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Application of XAFS in Tribology: P and S L-Edge XANES Spectroscopy of Antiwear Films

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Abstract: Antiwear additives are added to engine oils in the form of Zinc dialkyl dithiophosphates (ZDDPs). They form an antiwear (tribochemical) film on the rubbing surfaces. High resolution P and S L-edge X-ray absorption near edge (XANES) spectroscopy has been used to characterize the chemical nature of the films formed under air and inert atmosphere. The total electron yield and fluorescence yield detection methods have been employed to investigate the near surface and bulk composition of the films.

1. INTRODUCTION

Lubricant-derived surface films, generally known as antiwear (tribochemical) films result from the decomposition of Zinc dialkyl dithiophosphates (ZDDPs), added to engine oils. The tribochemical films (referred to as tribo-films) formed on the rubbing surfaces protect the engine from excessive wear and corrosion. Although these additives have been in use for over fifty years, the chemical nature of the species responsible for the antiwear function and the mechanism for the film formation is not well understood. Several surface techniques such as XPS and AES have been used in the past to characterize the nature of the antiwear films with limited success. Willermet et al. [1] have recently reviewed the subject and proposed a mechanism for the film formation. Yin et al. [2-3] have applied the phosphorus and sulphur L-edge X-ray absorption near edge (XANES) spectroscopy to characterize the chemical nature of the films and have forwarded a related mechanism for the antiwear film formation.

In this study, we have used the P and S L-edge XANES to study the chemical nature of tribo-films under air and nitrogen atmosphere. This is aimed to better understand the mechanism of the film formation.

2. EXPERIMENTAL

The antiwear agent used in this study was a commercial sec-dialkyl ZDDP, supplied by Imperial oil (Esso) Ltd. The tribo-films were generated using a Plint reciprocating wear machine [2]. The machine was equipped with an environment box which was used to prepare the tribo-films in an inert (N_2 or Ar) atmosphere. Nitrogen was bubbled through the oil containing ZDDP for 15 min to saturate the solution, before using it in the Plint machine. The box was flushed with nitrogen and kept at slightly positive pressure.

P L-edge and S L-edge X-ray absorption spectra were recorded at the Canadian Synchrotron Radiation Facility situated at the 1 GeV synchrotron storage ring, University of Wisconsin. Details of the data recording and analysis have been reported before [2-3].

3. RESULTS AND DISCUSSION

We have recently proposed a mechanism for the tribo-film formation [3]. This mechanism was based on the initial adsorption of ZDDP ($Zn(RO)_2P_2S_4$) on the rubbing contacts and its eventual thermo-oxidation reaction to form long chain polyphosphates. The following scheme is a modified mechanism to incorporate the effects of oxygen:

Reaction (1), (2), and (3) are balanced for P, Zn and O. Oxygen is present in oil during the reaction. Zinc metaphosphate ($Zn(PO_3)_2$) is known to have a long chain or a cyclic polyphosphate structure. Reaction (2) which produces short chain polyphosphate can also proceed with more of oxygen. Reaction (3) involves oxides on the contact surfaces. Several experiments have been performed under air and under nitrogen atmosphere to test the above mechanisms.

Figure 1 shows the P L-edge XANES spectra of tribo-films generated under nitrogen along with spectra of a film made under air and that of zinc polyphosphate. The XANES spectra were recorded in the total electron yield (TEY) (left side) and fluorescence yield (FY) (right side) modes. It has been shown that, in this energy region, the TEY technique probes ~ 50 Å depth of the surface and the FY method probes ~ 500 Å [4]. Comparing spectra A, B and C in Fig. 1 for films generated in 5 min, 30 min and 6 hr, respectively with the spectrum (E) of zinc polyphosphate, we notice that all the peak positions align very closely. However the intensity of peak *a* in the films is much higher than that of zinc polyphosphate. We have shown in the past that this increase in the intensity which is accompanied with shoulder *s*, is due to the presence of unchanged or partially decomposed ZDDP in the film [3]. Since the intensity of peak *a* is higher in spectrum (C), it suggests that there is more unchanged ZDDP on the surface of the 6 hr film than on the 30 and 5 min films. The corresponding spectra (F-H) recorded in the FY mode show similar results with small reduction in the intensity of peak *a*. This indicates that there is still significant amount of unchanged ZDDP in the bulk of the film.

For comparison, spectra (D) and (I) shown in Fig. 1 are for a 6 hr film generated in air and recorded in TEY and FY modes, respectively. From the intensity of peak *a* in spectrum (D) it is quite apparent that there is no or very little unchanged ZDDP on the surface of the film. The intensity of this peak in the TEY spectrum (D) is very close to the intensity of peak *l* in polyphosphate spectrum (E). In contrast, the intensity of peak *a* in the FY spectrum (I) is less intense than peak *l* of the polyphosphate spectrum (J). We have shown in the past that relative intensities of peaks *a/c* or *b/c* is a measure of the polyphosphate chain length [5]; the higher the ratio, the longer the chain length. From the intensity of peaks *a* and *b* in spectrum (D) and (I) we can conclude that film generated in air is composed of long chain polyphosphate on the surface and short chain polyphosphate in the bulk; in agreement with our previous findings [3].

Peak *b* is the spin orbit counterpart of peak *a*, and its intensity is much less affected by the presence of unchanged ZDDP. The intensity of this peak in the TEY spectra (A, B and C) is very similar to the intensity of that of the FY spectra (F, G and H). This observation suggest that films generated under nitrogen, in contrast to films formed under air, are composed of long chain polyphosphate throughout the film. There is very little difference between the surface and the bulk. The quality of the FY signal reveals that the film is relatively thick (>100 Å). In addition, as the intensity of peak *a* in the FY spectra suggest, films formed under nitrogen contain some unchanged ZDDP. In all our previous experiments carried out in air, the bulk of the sample contained short chain polyphosphate and was almost free of unchanged ZDDP [3].

Figure 2 shows the S L-edge XANES spectra of two 6 hr films generated under N_2 atmosphere and air as compared with the untreated ZDDP spectrum. The main peak of the film align closely with the main peak of untreated ZDDP. However the fine features are not well resolved in the film spectra. This observation does not necessarily suggest that unchanged ZDDP is present in the films. As has been shown in the past other sulphides, specially alkyl sulphides, show similar spectra in the same position [7]. What is

Figure 1: P L-edge XANES spectra of tribochemical films generated under air and nitrogen atmosphere and recorded in the TEY (left side) and FY (right side) modes.

important to note is the presence of sulphide on the surface as well as in the bulk for the film generated in N_2 (spectra A and B). In contrast, the sulphur signal in the bulk for the film generated in air is very weak (spectrum D).

These findings lead us to conclude that reducing the oxygen supply does increase the rate of polyphosphate formation (Reaction 1) versus short chain polyphosphate formation (Reaction 2). As we move from polyphosphate to orthophosphate, the O/P ratio increases. Thus, in order to produce short chain polyphosphate (reaction 2), we require more oxygen. It should be added that it is obvious from these results that, it has not been possible to remove all the oxygen from the system. Otherwise no polyphosphate could have been formed and ZDDP would have remained unchanged.

Willermet et al.[6] have conducted four-ball wear experiments under air and inert atmosphere. Using XPS and Auger spectroscopy, they have found that, compared with the original ZDDP, films generated under air were rich in oxygen and depleted in S. In contrast, films formed under inert atmosphere were depleted in O, Zn and P, but not S, as compared to the films formed under air. Our S L-edge XANES data agrees with their findings. Still the role of surface oxides (Reaction 3) is not clear. They may also take part in the reaction. More experiments are undergoing to investigate the interaction of the oxides in polyphosphate formation.

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Figure 2: S L-edge XANES spectra of tribo-films generated under air and under nitrogen and recorded in the TEY and FY modes as compared with the untreated ZDDP.