TRIBOFILES GENERATED FROM ZDDP AND DDP ON STEEL SURFACES: PART 1. GROWTH, WEAR AND MORPHOLOGY

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ABSTRACT
The growth and morphology of tribofilms, generated from zinc dialkyldithiophosphate (ZDDP) and an ashless dialkyldithiophosphate (DDP) over a wide range of rubbing times (10 seconds to 10 hours) and concentrations (0.1 to 5 wt % ZDDP), have been examined using atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and X-ray absorption near edge structure (XANES) spectroscopy at the O, P and S K-edges, and the P, S, and Fe L-edges. The physical aspects of the growth and morphology of the tribofilms will be presented here (Part I) and the chemistry of the films will be discussed in (Part II)

INTRODUCTION
A number of surface analytical techniques have been used to determine thickness and the morphology of tribofilms. Techniques such as XPS, AES, and SIMS in conjunction with ion etching, have been used to determine the physical film thickness (Minfray et al., 2004). Unfortunately, ion etching destroys the sample and thus the same sample cannot be used for other characterizations. On the other hand, the XANES technique is the only non-destructive method for thickness measurement (Suominen Fuller et al., 2000).

ZDDP tribofilms have also been investigated using imaging techniques such as atomic force microscopy (AFM) (Graham et al., 1999) and imaging nanoindenters (Bec et al. 1999; Nicholls et al. 2003) These techniques illustrate the morphology of the film and are all in agreement that the ZDDP antistrengthen film is laterally and vertically heterogeneous, being composed of ridge and valley regions. The ridge regions are composed of raised patches of film that have been termed antistrengthen pads. It has been suggested that these pads are responsible for bearing the load between the two rubbing surfaces and limiting the contact between the asperities, thereby reducing wear (Graham et al. 1999)

EXPERIMENTAL
Zinc dialkyldithiophosphate (ZDDP), ashless dialkyldithiophosphate (DDP) and the base oil used in this paper were commercial products. The tribological films (referred to as tribofilms) were generated in a Plint tribometer on 52100 steel coupons. Experimental details for film generation have been described before (Nicholls et al., 2003). The testing conditions were: temperature 100 °C; Speed 25 Hz; Load 225 N; Stroke 7 mm; rubbing time 10 seconds to 10 hrs.

RESULTS AND DISCUSSION
All AFM topography images of tribofilms were collected using a Nanoscope IIIa equipped with a Multimode head (Digital instruments, Santa Barabara, CA). The images of the antistrengthen films were recorded in contact force mode with V-shaped silicon nitride cantilevers possessing a nominal spring constant of 0.12 N/m.

Oxygen (K-edge), phosphorus (K- and L-edge), sulfur (K- and L-edge) and Fe L-edge (XANES) spectra were collected on the three Canadian Synchrotron Radiation Facility (CSRF) beamlines situated on the 1 GeV Aladdin storage ring, University of Wisconsin, Madison. Details are given elsewhere (Yamaguchi et al., 2003).

Fig. 1: P K-edge XANES spectra for ZDDP tribofilms from short rubbing times

At very short rubbing times, the ZDDP films are much thicker than the comparable DDP films: for example after 10 seconds rubbing, the ZDDP film is over 120 Å thick whereas the DDP film is barely detectable. After one minute of rubbing, the ZDDP film is well over 400 Å thick, whereas the comparable DDP film is about 200 Å thick.

The antistrengthen performance of ZDDP and DDP (1%) at different rubbing times was also investigated. The WSW was measured from the pin using a calibrated microscope. The wear
for the ZDDP additive for very short rubbing times (10-60 sec) is relatively small (~75 µm) and gradually increases to 130 µm after 1 hr rubbing. However, the WSW for DDP is always higher than those of ZDDP’s values. It starts at ~100 µm and reaches 180 µm after 1 hr rubbing. The antiwear performance of mixed ZDDP/DDP was also investigated. It was found that a very small concentration of ZDDP (0.1%) is sufficient to produce a thick film and give a good wear performance.

CONCLUSIONS
Using multiple analytical tools (XANES, XPS, and AFM), the average thickness and the morphology of tribofilms formed from ZDDP and DDP were investigated. For ZDDP, a phosphate film (about 100 Å thick) forms after only 10 seconds, while the rate of DDP film formation is much slower. The presence of a small amount of ZDDP in combination with DDP is sufficient to provide very good wear protection, and under all conditions used, antiwear performance of ZDDP was superior to DDP. The morphology of the tribofilms was measured using AFM. It was shown that at short rubbing times (10 sec), the ZDDP films are less uniform than the DDP films. However after 30 seconds rubbing, antiwear pads have formed for ZDDP and not for the DDP films. Despite the difference in chemistry and morphology of the films, the average thickness of both films is very similar after many minutes of rubbing.

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REFERENCES


