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ZDDP Tribofilm Formation and Removal

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1. Introduction

The role of lubricant antiwear additives such as Zinc dialkyldithiophosphates (ZDDPs) has become increasingly important to avoid surface failure including wear and scuffing by forming tribofilm since low viscosity oils have been commonly used. Together with tribofilm formation, its removal can also occur during ZDDP tribofilm growth. In some conditions tribofilm removal rate may exceed tribofilm formation rate so that the total tribofilm thickness decreases. To protect surface, tribofilm removal, especially drastic removal, must be understood and avoided. However, the mechanism of tribofilm removal is not well investigated. Therefore, the aim of this study is to understand what factors influence tribofilm removal by using a series of ZDDPs with varied alkyl structures and concentrations. Possible mechanisms of ZDDP tribofilm formation and removal are then suggested [1].

2. Test methods

Solutions of ZDDPs in a gas to liquid (GTL) base oil were studied. The base oil (GTL 3) had kinematic viscosity 9.9 mm^2/s at 40 °C and 2.7 mm^2/s at 100 °C. Four ZDDPs investigated and the contact conditions used in the MTM-SLIM tests are listed in Table 1. Selected tests were performed at ZDDP concentrations of 50, 100, 300 and 800 ppm phosphorus. The development of ZDDP tribofilm on the ball was monitored by SLIM measurements performed at set intervals throughout each 4 h test.

Table 1 Test oil and MTM test condition

Abbreviation	Alkyl group	Type
ZDDP2-C3/C6	prop-2-yl: 4-methyl-pent-2-yl = ratio 3:2	Secondary
ZDDP2-C4	but-2-yl	Secondary
ZDDP2-C6	4-methylpent-2-yl	Secondary
ZDDP1-C8	2-ethylhex-1-yl	Primary

Mean (entrainment) speed; $U = (U_{ball} + U_{disc})/2$	50 mm/s
Slide-roll-ratio (SRR); $SRR = 100*(U_{disc} - U_{ball})/U$	50%
Applied load	31 N (max Hertz pressure 0.95 GPa
Temperature	100 ºC
Rubbing time	4 h
Lambda ratio (minimum EHD film thickness / composite Rq roughness)	0.1

3. Results and Discussion

Figure 1 shows the evolution of ZDDP tribofilm thickness over 4 h rubbing tests. Four ZDDPs are compared, all at a concentration of 300 ppm P. ZDDP2C6(300) and ZDDP1-C8(300) gradually form tribofilm to reach *ca.* 140 nm after 2 h rubbing and *ca.* 80 nm after 2 h rubbing, respectively. By comparison, ZDDP2-C3/C6(300) and ZDDP2-C4(300) very quickly form *ca.* 120 nm tribofilm after 0.5 h rubbing, and then most of this tribofilm is removed before 1 h rubbing, to leave only ca. 25 nm. After this, no more tribofilm is developed until the end of the test so the tribofilm thickness stays at 25 nm. Figure 2 shows how MTM friction coefficient evolves with rubbing time. For ZDDP2-C6(300), the two characteristic features of friction behaviour with ZDDP tribofilm growth can be seen; (i) a shift of the mixed lubrication region of the friction curves to higher entrainment speed, and (ii) an increase in slow speed boundary friction. By comparison, ZDDP2-C3/C6(300) shows a similar trend as above until 0.5 h rubbing, then a different trend is observed; (i) a shift of the mixed lubrication regime of the friction curve to lower entrainment speed and (ii) a very high boundary friction at slow speed.

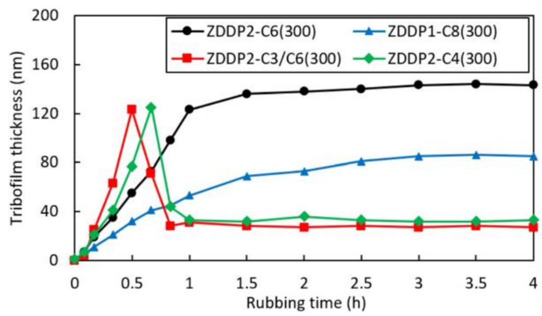


Fig. 1 The evolution of ZDDP tribofilm thickness during rubbing. Note that values quoted in the legend are ppm of P.

The effect of varying ZDDP concentration on tribofilm formation was studied for ZDDP2-C6 and ZDDP2-C3/C6 as shown in Fig. 3. For ZDDP2-C6 tribofilm formation rate increases steadily with rubbing time, with rate of formation increasing from 50 to 300

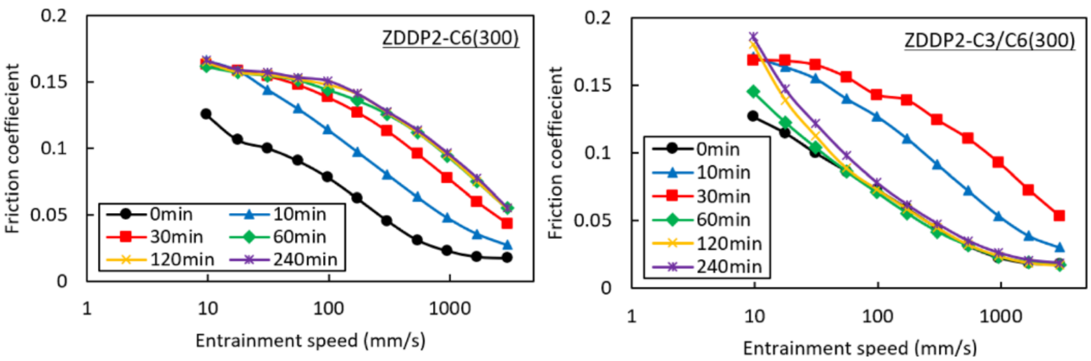


Fig. 2 Evolution of MTM friction coefficient with ZDDP2-C6(300) and ZDDP2-C3/C6(300)

ppm P concentration. By contrast, for ZDDP2-C3/C6, at low concentrations the rate of tribofilm formation increases with P concentration to reach 45 nm and 161 nm maximum tribofilm thickness at 50 ppm and 100 ppm P, respectively. No sudden loss of tribofilm is seen. However, at 300 ppm and 800 ppm P a tribofilm initially forms much more rapidly, and then tribofilm is partially removed after 30 min rubbing.

To identify any differences in chemical structure of the ZDDP tribofilms, the outermost few nanometers of some of the tribofilms on the balls were analysed using XPS. Figure 4 shows the Zn/O and BO/NBO ratios of the tribofilms (i) after 30 min rubbing of ZDDP2-C3/C6(300) before any tribofilm removal (ii) after 50 min rubbing of ZDDP2-C3/ C6(300) which is after tribofilm removal, and (iii) after 240 min rubbing of ZDDP2-C3/C6(100) without any tribofilm removal. XPS analysis shows significant differences in both Zn/O and BO/NBO and in particular it can be seen that prior to tribofilm removal in the test using ZDDP2-C3/C6(300), the Zn/O ratio is very low and the BO/NBO ratio is unusually high.

The theoretical Zn/O and BO/NBO ratios of the various phosphate structures can be calculated as listed in Table 2 [2]. Based on this the Zn/O ratios measured for the partial ZDDP2-C3/C6(300) after removal and for the ZDDP2-C3/C6(100) tribofilm that is not removed at all are both indicative of polyphosphate. However, the Zn/O for the ZDDP2-C3/C6(300) prior to removal is extremely low. It thus appears that the tribofilms that are formed very rapidly by the C3/C6 and C4 ZDDPs contain a significant proportion of ultraphosphate. By comparison, when tribofilm develops more slowly, a conventional tribofilm mainly consisting of short chain polyphosphates based on Zn and/or Fe cations is formed.

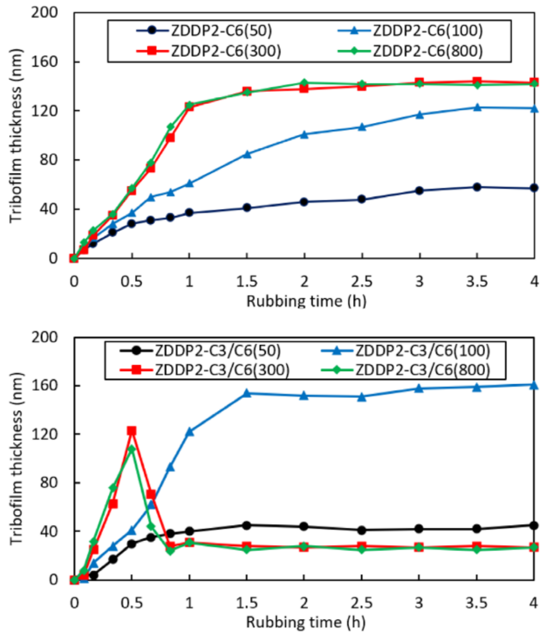


Fig. 3 The effect of ZDDP concentration on tribofilm thickness of a ZDDP2-C6 and b ZDDP2-C3/C6 (Note that values quoted in the legend are ppm of P).

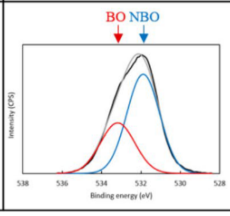
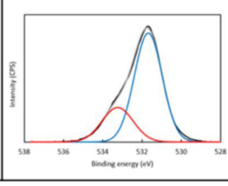
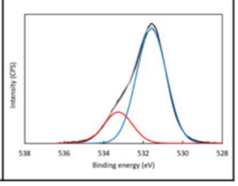
Sample	ZDDP2-C3/C6(300)	ZDDP2-C3/C6(300)	ZDDP2-C3/C6(100)
Rubbing time (minute)	30	50	240
Tribofilm thickness (nm)	123	28 *after a partial tribofilm removal	161
Zn/O	0.10	0.18	0.21
BO/NBO	0.54	0.33	0.27
O1s spectra			

Fig. 4 Zn/O, BO/NBO and O1s spectra of tribofilm of ZDDP2C3/C6 analysed by XPS

	Ortho-	Pyro-	Poly- (6P)	Poly- (12P)	Meta-	Ultra-
Zn/O	0.375	0.29	0.21	0.19	0.17	0
BO/NBO	0	0.17	0.36	0.42	0.5	1.5

Table 2 The theoretical Zn/O and BO/NBO of the various phosphate structures

4. Conclusions

The main findings can be summarised as follows;

1. While long chain secondary ZDDP2-C6 and primary ZDDP1-C8 form tribofilms whose thicknesses increases monotonically during extended rubbing, short chain secondary ZDDP2-C3/C6 and ZDDP2-C4 form very thick tribofilms extremely rapidly and then lose most of these tribofilms quite suddenly after about one hour of rubbing.
2. For ZDDP2-C3/C6 this sudden, partial loss of tribofilm thickness is concentration-dependent and only occurs at relatively high ZDDP concentrations. It also occurs more readily at high loads and temperatures and is thus most likely to occur when the tribofilm is formed very rapidly.
3. XPS analysis showed that rapidly-formed tribofilm of ZDDP2-C3/C6(300) present after 30 min has a very little Zn/O and high BO/NBO ratio. This suggests that such tribofilm contains some ultraphosphate, which is likely to have a relatively weak structure due to lack of stabilising cations. This results in the tribofilm being partially removed when it reaches a certain thickness. By comparison, the remaining tribofilm, and also tribofilms that form slowly, have high Zn/O and low BO/NBO. This suggests that they consist of relatively short chain phosphates and are thus stronger and more durable.

5. Reference

[1] Ueda, Mao, and Hugh Spikes. "ZDDP tribofilm formation and removal." *Tribology Letters* 72.4 (2024): 109.
[2] Spikes, Hugh. "The history and mechanisms of ZDDP." *Tribology letters* 17.3 (2004): 469-489.