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## Study of the effects of Ca sulfonate on antiwear film formation by X-ray absorption spectroscopy using synchrotron radiation

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X-ray absorption near edge (XANES) spectroscopy at the P and S L-edge and K-edges has been used to characterize antiwear films generated from combinations of the antiwear additives, zinc dialkyl dithiophosphates (ZDDPs), and the detergent additives, Ca sulfonates. The results clearly show the interaction of the detergent with the ZDDP in antiwear film formation. Zinc polyphosphate, in part, is converted to calcium phosphate. There are substantial differences between the effect of the neutral and overbased detergents. Wear is also affected by the presence of the detergent.

**Keywords:** ZDDP, P and S XANES, Detergents, Wear

### 1. Introduction

The antiwear/antioxidant additives, zinc dialkyl dithiophosphates (ZDDP's), are the most important of all chemically-active additives used in engine oil formulations today. In addition to ZDDPs, oil formulations generally contain other additives such as detergents and dispersant (Bart, 1993). While ZDDPs protect the rubbing parts of the engine from excessive wear by forming an antiwear film, detergents such as Ca sulfonate help to lift deposits from the surfaces and keep the engine surfaces clean. The interaction of ZDDP with detergents has been investigated in the past. (Inoue & Watanabe, 1983, Ramakumar et al., 1992). The ZDDP additive decomposes in oil solution and on the rubbing surfaces to give the so-called antiwear film (Yin et al., 1997a, Suominen Fuller et al., 1988). The rate of ZDDP decomposition can be retarded by detergents (Rounds, 1978). In addition, this additive could interfere with the ZDDP-derived antiwear films by co-adsorbing on the surface (Inoue & Watanabe, 1983, Rounds, 1986). In a previous investigation using the P and S L-edge X-ray absorption near edge (XANES) spectroscopy, we briefly investigated the effect of neutral Ca sulfonate on antiwear film formation [Yin et al., 1997b]. In this paper we report the effect of calcium sulfonate on antiwear film and wear performance of neutral and overbased calcium sulfonate. P and S L-edge and K-edge XANES spectroscopy is used to characterize the chemical nature of P and S species in the antiwear film.

### 2. Experimental

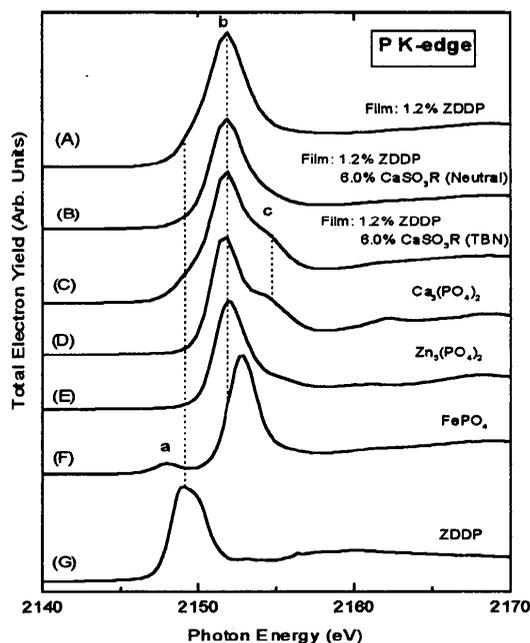
All additives and model compounds used in this study were commercial products: a sec-ZDDP, Calcium sulfonate (neutral) and calcium sulfonate (overbased, 400 TBN). Total Base Number (TBN) is a measure of the alkalinity of an additive and is equivalent to mg of KOH per a gram of additive. All the additives were supplied in a concentrated form in oil. The additive concentrates were diluted in MCT-10 base oil in the following concentrations: sec-ZDDP, 1.2 wt.%; detergents, 2 and 6 wt.%. The antiwear films were generated on 52100 steel coupons. Prior to film generation, the 52100 steel coupons were polished using 3 µm diamond paste. The coupons and cylindrical pins were cleaned in an ultrasonic bath using a light hydrocarbon solvent (hexane). The antiwear films were prepared using a Plint reciprocating wear tester. Data acquisition and data analysis have been described elsewhere [Yin et al., 1997a].

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### 3. Results and Discussions

#### 3.1 XANES Spectra

In order to determine the chemical nature of P and S in the antiwear films, it is crucial to compare the XANES spectra of films with those of various model compounds in which the local chemical environments of P and S are known [Yin et al., 1997a]. In this study we have taken advantage of P and S XANES spectroscopy, both at the L-edge and K-edge, to investigate the effects of Ca sulfonate detergents on antiwear film formation. The Total Electron Yield (TEY) and Fluorescence Yield (FY) techniques have been used at both the K-edge and L-edge to probe the surface and the bulk chemistries of the film [Kasrai et al., 1993, Kasrai et al., 1996]. Two types of Ca sulfonates, namely neutral and overbased, were used in this study. The overbased detergent is loaded with the amount of CaCO<sub>3</sub> required to meet the desired TBN.



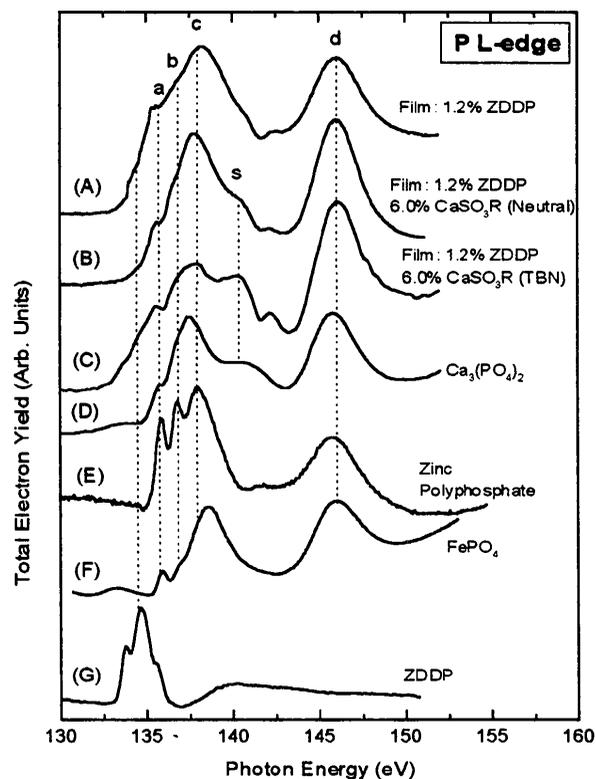
**Figure 1** Phosphorus K-edge XANES spectra of antiwear films as compared with model compounds.

First we consider the P K-edge spectra. Figure 1 shows the P K-edge total electron yield XANES spectra for several model compounds and antiwear films generated from ZDDP alone and in combination with the detergents. Spectrum (A) is of a film generated from the ZDDP additive alone. Spectra (B) and (C) are of films generated from ZDDP with neutral and overbased calcium sulfonate, respectively. Spectra (A) and (B) are identical, and both are very similar to spectrum (E) of the model compound, zinc polyphosphate. Spectrum (C) of a film generated from ZDDP and overbased calcium sulfonate has a unique feature not found in spectra (A) and (B). A shoulder is found at point c, which aligns well with the shoulder in spectrum (D) of the model compound, calcium phosphate. This indicates that when the overbased detergent is used in conjunction with ZDDP, considerable calcium phosphate is formed and is incorporated into the film. Replacement of Zn for Ca in the antiwear film has been suggested in the past (Willermet et al., 1995). To our knowledge, this is the first direct spectroscopic evidence for the formation of Ca phosphate from a mixture of ZDDP and overbased Ca sulfonate. Spectrum (F) of iron phosphate is quite different from any of the tribofilm spectra, since peak a is absent in the tribofilm spectra and peak b has shifted  $\sim 1.5$  eV to lower energy (Kasrai et al., 1998). Thus the presence of  $\text{FePO}_4$  in any of the films is unlikely. All of the antiwear film spectra show a weak shoulder at around 2150 eV which is absent in all of the phosphate model compound spectra. This shoulder could be the result of some unreacted ZDDP in the film since it corresponds closely to the main peak in spectrum (G) of ZDDP.

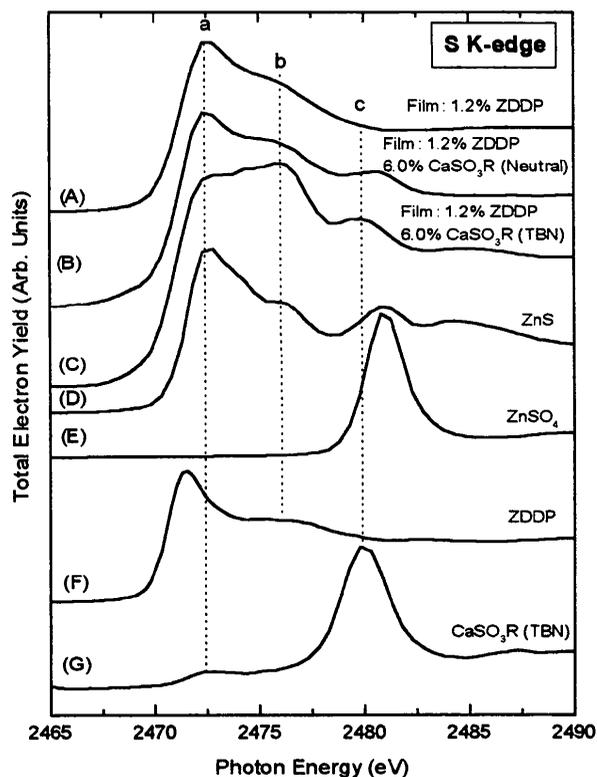
Spectrum (B) of a film generated from ZDDP in combination with neutral calcium sulfonate is similar to that of the film generated from neat ZDDP. This indicates that the Ca from calcium carbonate in the overbased detergent, and not the Ca from the calcium sulfonate, is responsible for the cation exchange. Previous studies have shown that, in the absence of overbased detergent, the films are essentially composed of zinc phosphates. Addition of overbased detergent results in partial displacement of zinc by the metal (calcium in this study) from the detergent (Willermet et al., 1995). Spectra recorded in FY mode (not shown) for the P K-edge were remarkably similar to the spectra in Figure 1 indicating a uniform film structure.

The corresponding P L-edge XANES spectra of the films and model compounds are shown in Figure 2. In general, because of better photon resolution and narrower line widths at the L-edge, more chemical information can be obtained from the P L-edge XANES (Yin et al., 1997a). We notice that peaks b, c and d in spectrum (A) (ZDDP film) correspond remarkably well to those of spectrum (E) of zinc polyphosphate. On the other hand, the same peaks in spectra (B) and (C) correspond more closely in intensity and peak positions to those in spectrum (D) of the model compound,  $\text{Ca}_3(\text{PO}_4)_2$ . Also, shoulder s in spectra (B) and (C) aligns well with that of  $\text{Ca}_3(\text{PO}_4)_2$ . In contrast to the results obtained from the P K-edge spectra (Fig. 1), the shoulder s is noticeable in spectrum (B) in Fig. 2, indicating some interaction of the neutral calcium sulfonate with ZDDP. However, we should remember that TEY at the L-edge probes  $< 5$  nm compared to 25 nm at the K-edge. Thus, the reaction of the neutral calcium sulfonate with the ZDDP is a surface reaction. As was obtained from the P K-edge, the iron phosphate spectrum (F) does not correspond to any of the film spectra, and the formation of  $\text{FePO}_4$  is ruled out.

The S K-edge XANES spectra of the films and model compounds are presented in Figure 3. The film spectra (A, B and C) are quite similar to the ZnS spectrum (D), indicating that the films are mainly composed of reduced sulphur species. The sulphur signal is much weaker than the phosphorus signal, in



**Figure 2**  
Phosphorus L-edge XANES spectra of antiwear films as compared with model compounds.



**Figure 3**  
Sulfur K-edge XANES spectra of antiwear films as compared with model compounds.

particular, for films generated in the presence of sulfonate detergent. Comparison of the film spectra (A,B and C) with that of the calcium sulfonate starting material (G) indicates that very little if any of the unreacted material is present in the film. However, peak b in spectrum (C) indicates that the sulfonate has been reduced to a new sulphur species. The nature of this species has not yet been determined. Its oxidation state is somewhere between a sulfoxide and a sulfone.

The S L-edge spectra (not shown) yielded similar results. In addition, the Ca L-edge (2<sup>nd</sup> order) XANES indicated the presence of calcium in the films. The signal was much stronger for the overbased film. This is further proof for the exchange of Ca for Zn in the phosphates.

### 3.2 Wear Measurements

Each sample was prepared by rubbing a steel coupon with a cylindrical steel pin (line contact). Metal is worn away from the pin and results in a flat region (wear scar). The width of wear scar indicates the lubricating ability of the antiwear film formed from each oil formulation. The smaller the width of the wear scar, the better the film is at protecting the steel substrate beneath it.

Wear was greater when the ZDDP and neutral calcium sulfonate additives were used together than for ZDDP on its own (200 vs. 80  $\mu\text{m}$ ). Solutions containing both ZDDP and detergent yielded less wear when the overbased calcium sulfonate, rather than neutral was employed (105 $\mu\text{m}$ ). It must be noted that all solutions prepared with the overbased calcium sulfonate gave less wear when the lower concentration of 2% instead of 6% was used (105 vs. 130  $\mu\text{m}$ ). Possibly the 2% concentration is more optimal for forming antiwear films. Further studies need to be done to confirm this. Overall results point to the fact that the chemical nature of the antiwear film (zinc phosphate vs. calcium phosphate) plays an important role in wear control.

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