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Studies on ZDDP anti-wear films formed under the different conditions by XANES spectroscopy, atomic force microscopy and 31P NMR

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ABSTRACT

Antiwear (AW) films, generated from a mineral base oil containing zinc dialkyl dithiophosphate (ZDDP) additive, were extensively studied. These films were formed at various conditions such as different temperatures, various loads and rubbing times. The surface morphology of these films was investigated using atomic force microscopy (AFM) and the surface roughness of these films has been calculated from the images. X-ray absorption near edge structure (XANES) spectroscopy has been used to characterize the chemistry of these films. The intensity of phosphorus K-edge was also used to monitor the thickness of these films. Phosphorus L-edge spectra show that these films have slightly variable chemical natures. 31P Nuclear magnetic resonance (31P NMR) was used to study the ZDDP components in the residue oils. The spectra show that the primary and secondary ZDDP decompose quite differently at the various conditions. Tribological characteristics of these AW films were probed by measuring the coefficients of friction and the wear scar width of the counter faces.

INTRODUCTION

Phosphorus-based antiwear additives, and in particular, ZDDPs have been widely used in engine lubricants since the 1950s[1]. It is widely accepted that ZDDPs break down in certain conditions and create sacrificial films that are responsible for minimizing asperity contact which can eventually lead to wear. Much work has been published concerning the role of ZDDP and explaining its behaviour at a fundamental level. To date, ZDDPs have been the focus of several reviews [1-3], which have nicely summarized the evolution of this important class of molecules, and discussed the history of earlier studies of ZDDPs with regard to the AW films they form. Because of the concerns about the impact of phosphorus-containing additives on exhaust after-treatment catalysts, there have been considerable efforts to replace these additives by phosphorus-free alternatives. This has met with relatively little success and one of the main reasons is the physical and chemical processes responsible for the formation and function of antiwear films are general unknown.

In this paper, AW films generated from the ZDDP solution and wear performances were investigated as an entire system. These studies help reveal the nature and properties of AW films and are directed to help solve the real problem of reducing the concentration of phosphorus-containing additives, and also of optimizing the performances of additive packages.

EXPERIMENTAL

ZDDP antiwear film preparation

The ZDDP tribofilms were formed by a Plint TE77 high speed friction machine in pin-on-flat configuration with line contact (Figure 1). Pins and coupons used in these experiments were made from AISI-52100 steel. The ZDDP used in this study is a commercial ZDDP supplied by Imperial Oil, Canada. It contains secondary butyl (85%) and n-octyl (15%) groups. ZDDP oil solutions with 1.2 mass % ZDDP (providing approximately 0.1 mass % P), were prepared by mixing ZDDP concentrate in MCT-10 base oil. The experiment parameters are listed in Table 1.

Table 1. Physical parameters of the wear tests

Experimental parameters	Conditions
Rubbing Temperature(°C)	40, 100, 150
Rubbing Time(hour)	1 or 4
Applied force (N)	60 or 220
Sliding speed (m/s)	0.35

RESULTS AND DISCUSSION

AFM images and surface roughness

The morphology and the surface roughness of the AW films are dependent on the conditions of formation. The AFM images are shown in Figure 1.

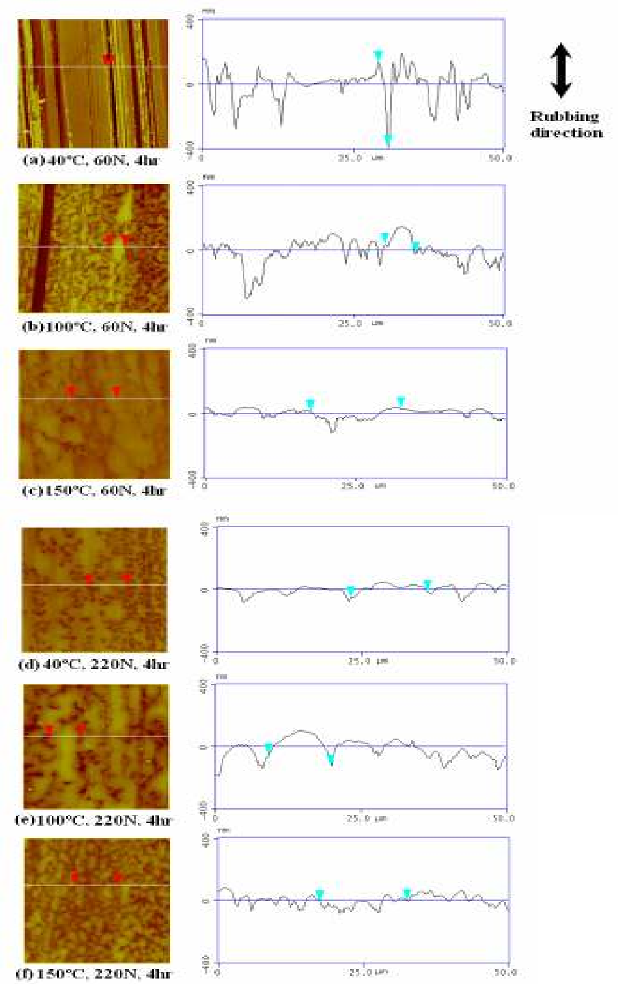

Figure 1. Representative AFM images and section analyses of AW films formed under different conditions.

Phosphorus K-edge XANES and film thickness

The chemistry of the AW films can be obtained from XANE spectra. The method developed by Fuller et.al.[4] was usd to monitor the AW film thickness. The data are plotted in Figure 2. It is clear that the film thickness is dependent on the running conditions.

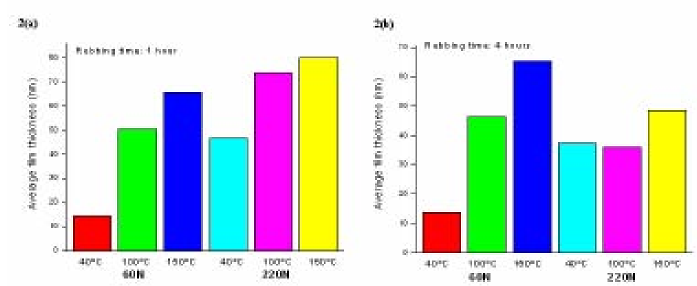

Figure 2. The average film thickness formed under the indicated conditions.

Phosphorus L-edge XANES (detailed in manuscript text)

XANES P L-edge spectra show that the AW films have similar chemical nature in that they are all polyphosphate glasses but with chains of varying lengths. Low temperatures and low loads are unfavourable for the formation of long chain polyphosphates. High temperatures and loads favour the formation of the AW films but the depletion of ZDDP in the solution causes the problem of wear for longer rubbing times as AW films can no longer be rapidly formed.

31-Phosphorus NMR

The commercial ZDDP contains iso-butyl (85%) and n-octyl (15%) groups and 31P NMR technique was used to probe these two ZDDPs after the rubbing experiments. It was found that the reaction rates of the primary ZDDP and the secondary ZDDP are different. The secondary ZDDP (94.8 ppm) decomposed faster than the primary ZDDP (100.5ppm) at the lower load and temperature while the primary ZDDP discomposed faster at the higher load and temperature, shown Figure 3.

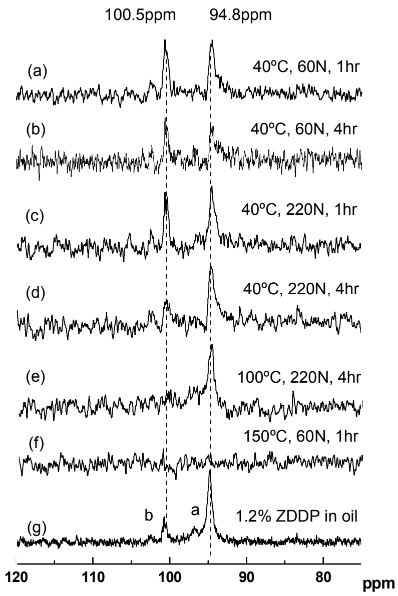

Figure 3. 31P NMR spectra of 1.2% ZDDP in oil and ZDDP oil residues collected after rubbing under the different conditions.

Wear scar width measurements

The wear scar width (WSW) measurements made on the pins are plotted in Figure 4. For 1 hour rubbing experiments, the relatively larger WSW numbers were found at 220N load conditions, in Figure 4(a). For the 4 hour rubbing time, the larger WSW values were found at conditions of 40ºC and 100ºC with a load of 60 N, and at 150ºC with a load of 220 N. It is clear that ZDDPs only operate optimally as anti-wear agents under particular and favourable conditions.

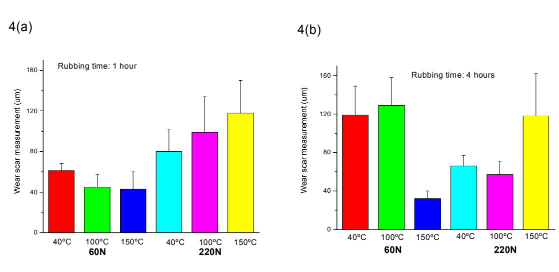

Figure 4. Wear scar widths of pin as a function of the different rubbing conditions.

CONCLUSIONS

The chemistry and morphology of the AW films formed in ZDDP oil solution under various conditions has been investigated and has provided insight into the functionality and limitations of ZDDPs as an AW agent. All the data from XANES, AFM, 31P NMR and optical microscopy, we have found that:

1) The AW films formed under various conditions showed the different morphology and surface roughness;

2) The thickness of these films is highly dependent on the formation conditions of the films;

3) Iso-butyl ZDDP and n-octyl ZDDP have shown the different reactivity under the various conditions. Iso-butyl ZDDP shows the better thermal stability at the higher temperature and higher reaction rate at the low load and low temperature condition compared with n-octyl ZDDP.

4) ZDDP did not show the expected antiwear protection in 2 regimes: (1) low load and low temperature conditions; (2) severe conditions of long duration.

The focus of this manuscript is an integration of chemical analyses of AW films and oil residues, and more importantly a progress towards expanding our knowledge of ZDDPs and their performances.

REFERENCES

[1] H. Spikes, *The history and mechanisms of ZDDP.* Tribology letters, 2004. **17**(3): p. 469.

[2] A. M. Barnes, K. D. Bartle and V. R. A. Thibon, *A review of zinc dialkyldithiophosphates (ZDDPS): characterisation and role in the lubricating oil.* Tribology International, 2001. **34**: p. 389.

[3] M. A. Nicholls, T. Do, P. R. Norton, M. Kasrai and G. M. Bancroft, *Review of the lubrication of metallic surfaces by zinc dialkyl-dithiophosphates.* Tribology International, 2005. **38**(1): p. 15.

[4] M. L. Fuller, L. R. Fernandez, G. R. Massoumi, W. N. Lennard, M. Kasrai and G. M. Bancroft, *The use of x-ray absorption spectroscopy fro monitoring the thickness of antiwear films from ZDDP.* Tribology Letters, 2000. **8**: p. 187.