ZDDP Tribofilm Formation on Non-Ferrous Surfaces

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1. Introduction

The current trend for using lower viscosity lubricants with the aim of improving fuel economy of mechanical systems means that machine components are required to operate for longer periods in thin oil film, boundary and mixed lubrication conditions, where the risk of surface damage is increased. In addition, non-ferrous materials are increasingly being introduced in machine components to reduce wear and increase efficiency. Thus, understanding of the Zinc Dialkyldithiophosphate (ZDDP) antiwear tribofilm formation on both ferrous and non-ferrous surfaces is increasingly important in order to formulate lubricants that give desired antiwear performance with both types of materials. In this paper the effect of ferrous and non-ferrous rubbing materials, steel, Si_3N_4, WC, SiC and a-C:H DLC coating, on ZDDP tribofilm formation was investigated [1].

2. Test methods

A mini traction machine (MTM) and an extreme pressure traction machine (ETM) were employed to observe the ZDDP tribofilm growth. Both are ball on disc tribometers with a similar configuration shown in Fig. 1. The test conditions are shown in Table 1. By using a very low entrainment speed, MTM tests were controlled to an initial theoretical lambda ratio of less than 0.1, thus providing boundary lubrication conditions. Load was set at values that gave a maximum Hertz pressure of 0.95 GPa for all material combinations. ETM was set to achieve a full elastohydrodynamic lubricant (EHL) film. These tests therefore evaluate the ability of ZDDP to adsorb and react to form tribofilms in full film, high shear stress EHL conditions without any asperity contact. For test oils, a single, secondary C6 ZDDP was used at a concentration of 800 ppm of P in all tests. For MTM studied, to ensure thin film and thus boundary lubrication conditions polyalphaolefin (PAO) with a relatively low viscosity was used. For ETM studies, polyisobutene (PIB) having a relatively high viscosity was used to ensure full-film EHL conditions. After the tests, chemical and physical properties of tribofilms on discs were analyzed.

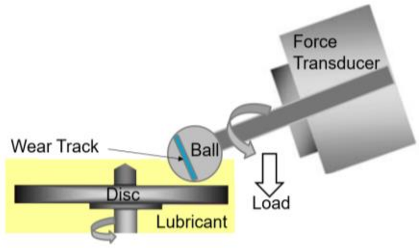
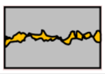


Figure 1 A schematic illustration of the MTM and ETM ball-on- disc set-up

Table 1 MTM and ETM test conditions

	MTM	ETM (Extreme pressure)
Lambda ratio	< 0.1 (Boundary) 	5 – 10 (Full-film EHL) 
Mean entrainment speed	50 mm/s	750 mm/s
Slide-roll-ratio (SRR)	50%	2%
Max Hertz pressure	1 GPa	3 GPa
Lubricant Temperature	100 ºC	100 ºC
Lubricant	PAO (KV 100: 4.1 mm^2/s) + Sec-ZDDP (P: 800ppm)	Polyisobutene (KV100: 15.3 mm^2/s) + Sec-ZDDP (P: 800ppm)

3. Results

3.1 Tribofilm formation in boundary lubrication conditions

The effect of surface material on ZDDP tribofilm formation in boundary lubrication conditions was investigated using MTM. Figure 2 shows optical micrographs and AFM profiles of tribofilms on the discs after 3 hours rubbing with all five tribopairs. On AISI 52100 steel discs, tribofilm forms on all parts of the wear track, with a pad-like topography and a maximum tribofilm thickness of 190 nm. In contrast, with Si_3N_4 and WC specimens tribofilms formed only on some parts of the wear track and consisted of large, relatively smooth lumps, rather than the fine, pad structure seen on the steel specimens. The maximum thickness of tribofilm was 700 nm and 250 nm on Si_3N_4 and WC, respectively. No measurable tribofilms were observed on SiC

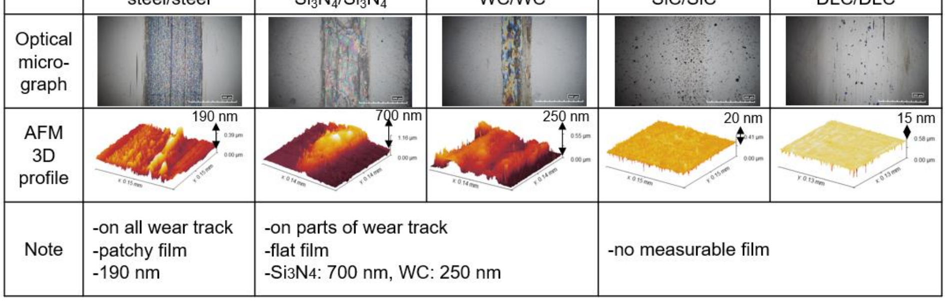


Fig. 2 Optical micrographs and AFM profiles of ZDDP tribofilm on the disc of each material after 3 hours rubbing

and DLC. It is difficult to ascertain whether tribofilm cannot form on SiC and DLC or whether tribofilm can form but is immediately removed.

3.2 Tribofilm formation in full film EHL conditions

Since tribofilm appeared to be relatively easily removed from the non-ferrous surfaces in thin film, boundary lubrication conditions, ZDDP's ability to form tribofilms on non-ferrous surfaces could not be reliably quantified, making it difficult to understand the mechanism of tribofilm formation. To overcome this problem, tribofilm formation was studied in high shear stress EHL conditions which eliminate the possibility of tribofilm removal by asperity contacts. The ETM rig was used for these studies as it is capable of reaching very high pressures, and hence shear stresses, with all of the tribopairs employed here. Figure 3 shows optical micrographs and AFM profiles of tribofilms formed after 3 hours rubbing on the disc. Tribofilms covering almost the whole wear track were formed on steel, Si_3N_4 and WC, with maximum tribofilm thickness of 180 nm, 160 nm and 40 nm respectively. The tribofilms all had a similar topography and a smaller variation of thickness than the equivalent tribofilms formed in boundary lubrication conditions. No measurable tribofilms were found on SiC and DLC. These results suggest that, in contrast to what was observed in boundary lubrication, tribofilms formed on Si_3N_4 and WC in full EHL conditions are not being continuously removed. This allows quantitative comparison of the ZDDP's ability to adsorb and react to form tribofilms. The thickness of the ZDDP tribofilms formed on the five materials after 3 hours rubbing was in the following order; steel > Si_3N_4 > WC > SiC and DLC. These observations suggest that ZDDP adsorption and reaction to form tribofilm does occur on Si_3N_4 and WC; however, in boundary lubrication these tribofilms are easily removed because of their weak adhesion to surface. By contrast, tribofilm did not form well on SiC and DLC either because ZDDP did not adsorb or because, although adsorbed, it did not react to form polyphosphate.

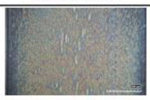
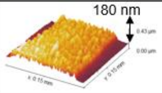
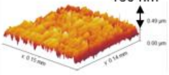
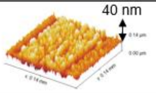
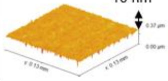
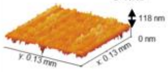
	steel/steel	Si_3N_4/Si_3N_4	WC/WC	SiC/SiC	DLC/DLC
Optical micro-graph					
AFM 3D profile					
AFM 3D profile	-tribofilm formed on all wear track -similar morphology -steel:180 nm, Si3N4: 160 nm, WC: 40 nm			-no measurable film	

Fig. 3 Optical micrographs and AFM profiles of ZDDP tribofilm on the discs of each material after 3 hours

Based on the tribofilm development and various analyses, results suggest that a potentially important factor in formation of ZDDP films on non-ferrous surfaces is the presence and concentration of metal atoms or ions at the surface. The metals present in Si_3N_4 and WC may act as adsorption sites for ZDDP in a similar manner to Fe in steel, forming ionic bonds between these cations and the sulphur atoms in ZDDP molecules. However, in the case of non-ferrous substrates such bonds appear to be less strong than with steel, resulting in weak adhesion of the tribofilm to the substrate, and hence its easier removal.

4. Conclusions

This study has used MTM and ETM ball on disc tribometers combined with tribofilm analysis to show that ZDDP forms tribofilms in both ferrous/ferrous and non-ferrous/non-ferrous rubbing contacts. Key conclusions are as follows.

- In the boundary lubrication conditions, ZDDP tribofilms formed on Si_3N_4 and WC surfaces were thicker but less adhesive than those formed on steel, while no measurable tribofilms formed on SiC and a-C:H DLC coating. Tribofilms on Si_3N_4 and WC were easily removed by rubbing in pure PAO base oil, indicating their weak adhesion to the substrate.
- In full-film EHL conditions, thick tribofilms formed, in the order of decreasing thickness, on steel, Si_3N_4 and WC and no apparent tribofilm removal was observed in this case. Once again, no measurable tribofilms formed on SiC and a-C:H DLC coating.
- Tribofilms on Si_3N_4 and WC formed in the boundary lubrication regimes were composed of phosphate reaction films and a large amount of carbon-based material. This carbon might be attributed to unreacted ZDDP, resulting in the formation of relatively thick tribofilms.
- The fact that metals, including iron but also other metals, affect tribofilm formation has practical implications for optimizing lubricants and the composition of non-ferrous rubbing materials for improved antiwear performance of machines.

5. Reference

[1] M. Ueda, A. Kadiric, H. Spikes, ZDDP Tribofilm Formation on Non-Ferrous Surfaces, Tribol. Online. 15 (2020) 318–331.