J. Synchrotron Rad. (1999). **6**, 740–742

Study of the interaction between antiwear, extreme pressure and rust inhibitor agents in the formation of protective films by X-ray absorption spectroscopy

Greg Canning,[a] Masoud Kasrai,[a*] G. Michael Bancroft[a] and David Andrew[b]

[a]Department of Chemistry, University of Western Ontario, London, Ontario N6A 5B7, Canada, [b]Imperial Oil Products Division, Sarnia Research Centre, P.O. Box 3022, Sarnia, Ontario N7T 7M1, Canada.
Email:MKASRAI@UWO.CA

X-ray absorption near edge structure (XANES) spectroscopy at the P and S K-edge has been used to characterize thermally generated films from antiwear (AW)/extreme pressure (EP) agents such as organic phosphates and disulfides along with rust inhibitors such as alkylated organic acid/esters. The analysis revealed that the AW additive formed an iron phosphate-like film on steel and the EP agent formed an iron sulfate film on steel. From fluorescence yield XANES spectra, it was found that there exists a competition between the AW and EP agents.

Keywords: P and S K-edge, EP additives, Thermal films

1. Introduction

In order for lubricants to perform effectively in today's equipments, certain chemical additives must be present in the base oils. These so called "performance additives" which improve the chemical characteristics of the oil, include friction modifiers, extreme pressure (EP) agents, antiwear (AW) additives, anti-oxidants, detergents-dispersants, rust inhibitors, and metal deactivators (Herndan, 1997; Sarin *et al.*, 1997; Wei, 1995). Antiwear additives decompose on the metal surface to form a protective film. Under severe sliding conditions, AW additives cannot function and EP additives are required. The EP additives react chemically with the metallic surfaces, forming an inorganic surface coating, to prevent welding and halt the catastrophic wear process. Most EP additives contain S, Cl, P, or a combination of these elements. Protection of metallic surfaces from corrosion is another important function of lubricant additives. A corrosion inhibitor is required for this function.

This study concentrates on the interaction of certain EP additives, AW additives, and rust inhibitors and their film formation on steel surfaces using X-ray absorption near edge spectroscopy(XANES) at P and S K-edges

2. Experimental

2.1 Sample Preparation

The AW and EP thermal films were prepared using 52100 steel coupons, polished with 3μ diamond paste, and ultrasonically cleaned in light hydrocarbons. Oil solutions were prepared by dissolving the concentrated (Irgalube 349, Lubrizol 859, and Mobilad C170) (see Figures 1-3 for structures) in MCT-30 base oil. The oil was then heated to the appropriate temperature and the coupon was suspended in the oil bath for 18 hours, removed from the oil bath, and then gently blotted with a tissue paper prior to storage for analysis.

2.2 X-ray Absorption Spectroscopy

Photoabsorption spectra of the films were recorded using the fluorescence yield (FY) and total electron yield (TEY) detection modes at the Canadian Synchrotron Radiation Facility (CSRF)- Madison, Wisconsin. For the P and S K-edge measurements, the double crystal monochromator (DCM) beamline was used. The energy scale in the S and P regions were calibrated using pyrite (FeS_2) (2471.3 eV) and $FePO_4$ (2153.0 eV). Details of the analysis have been described elsewhere (Yin *et al.*, 1993)

3. Results and Discussion

3.1 Irgalube 349

The thermal films were prepared at different temperatures from a 0.5wt.% Irgalube solution. Irgalube is an organic phosphate and it can interact with the steel surface to form iron phosphate. To investigate this possibility, the P K-edge XANES spectra of Irgalube films are compared with that of $FePO_4$ in Figure 1.

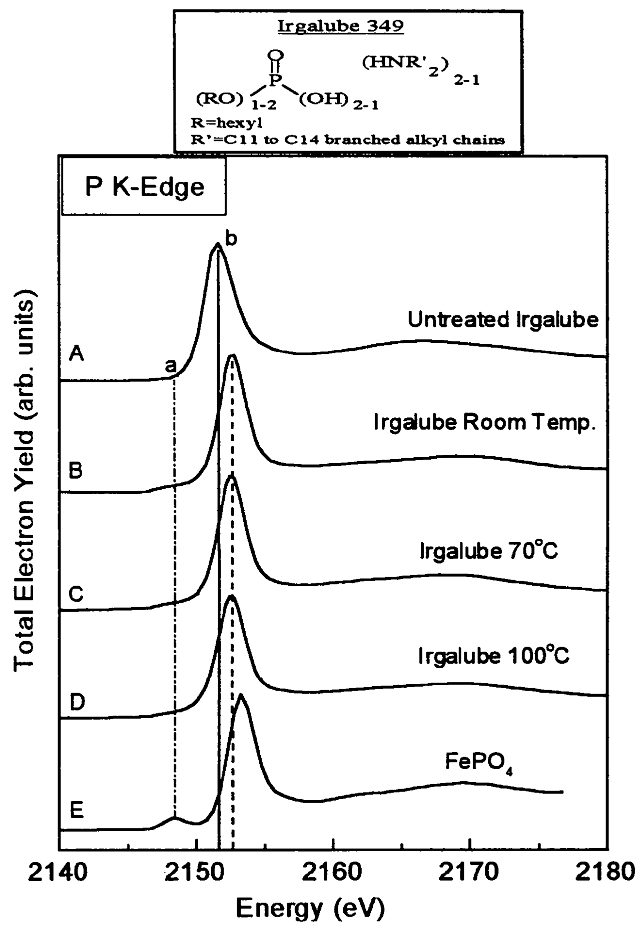

Figure 1
P K-edge spectra of Irgalube interaction with steel substrate

Spectrum A is for Irgalube in a thin oil layer (untreated.). Spectra B-D are for films generated at room temperature, 70 ^{0}C, and 100 ^{0}C, respectively. Spectrum E is for $FePO_4$.

Spectra B-C of thermal films are identical and have shifted to high energy by ~ 0.9 eV compared with untreated Irgalube. This indicates that Irgalube has reacted with the substrate. However, the spectra are different from $FePO_4$ spectrum E. Peak b in spectra E is shifted to higher energy by ~ 0.5 eV and peak a in the film spectra is very weak.. The 0.9 eV shift and the presence a weak peak a in the film indicates a partial substitution of Fe for the R group in Irgalube and formation of an iron phosphate-like film. The TEY and FY spectra of the films (not shown), were very similar indicating a uniform chemistry throughout the film. As no appropriate model compound, was available at this stage, further identification is not possible.

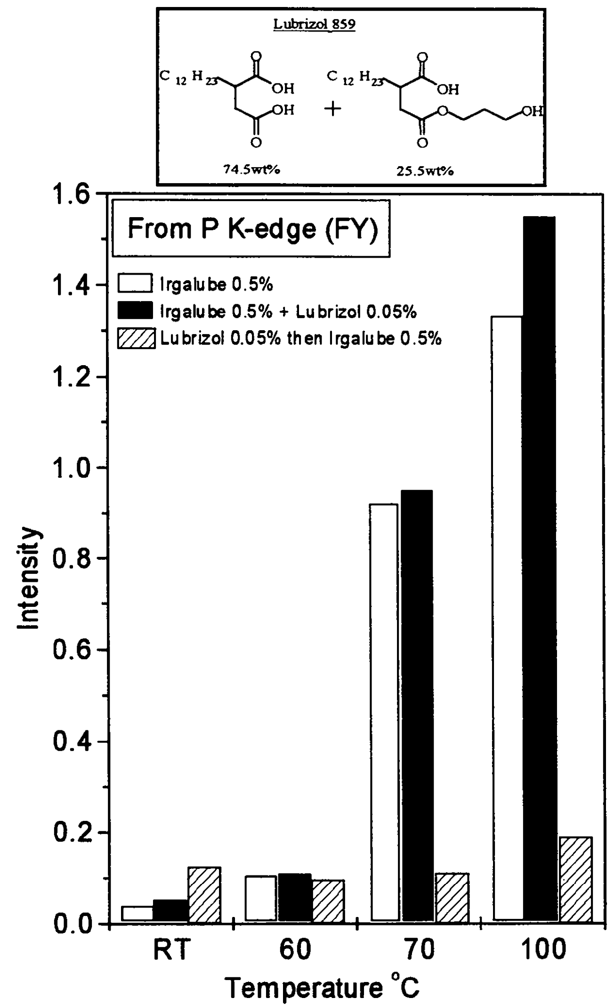

Figure 2
Fluorescence yield intensity of phosphate K-edge peak comparing the interaction between Irgalube and Lubrizol.

3.2 *Irgalube and Lubrizol*

The effect of the rust inhibitor Lubrizol was investigated in combination with Irgalube. Three similar sets of experiments were performed at 4 different temperatures. 1. Films were generated from Irgalube (0.5wt%). 2. Films were generated from a mixture of Lubrizol (0.05wt.%) and Irgalube (0.5wt.%). 3. The steel coupon was immersed in Lubrizol (0.05wt.%) for 18hrs, and then immersed in Irgalube (0.5wt.%) for 18hrs. The P K-edge XANES spectra of films generated from experiments 1-3 were identical. However, the peak intensity of the FY spectra which is a measure of the film thickness (Kasrai, *et al.*, 1996; Suominen Fuller, *et al.*, 1998) was different. The FY intensity of the films is plotted versus the reaction temperature in figure 2. As the temperature increases, the phosphate signal increases, suggesting a thicker film. The only difference is seen when the Lubrizol is introduced first. The FY signal is much weaker illustrating that Lubrizol coats the surface and inhibits phosphate film formation. Irgalube requires direct interaction with the metal substrate to form a substantial phosphate film. This is in agreement with the above suggestion that Irgalube reacts with the surface to form an iron phosphate-like film.

3.3 *Irgalube and Mobilad*

The effect of the EP additive Mobilad alone and in combination with Irgalube was investigated. A solution of 1wt.% Mobilad alone and in combination with 0.5wt.% Irgalube was used in this experiment. In Figure 3 the S K-edge XANES spectrum of untreated Mobilad (A) is compared with the spectra of film generated from Mobilad alone (B), a mixture of Irgalube/Mobilad (C) and $FeSO_4$ (D) . It is very clear from the spectra in Figure 3 that Mobilad decomposes to sulfate in contact with steel, with or without Irgalube present. There is enough oxygen in the oil and in the surface oxide layer of the steel to provide oxygen for the oxidation reaction, but the mechanism by which this oxidation takes place requires further investigation.

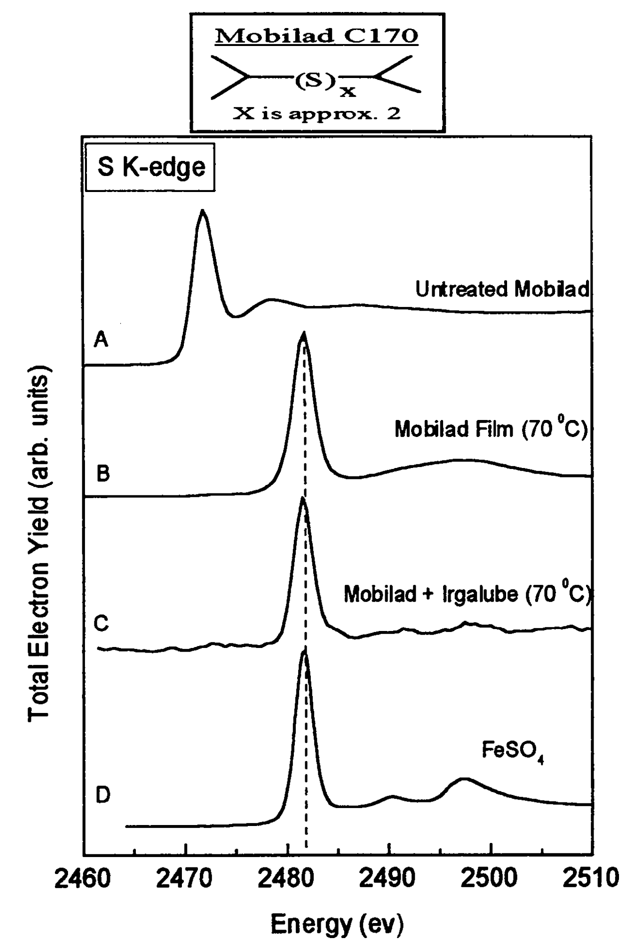

Figure 3
S K-edge spectra of Mobilad interaction with steel substrate at 70 ^{0}C.

The P K-edge spectrum of the mixture (not shown) indicated that there was no effect on the phosphate structure when Mobilad was present in the film. However, the P and S FY XANES spectra showed that the intensity of the P and S signals in the mixed system decreases greatly from the samples with only one of the additives. This illustrates that the additives are competing for surface sites. If one additive was dominating then its FY signal intensity would approach that of the additive by itself. The total intensity of the mixture is also much less that of the individual additives indicating that this competition hinders film growth.

4. Conclusion

The following general conclusions can be drawn from the above results.

1. The AW agent Irgalube forms an iron phosphate-like film on steel when thermally decomposed. This film increases in thickness with increased reaction temperature. When a rust inhibitor is introduced, prior to Irgalube, it impairs the ability of Irgalube to form a phosphate film on steel.
2. The EP additive Mobilad forms a sulfate film on steel. When Irgalube and Mobilad are used together they compete for surface sites, thus producing a very thin film of phosphate and sulfate.

This study was supported by Materials and Manufacturing Ontario (MMO), Imperial Oil, and the NSERC of Canada. The authors are grateful to Kim Tan and Greg Retzlaff from CSRF and the staff of SRC, University of Wisconsin-Madison for their technical support and the National Sciences Foundation (NSF) for supporting the SRC under Award No. DMR-95-31009.

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(Received 10 August 1998; accepted 23 November 1998)