosphate, ZnDTP : Zinc-dialkyl dithiophosphate) and the role of reacted surface film on the friction behavior of MoDTP (molybdenum dialkyl dithiophosphate), a friction experiment using a dual circular pipe edge surface type friction tester and XPS (X-ray photoelectronic spectrum) surface analysis were conducted.

Friction reduction with MoDTP lubricant was proved to be greatly influenced by co-existing additive species. It was dependent on the properties of the film formed through the reaction between the additive and the surface. Phosphate film reduced the friction coefficient of MoDTP through suppression of diffusion of Mo compounds towards the metal substrate. On the other hand, sulfate film, which is inherently rich in lattice defects, did not lead to any appreciable friction reduction with MoDTP since the diffusion of the Mo compound towards the metal substrate was not effectively suppressed. With ZnDTP additive, the sulfide film formed through decomposition greatly influenced the lubricating performance of MoDTP. As such, properties of surface films formed from additives were proved to yield significant influence on the lubrication performance of MoDTP.

1. INTRODUCTION

It is a common practice to use some additive in automotive engine oil and other lubricating oils, in order to enhance their performance. It is also widely recognized that, through a careless selection of co-existing additives, the opposite effect might come about and that these additives can actually worsen an engine's lubrication performance. Development of the lubricating oil has recently been focussed on the further reduction of viscosity, multigrading and addition of FM (friction modifier)[1-3]. Matsuo[4] reported that the performance of gear based Sulfure-phosphate was generally worsened through the addition of an oil-soluble Mo compound. As represented by Matsuo's publication, the effects of Mo-containing FM have been mainly investigated from the pragmatic point of view[5,6].

We investigated the fundamental aspects of friction reduction gained by MoDTP, one of the representative FMs, and reported[7] that the friction reduction by the MoDTP additive was closely related to the formation of MoS_2 film formed on the frictional surface. The desired friction reduction was not gained when Mo from the MoS_2 surface film was easily diffused into the metal substrate. In this research, there was an effort to clarify the influences of a second critical pressure additive such as S-compound, P-compound or thiophosphate-compound on the friction reduction performance gained with the MoDTP additive. The influences of the surrounding atmosphere on the performance under pressure of the co-existing additives were also examined. Through analysis of these experimental results, the mechanism of friction reduction by MoDTP was evaluated.

2. EXPERIMENT

2-1. Test apparatus

A frictional test was conducted using a dual cir-

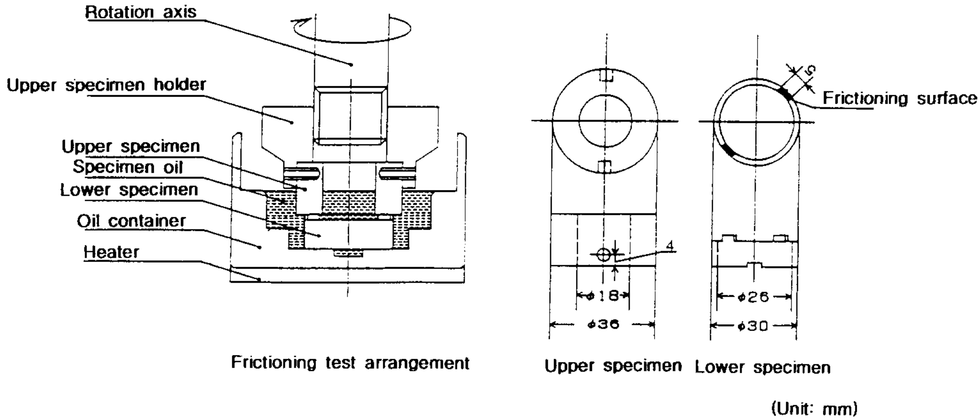

Fig. 1. 5/Frictioning test arrangement and specimen dimensions.

cular pipe edge surface friction tester, as depicted in Fig. 1. Both upper and lower test pieces were S45C carbon steel. The upper test piece was subjected to heat treatment to enhance its hardness. The test was conducted under a load of 631N and a circumferential velocity of 44 mm/s at 60℃. Further detailed test procedures are listed elsewhere[7].

2-2. Specimen oil and additives

As a representative of Mo-containing FM we chose MoDTP, which possesses 2-ethylhexyl-base as the alkyl-base. The additive which co-existed with MoDTP was chosen from the following ranges of compounds: pure S (S_8), TBP (tributyl phosphate) and ZnDTP (Zinc 2-ethylhexyl-dithio-phosphate). Refined paraffinic mineral oil was used as a base oil[7].

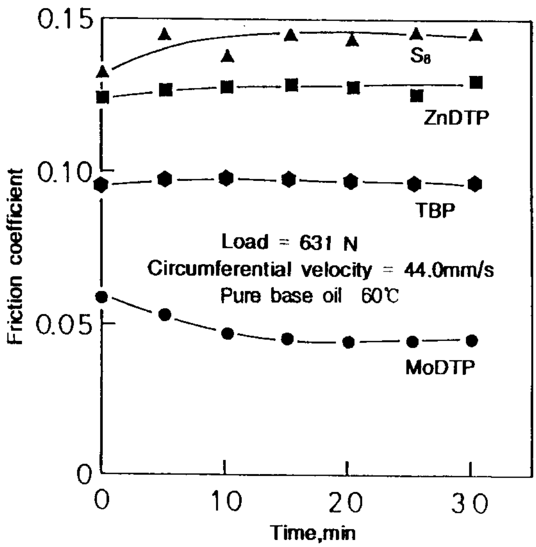

Fig. 2. Friction performances of individual additives.

3. RESULTS AND DISCUSSION

3-1. Friction performance of individual additives

Fig. 2 compares the friction performance of individual additives examined in this study; S_8 (5 mmol/*l*), TBP (5 mmol/*l*), ZnDTP (10 mmol/*l*) and MoDTP (10 mmol/*l*). The friction coefficients of S_8, ZnDTP and TBP were appreciably higher (0.1~0.15) than that of MoDTP (0.05).

3-2. Friction performance under co-existence of MoDTP and S_8

A specimen oil containing 10 mmol/*l* MoDTP and 5 mmol/*l* S_8 (in the following, simply referred to as MoDTP 10 mmol/*l* + S_8 5 mmol/*l* oil) was prepared for examination of the friction performance. Tests were conducted in both air and N_2 atmosphere. Tests in the N_2 atmosphere were conducted for both the standard metal test specimen and the preliminary surface-oxidized specimen[7]. Test results are summarized in Fig. 3. The friction coefficients of the oils with co-existing MoDTP and S_8 appeared to be appreciably higher than that of oil with the MoDTP single additive, no matter what

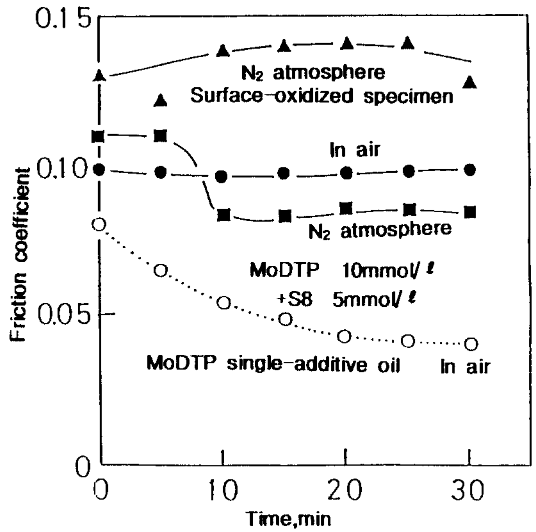

Fig. 3. Friction performances in MoDTP+S_8 oil.

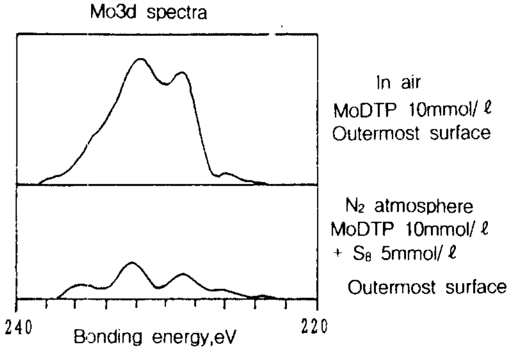

Fig. 4. Mo3d spectra (I).

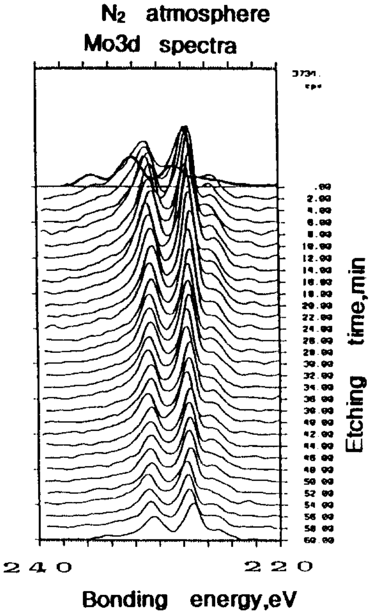

Fig. 5. Mo3d spectra depth profile for the specimen frictioned in MoDTP+S_8 oil (I).

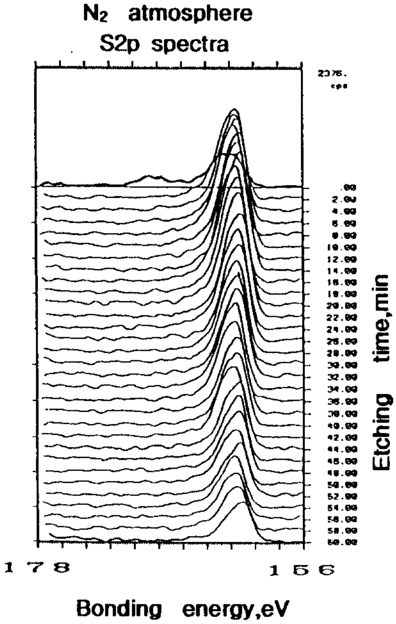

Fig. 6. S2p spectra depth profile for the specimen frictioned in MoDTP+S_8 oil (I).

the atmosphere was. After test runs with the co-existing additives, black wear powders were detected in the oil.

Fig. 4 shows the XPS analysis result (Mo3d spectrum) for the specimen surface tested in the oil in the presence of co-existing additives in N_2 and the reference Mo3d spectrum obtained for the specimen in oil with the MoDTP additive alone with an air atmosphere. This comparison shows clearly that Mo content in the former was appreciably lower than the latter. Fig. 5 plots Mo3d spectra depth for the former, and Fig. 6 plots the corresponding S2p spectra. Fig. 5 shows that the penetration depth of zero-valent Mo (226.9 eV, 230 eV) is quite deep. Judging from this, together with the friction test results, in MoDTP 10 mmol/l+S_8 5 mmol/l, the sul-

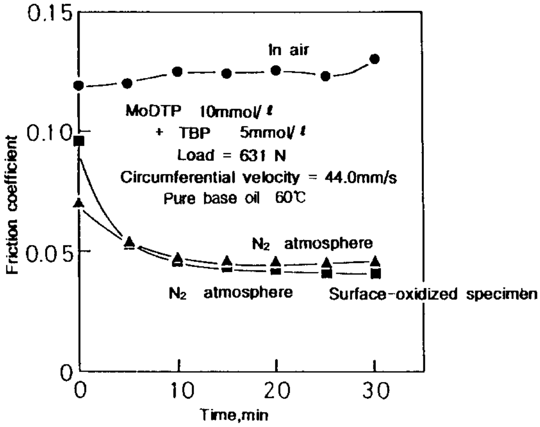

Fig. 7. Friction performances in MoDTP+TBP oil.

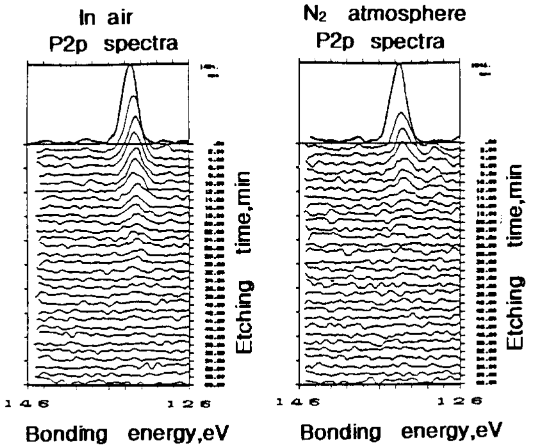

Fig. 8. P2p spectra depth profile for the specimen frictioned in MoDTP+TBP oil (III).

fidizing surface reaction must be stimulated due to the existance of highly reactive sulfur to form an MoS_2 film, and MoS_2 diffused into the metal substrate readily. In consequence, the desired lubrication effect from MoS_2 was not gained. The occurence of a surface corrosion reaction was also evidenced due to the odserved black wear powders in the oil after the test.

Even if a protective surface oxide film was preliminary prepared on the specimen surface, the highly reactive S stimulated a sulfidizing surface reaction in MoDTP+S_8 oil. This caused a subsequent loss of formed MoS_2 from the surface through diffusion towards the metal substrate. Therefore, an appreciable worsening of the lubrication perform was caused by adding S_8 to the MoDTP-containing oil lubricant.

3-3. Friction performance with MoDTP and TBP co-existing

Fig. 7 plots the friction test results obtaind in MoDTP 10 mmol/l+TBP 5 mmol/l oil. In the MoDTP single-additive oil, the friction coefficient was smaller in air than in an N_2 atmosphere[7]. Contrary to this, in MoDTP+TBP oil the friction coefficient in N_2 (0.045) was appreciably smallar than that in air (0.12). A preliminary surface-oxidized specimen also exhibited a relatively low friction coefficient in N_2 (Fig. 7). In MoDTP+TBP oil, low friction was observed for both the standard metal test specimen and the preliminary surface-oxidized specimen under an N_2 atmosphere. Therefore, the relatively high friction observed with this oil in air cannot be readily interpreted in terms of inhibited formation of surface MoS_2 through the occurrence of a certain reaction between MoDTP and TBP.

It is commonly accepted[8] that P-containing additives would lead to the formation of a phosphate surface film. Therefore, it is probable that these results obtained in MoDTP+TBP oil were influenced by the phosphate film formed due to the existence of TBP. To examine this idea, an XPS surface analysis was carried out. These results are summarized in Figs. 8~10. Judging from the P2p spectra shown in Fig. 8, the existence of phosphate (133 eV) was confirmed. The phosphate seemed to exist only on the surface skin, and the amount of phosphate formed in the N_2 atmosphere and that formed in air were comparison. Fig. 9 compared to the Mo3d spectra. The major component of the surface film formed in MoDTP+TBP oil in air was MoO_3. On the other hand, a mixture of the MoO_3 spectra depth profile in Fig. 10, a localized existence of Mo-compounds near the surface occurred no matter what the atmosphere.

In MoDTP+TBP oil, the formed phosphate film inhibited the diffusion of Mo-compounds toward the

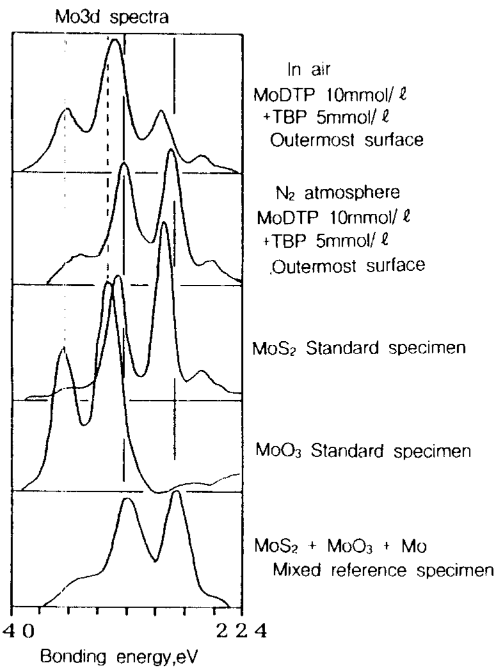

Fig. 9. Comparative Mo3d spectra (III).

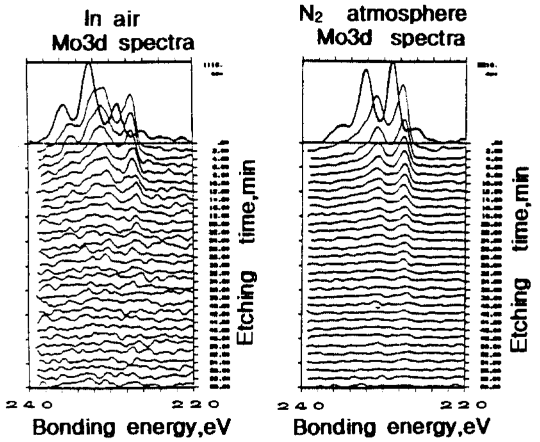

Fig. 10. Mo3d spectra depth profile for the specimen frictioned in MoDTP+TBP oil (IV).

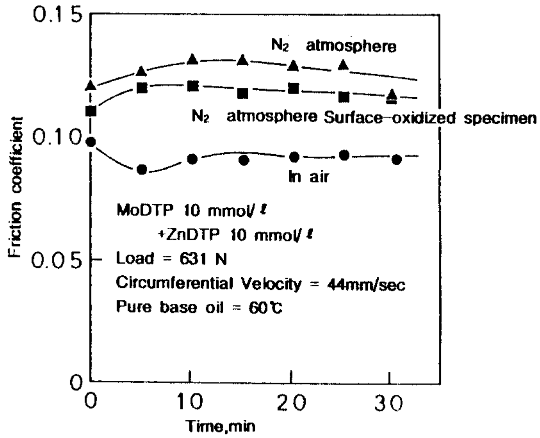

Fig. 11. Friction performances in MoDTP+ZnDTP oil.

metal substrate. Thus, in air, MoS_2 on the friction surface was further oxidized to MoO_3 which lead to an appreciably higher friction coefficient (Fig. 7). On the other hand, in the N_2 atmosphere, MoS_2 remained stably on the friction surface without being oxidized, so that a favorable lubrication effect was gained. In the N_2 atmosphere, even a preliminary surface-oxidized specimen in MoDTP+TBP exhibited a lubrication performance comparable to that of the standard metal specimen. This implies that the stably existing phosphate film effectively inhibited the diffusion of MoS_2 (which existed on the surface), toward metal substrate.

These experimental results reassured us that the key factor leading to reduction of the friction coefficient in MoDTP-containing lubricant is the stimulated formation of MoS_2 to MoO_3 was accelerated by the MoDTP-containing solution which co-existed with the P-compound in air for the monent. This point must be clarified by further evaluation.

3-4. Frictiion performance under co-existing MoDTP and ZnDTP

Fig. 11 summarizes the friction test results obtained in MoDTP 10 mmol/l+ZnDTP 10 mmol/l oil. In air and in this oil, the standard metal specimen exhibited a friction coefficient apperciably higer than that in the MoDTP single-additive solution. The friction coefficients of both the standard metal and the preliminary surface-oxidized specimens in this oil in the N_2 atmosphere were even higher than that of the standard metal specimens in air. The observed difference in the friction behaviors is due to the oxide film formation in air which suppresses MoS_2 diffusion toward the metal substrate

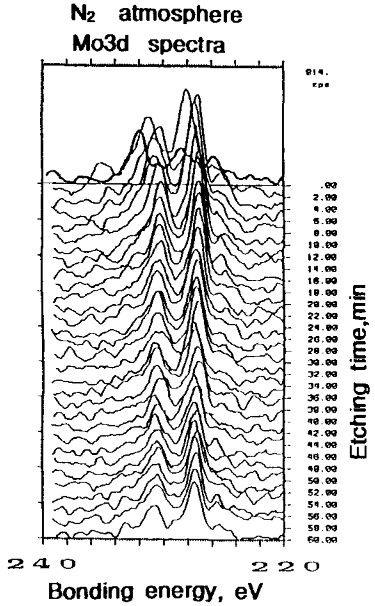

Fig. 12. Mo3d spectra depth profile for the specimen frictioned in MoDTP+ZnDTP oil (V).

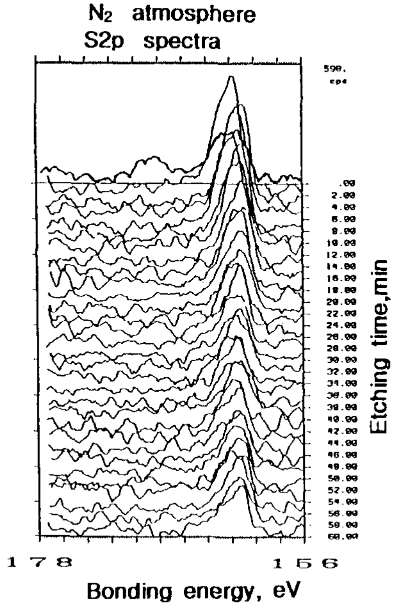

Fig. 13. S2p spectra depth profile for the specimen frictioned in MoDTP+ZnDTP oil (VI).

compared to the absence of oxide film in an N_2 atmosphere.

The XPS Mo3d spectra depth profile, in Fig. 12, shows that in the N_2 atmosphere the Mo-compound formation on the surface was rather limited in MoDTP+ZnDTP oil, and that Mo tended to diffuse deeply into the metal substrate. The XPS S2p spectra depth profile in Fig. 13 shows the tendency of deep penetration of P into the metal substrate in MoDTP+ZnDTP oil in the N_2. In these oil, sulfides are generated as the decomposition products from MoDTP and ZnDTP. These sulfides stimulate the MoS_2 formation on the friction surface and its diffusion toward the metal substrate simultaneously. Therefore, as with MoDTP+S_8 oil, the reduction of the friction coefficient was not gained in MoDTP+ZnDTP oil. The same cause explains the failed lubrication enhancement for the preliminary surface-oxidized specimen in this oil in the N_2 atmosphere.

3-5. Influence of surface film

Through analysis of three different co-existing additive systems in 3.2~3.4, it became evident that the extent of friction reduction gained by the MoDTP additive was greatly influenced by the co-existing second additive species. It was concluded that the observed different behaviors were explicated in terms of the quality of surface films formed through the influence of the second co-existing additive. In order to examine the validity of this theory, we conducted friction experiments in 10 mmol/*l* MoDTP oil in an N_2 atmosphere for test specimens which had surface films preliminary prepared by low-load (196N) frictioning in the N_2 atmosphere in oils containing S_8, TBP or ZnDTP. The specimen with preliminary prepared film in S_8-containing oil shall be referred to in the following as the S-specimen, that in TBP oil as the P-specimen and that in ZnDTP as the Zn-S-P-specimen. The experimental results obtained for these specimen are summarized in Figs. 14~16. As clear from these results ,the friction reduction effect of MoDTP was not gained for the S- and Zn-S-P-specimen. On the other hand, the P-specimen exhibited an appreciable friction reduction the MoDTP oil even in the N_2 atmo-

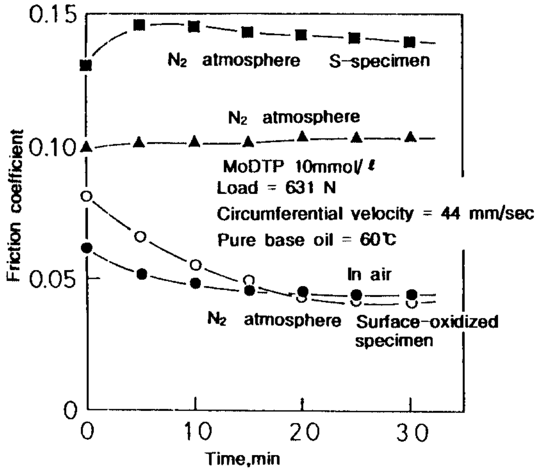

Fig. 14. Friction performances of the S-specimen.

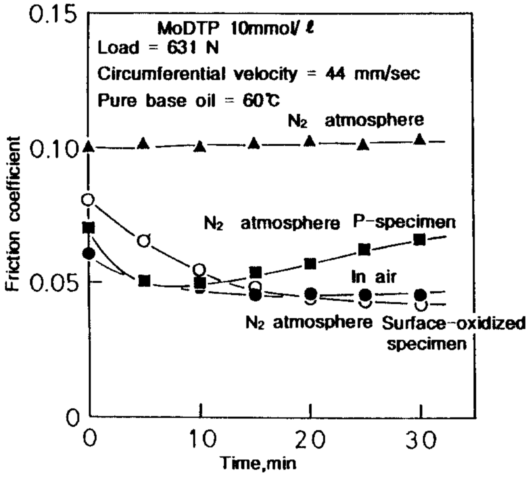

Fig. 15. Friction performances of the P-specimen.

sphere. Since sulfide film is inherently rich in lattice defects[9], even once-formed MoS_2 lubricating compound on the surface can easily be lost through diffusion toward the metal substrate. Therefore, the S-specimen did not show any improvement of lubrication performance. The phosphate film as well as the oxide film seemed to functions an effective barrier against the diffusion of MoS_2 toward the metal substrate. With the Zn-S-P-specimen, the formation of polymer film from ZnDTP[10]. and the sulfidizing of the friction surface occurred simultaneously. This sulfide somehow did not yield a good influence on the friction reduction mechanism of MoDTP. Therefore, as observed, the friction performance of the Zn-S-P-specimen in MoDTP oil was rather disappointing.

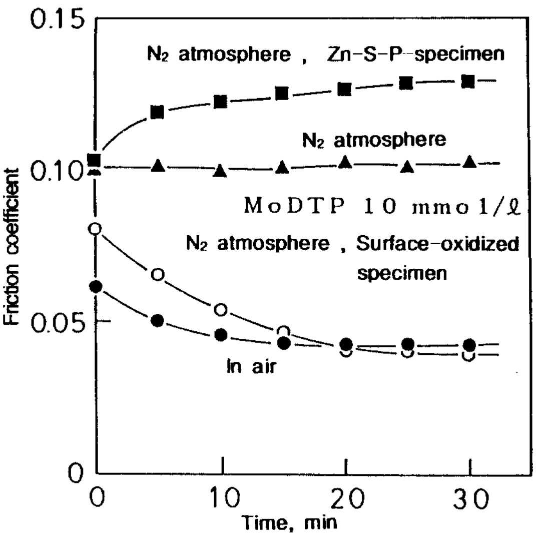

Fig. 16. Friction performances of the Zn-S-P-specimen.

4. CONCLUSION

We investigated the influences of co-existing second additives on the friction reduction effect by an MoDTP additive in both air and N_2 atmospheres. It was clearly shown that the extent of friction reduction by the MoDTP additive was greatly influenced by co-existing additives. Depending on the co-existing additives, the quality of surface film formed on the friction surface varied greatly and, in terms of this, the different MoDTP were interpreted. The phosphate film formed in the MoDTP+TBP oil appeared to work as an effective barrier against the diffusion of the lubricating MoS_2 from the friction surface toward the metal substrate. In consequence, a favorable enhancement of lubrication performance was gained in this oil. On the other hand, the inherently lattice defect-rich sulfide film failed to yield a barrierr so that the MoS_2 formed on the friction surface in the MoDTP+S_8 oil was easily lost through diffusion toward the metal the substrate, and the lubrication performance remained at a rather disappointing level.

In short, we concluded that the influence of the co-existing additive on the lubrication performance of MoDTP occurred through the influence of the co-existing additive on the quality of the film formed on the frictioning surface.

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