Research Article

SURFACE and INTERFACE ANALYSIS

Received: 29 December 2008 Revised: 6 June 2009 Accepted: 6 June 2009 Published online in Wiley Interscience: 7 August 2009

(www.interscience.wiley.com) DOI 10.1002/sia.3092

XANES characteristics of tribofilms generated by dithiophosphate additive in water at different test temperatures and durations

Haibing Ma, Rui Qiao, Yilin Li, Huan Chen and Tianhui Ren*

Water-based lubricants and metal-working fluids are becoming more and more popular in modern manufacturing due to environmental concerns. Owing to the poor lubricating properties offered by pure water, additives are generally needed to improve the antiwear and extreme pressure properties. In the present work, the tribological behaviors of synthesized additives in water-based lubricants are studied for different durations and temperatures by a four-ball machine, and the worn surfaces were analyzed by scanning electron microscopy (SEM) and X-ray absorption near-edge structure (XANES) spectroscopy. It was found that the tribological properties changed with the duration and temperature, and the tribofilms mainly consisted of an adsorbed layer and a tribochemical layer. The compositions of tribofilms also changed with duration and temperature, and the different compositions of tribofilms would result in different tribological properties accordingly. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: water-based lubricant; metal-working fluids; thermal films; tribofilms; XANES; mechanism

Introduction

Lubricants can contribute substantially to reduce the mechanical damages and consumption of fossil fuels. They help in reducing the tribological damages and decreasing the emission of carbon dioxide. In recent years, as a substitute for the oil-based lubricants water-based lubricants have been widely used in metal-working fluids and hydraulic systems.[1–3] Many advantages, such as dispersing heat easily, effortless cleanouts, low toxicity and fire-resistance, are possessed by water-based lubricants relative to oil-based lubricants. The related research work has also progressed rapidly.[4–7]

In a water-based lubricant, the lubricating additive is a very important component because of the poor lubricating properties possessed by water. Thiophosphate is such an important kind of water-soluble additive, which contains active elements such as sulfur and phosphorus, and can exhibit excellent tribological properties.

In the process of metal working, the temperature of the contact area between two mating parts can instantaneously reach hundreds of degree centigrade, and the additive molecule will react with the metal surface, forming tribofilms quickly. In the past few years, much effort has been put into understanding the mechanism of tribofilms, but there are still questions concerning the film formation, the reacting species, the reaction kinetics and film compositions. Relative to the earlier works, which mainly concentrated on the tribological properties, the present work mainly focuses on the influence of the duration and temperature on the tribological properties. All the compositions of tribofilms are analyzed by X-ray absorption near-edge structure (XANES) spectroscopy, which is a very important tool and has been used in tribology and thin-film research work in recent years.[8–11] High atom sensitivity and speed, as well as perfect accuracy, are all its advantages. Total electron yield (TEY) and fluorescence yield (FY) are two modes of detection, and provide the surface and near-surface (about 5 nm) and bulk (about 2000 nm) chemistry of the films, respectively. The mechanism of tribofilm formation of this kind of additives is also discussed in the present work.

Experimental

Preparation and characterization of the additive

The additive *O*,*O*-di-(AEO-3) phosphorodithioic acid (DAPA) was prepared in our laboratory according to Refs [12,13], and the pathway is outlined in Fig. 1. The processes are as follows: 2 mols of pentasulfide was added in small portions to 8 mols of AEO-3 at 70–80 °C, whereupon the temperature rose gradually until the reaction became violent. The flask was finally heated in an oil bath at 100–110 °C for 2 h. The reaction was accompanied by copious evolution of hydrogen sulfide. The reaction mixture was treated with charcoal and filtered. Titration with standard alkali indicated a purity of 90%. The products were used for tribological tests directly and without further purification. Triethanolamine was added in order to neutralize the acids and increase the water solubility.

Tribology measurements and preparation of tribofilms

The friction coefficients of the 3.0% additive-containing lubricant are generated for different durations, at 25 ± 5 °C and at a rotation rate of 1450 rpm. The antiwear and friction-reducing properties of DAPA in water at different concentrations were evaluated

* *Correspondence to: Tianhui Ren, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China.*
E-mail: thren@sjtu.edu.cn

School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai 200240, China

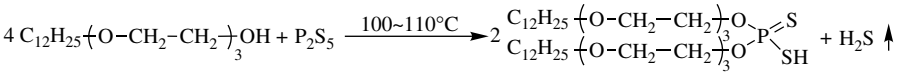

Figure 1. Preparation pathway of DAPA.

by using a four-ball machine with a test duration of 10 min at different temperatures and a rotation rate of 1450 rpm. The testing temperature was controlled by an annular heater surrounding the oil bath, similar to that in Refs [14,15]. The balls were made of GCrl5 bearing steel and had a diameter of 12.7 mm and hardness (HRC) in the range 59–61. The wear-scar diameters (WSDs) on the three lower balls were measured using an optical microscope. The friction coefficient values were recorded automatically and were averaged throughout the test. After the tribology test, the lower balls were washed ultrasonically with ethanol and dried with tissue paper, and they were used to analyze the worn surface directly.

Preparation of thermal films

The method of preparation of the thermal films is according to Ref. [16]. The process was as follows: the balls were put into the 5.0% additive-containing lubricant, keeping reaction for 6 h at 40, 60 and 80 °C, respectively. The balls were then used for the film analysis after ultrasonic cleaning with ethanol and drying with tissue paper.

Worn surface analytical method

After the tribology test, the ball was washed ultrasonically with ethanol and dried with tissue paper, then was used to study the worn surface.

A scanning electron microscope (SEM) JSM-5600Lv was used to study the worn surface. XANES data were obtained from the Institute of High-Energy Physics (IHEP), Chinese Academy of Sciences. Phosphorus and sulfur *K*-edge spectra were obtained on a double-crystal monochromator (DCM) covering an energy range of 1900–6000 eV with photon resolution of 0.5 eV. The photon absorption spectra for the model compounds and samples were recorded in the FY mode spectra for bulk sensitivity. The assignment of the fine structure in XANES was obtained by using the spectra of model compounds obtained by the authors or from previously published data.[16,17]

Results and Discussion

Influence of duration on the tribofilms

Tribology

Generally, tribological properties will exhibit differences with different durations. Figure 2 shows the variations of the friction coefficient with duration. It can be seen that the friction coefficient values vary in a broad range from 0.077 to 0.135 approximately at different durations. The friction coefficient value increases with time, reaching a maximum in about 35 min, and then decreases to the original values, and a new cycle begins. It can be seen that the friction coefficients at the beginning (about 0–15 min) and at the end (about 50–60 min) of the friction are smaller than that at the medium duration (15–50 min) of the friction. The reason for these phenomena may be formation of efficient films at the beginning of the friction, and the destruction of the efficient film gradually with the time. At a certain time (about 50–60 min), the new film-changing process restarts.

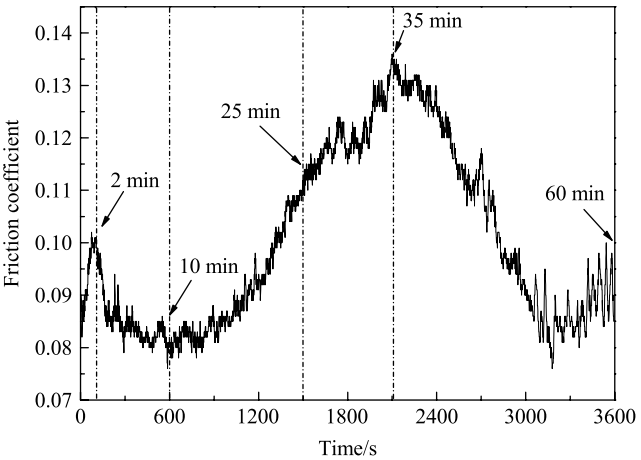

Figure 2. Relationship of the friction coefficient with time from 0 to 60 min at 25 ± 5 °C.

XANES spectroscopy of tribofilms at different durations

The tribofilms formed on the lower ball at different durations were analyzed by the FY mode of XANES, which can provide information about the chemical state of the surrounding of the sulfur and phosphorus atoms in the bulk.

Sulfur characterization. The S *K*-edge XANES spectra of tribofilms generated at 25 ± 5 °C from 3.0% DAPA at different frictional durations are shown in Fig. 3(a), and the spectral data are listed in Table 1 along with XANES spectra of iron sulfide, sodium sulfide and iron sulfate for spectral comparison. It can be seen that the

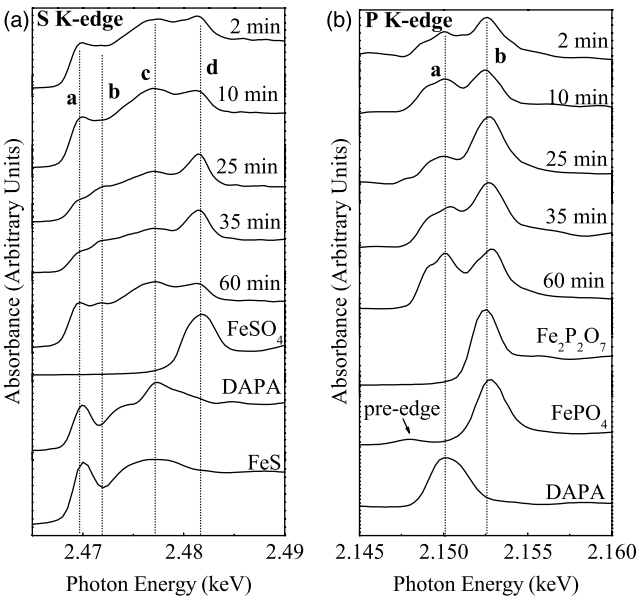

Figure 3. S *K*-edge (a) and P *K*-edge (b) spectra of tribofilms generated by 3.0% DAPA at different times.

SURFACE and INTERFACE ANALYSIS

Table 1. Peak positions of the S K-edge and P K-edge XANES (FY) spectra of tribofilms for various rubbing times and model compounds

	S K-edge (eV)				P K-edge (eV)	
Sample	*a*	*b*	*c*	*d*	*a*	*b*
2 min	2469.7	–	2477.5	2481.4	2150.0	2152.6
10 min	2470.0	–	2476.9	2481.1	2150.0	2152.4
25 min	–	2472.1	2476.9	2481.4	2150.0	2152.8
35 min	–	2472.1	–	2481.4	2150.4	2152.6
60 min	2469.7	2472.1	2477.2	2481.4	2150.0	2152.8
DAPA, 40 °C	–	–	2477.1	2481.9	2150.0	2152.6
DAPA, 60 °C	2470.2	2472.6	2477.7	2481.9	2150.0	2152.8
DAPA, 80 °C	2470.5	–	2477.7	2481.9	–	2152.6
$FeSO_4$	–	–	–	2481.7	–	–
Na_2SO_3	–	–	2477.2	–	–	–
FeS	2470.0	–	–	–	–	–
$Fe_2P_2O_7$	–	–	–	–	–	2152.6
$FePO_4$	–	–	–	–	–	2152.9
DAPA	2469.9	–	2477.4	–	2150.2	–

additive could react with the iron substrate and produce different sulfur-containing compounds. The peak *d* situated at 2481.4 eV corresponds to sulfate, which exists in the whole frictional process. The peaks of adsorbed and unreacted additive molecules also exist more or less in the tribofilms, which can be found at 2472.1 eV. At the initiation of the friction (2 and 10 min), several different forms of sulfur are introduced to the metal surface. Peaks *a*, *b* and *c* situated at 2470, 2477 and 2481 eV correspond to sulfide, sulfite and sulfate, respectively. It may also include adsorbed molecules of DAPA. In the middle duration of friction (25 and 35 min), the sulfide and sulfite in the tribofilms are oxidized to sulfate as can be seen from the decreasing peak intensity of peak *a* and *c* from initial duration to the middle duration. The spectrum generated at 60 min is similar to those generated at the beginning of the friction, which means that the components of sulfur in the films are the same, too. Recalling the tribological results generated at different durations, the mixtures of sulfur compounds such as sulfide, sulfite and sulfate can form efficient tribofilms, which can result in good antifriction properties, but the reducing of sulfide and sulfate in the tribofilms will result in higher friction coefficients.

Phosphorus characterization. Fig. 3(b) shows the P *K*-edge XANES spectra of tribofilms generated by the additive-containing solution at different durations. XANES spectra of iron phosphate and polyphosphate are also shown in order to characterize the tribofilms. Peaks *a* and *b* situated at 2150 and 2152 eV can be assigned to the adsorbed additive and polyphosphate. At the beginning (2 and 10 min) and end (60 min) of the friction, a higher percentage of adsorbed additives is contained in the tribofilm than at medium duration (25 and 30 min), according to the higher intensity of peak *a* than that of *b*. Associating these results with antifriction properties, the conclusion can be drawn that the tribofilms are composed of an adsorbed layer and a tribochemical layer, and a proper ratio of the mixtures of the adsorbed molecule and tribochemical products in the tribofilms will produce better antifriction results than a single component. As can be seen from the spectroscopy of tribofilms, there is no or only a weak pre-edge feature at approximately 2148.0 eV (the peak is the characteristic of Fe(III) phosphate according to the Refs [18,19]), which indicates that the cation in the films is mainly Fe(II) and not Fe (III).

It can been seen from the S *K*-edge and P *K*-edge spectra that in the process of friction the lubricating films formed on the surface of friction pairs are the main reason for the antiwear and antifriction exhibited by DAPA. 'Active elements' such as S and P in these lubricating films are mainly composed of an adsorbed layer and a tribochemical layer, and these layers are multilayers in general. All the forming and destroying processes of these films may continue during the whole friction process. Since most of the film thickness formed in the oil-based lubricant is about 30–70 nm,[20–22] we estimated that the thickness of the film formed in the water-based lubricant is about 10 nm because of the film degradation caused by dissolution of some S or P-containing compounds in the films.[23]

Influence of temperature on the tribofilms

Temperature has a significant influence on lubrication. It may result in decomposing the additive, accelerating the reaction speed or changing the mechanisms of the reaction process. In the oil-based lubricants, the influence of temperature on the compositions of tribofilms has been investigated widely in Refs [24–26], but little work has been done on water-based lubricants. In the present work, the tribofilms generated at 20, 40, 60 and 80 °C were analyzed for the water-based lubricant in order to ascertain the influence of temperature on the tribofilms' compositions.

Tribology

The dependence of WSD and friction coefficient on different temperatures is presented in Fig. 4(a) and (b), respectively. It is interesting to note that the values of WSD and friction coefficient are lower at higher temperatures than that at low temperatures, and they reach the lowest values at 60 °C.

Normally, the additive can be adsorbed on and react with the friction pair to form the tribofilms, which would have dominant influences on the lubricating process. A certain proportion of additive adsorption and tribochemical reactants in the tribofilms will result in good tribological properties. Lower temperature is favorable to physical adsorption, but higher temperature is beneficial to tribochemical reaction. In order to balance the adsorption and tribochemical reaction processes, an appropriate temperature should exist. In the present work, 60 °C is approximately the temperature which can balance the adsorption and tribochemical reaction to form a suitable tribofilm, which can result in good antiwear and friction-reducing properties.

Morphology of the worn surface

Figure 5 clearly shows the morphologies of the worn surfaces generated at different temperatures. It can be seen that the morphology generated at 60 °C is obviously different from that generated at other temperatures. The films have the areas within the scar which are comprised of glassy pads; between the glassy pads are areas of what appears to be the steel substrate. Normally, these glassy pads in the tribofilms could result in better antiwear and friction-reducing properties.[27]

XANES spectroscopy of tribofilms at different temperatures

Sulfur characterization. The S *K*-edge spectra of tribofilms generated from the additive-containing lubricant at 20, 40, 60, 80 °C along with model compounds are shown in Fig. 6(a), and the spectral data are listed in Table 1. Peaks *a*, *b*, *c* and *d* in each

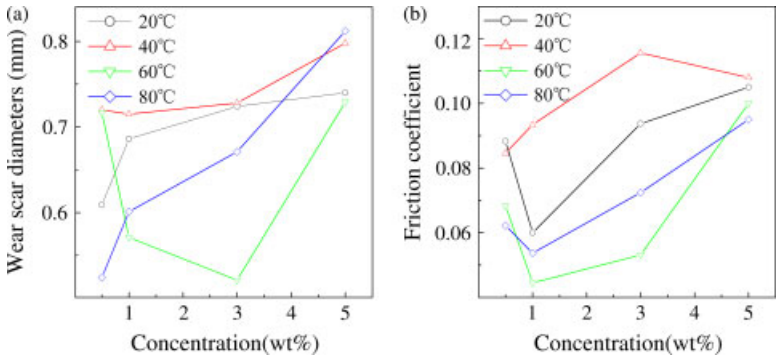

Figure 4. Variations of WSD and friction coefficient with 1–5% additive concentration at 20, 40, 60 and 80 °C. This figure is available in colour online at www.interscience.wiley.com/journal/sia.

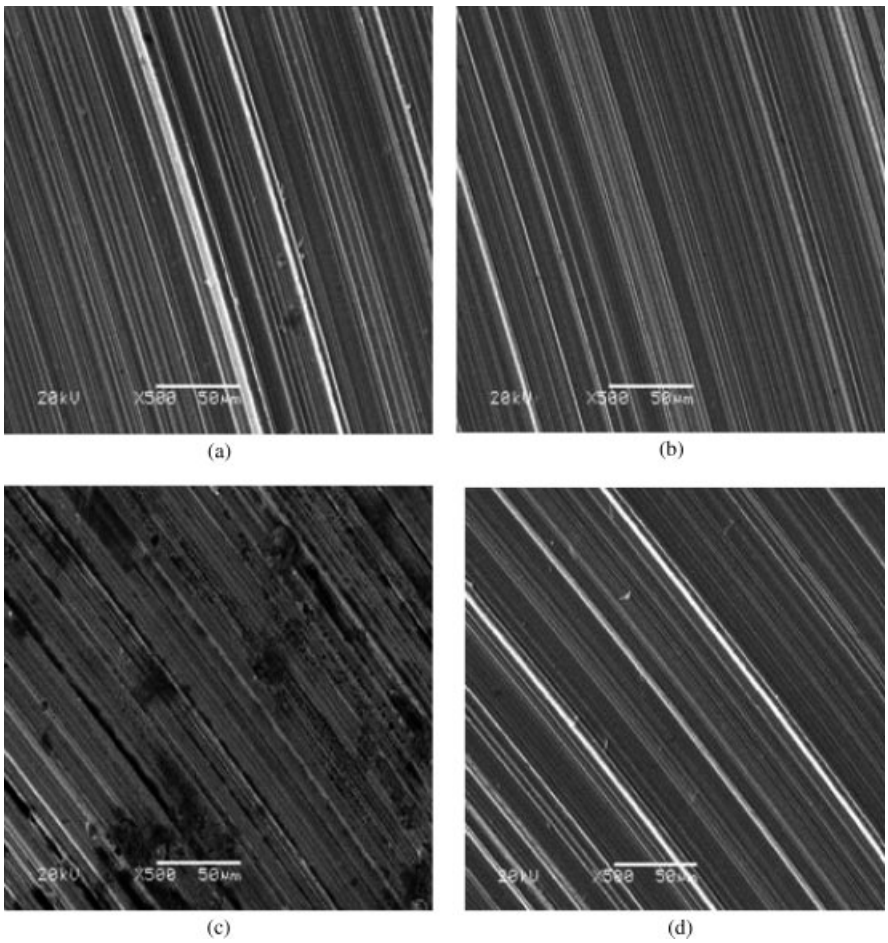

Figure 5. Scanning electron micrographs of the worn surface at different temperatures: (a) 20 °C; (b) 40 °C; (c) 60 °C; (d) 80 °C.

spectrum correspond to iron sulfide, alkylsulfur,[28] sulfite and sulfate, respectively. It can be seen that temperature has some influence on the components of tribofilms. First, it influences the peak position. For example, with the increasing of temperature from 20 to 80 °C, the peak energy of peak *d* is obviously moving to a higher value. Second, the temperature can influence the peak intensity, which corresponds to the relative content of sulfur-containing compounds in the tribofilm. With the increase of temperature, the intensity of peak *a* becomes strong first, and then turns weak at medium temperature, but it becomes strong again at 80 °C. But peak *b*, which corresponds to alkylsulfur, exists only at 40 and 60 °C. Recalling the tribological properties in Fig. 4, the conclusion can be drawn that sulfate and sulfide are two basic compounds in the tribofilm at different temperatures, and the content of iron sulfate (FeS) in the tribofilm is an uncertain factor to the tribological properties, but a higher content of alkylsulfur will result in better antiwear and friction reduction.

Phosphorus characterization. Fig. 6(b) shows the P *K*-edge XANES spectra at different temperatures. It can be seen that there are two basic peaks in the spectra, peak *a* situated at 2150 eV corresponding to the adsorbed additive and peak *b* situated

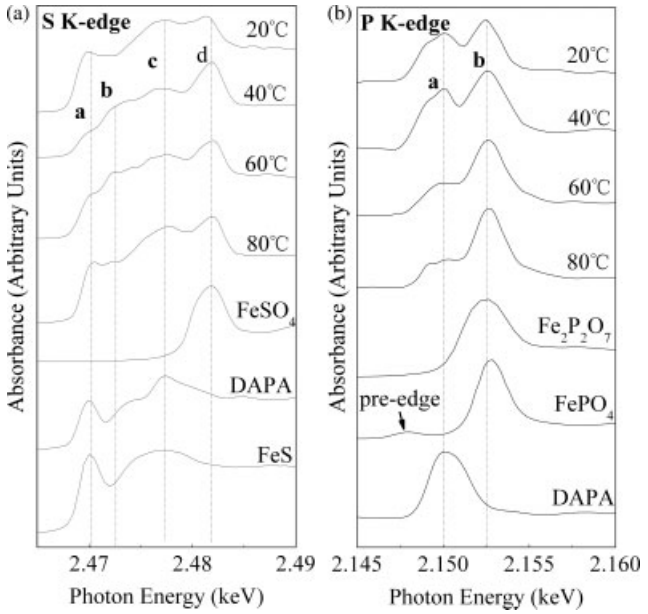

Figure 6. S *K*-edge (a) and P *K*-edge (b) XANES of tribofilms generated by 3.0% DAPA at different temperatures.

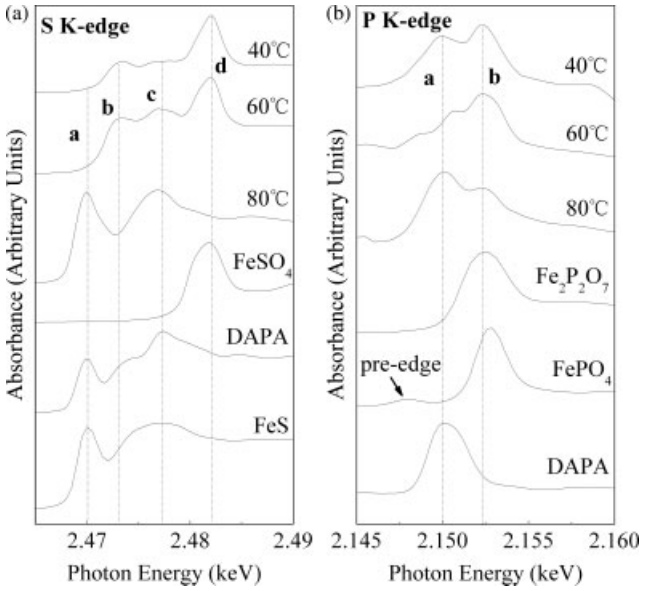

Figure 7. S and P *K*-edge XANES spectra of thermal films generated by DAPA at different temperatures.

at 2152 eV corresponding to polyphosphate. The phosphate exists always in tribofilms at different temperatures, but the intensity of peak *a* at different temperatures is different. At lower temperatures (20 and 40 °C), the intensity of peak *a* is stronger than that at higher temperature (60 and 80 °C), which means that the content of adsorbed additive at higher temperatures is lower than that at lower temperatures. This phenomenon maybe due to the fact that more adsorbed additives will react with the metal surface at higher temperatures than the lower temperatures. Considering the results with the tribological properties, a lower content of the adsorbed additive will result in better antiwear and friction-reducing properties. This result is opposite to the relationship between the content of adsorbed additive and the antiwear and friction-reducing properties at room temperature.

S and P K-edge XANES spectra of thermal films

An analysis of the thermal films generated from a fresh additive can allow insights into the chemical properties of the tribofilms. It can provide some useful information about the additive to understand the pathways of decomposition taking place prior to the friction process. S and P *K*-edge XANES spectra of the thermal films at different temperatures are shown in Fig. 7(a) and (b), respectively. The spectra of some model compounds are also listed in the figure. The peak position of each spectrum is shown in Table 2. It can be seen that the additive molecules could react with metal surface and produce different tribochemical reactants, and the spectra are clearly different from each other.

Figure 7(a) shows the S *K*-edge spectra of the thermal films. At 40 and 60 °C, peak *b* situated at 2473.4 eV corresponds to alkyldisulfide according to Ref. [25,28], and the alkyldisulfide comes from the decomposition of the additive molecule. Peak *c* situated at 2477.0 eV corresponds to sulfite, and peak *d* situated at 2482.1 eV corresponds to sulfate. Relative to the spectra generated at 40 and 60 °C, the spectra generated at 80 °C exhibit a peculiar characteristic: there is no obvious peak of sulfate existing in the film, but peak *a* (situated in 2470 eV corresponding to the sulfide) and peak *c* are the main components of the film.

Table 2. Peak positions of the S K-edge and P K-edge XANES (FY) spectra of untreated additives, thermal films generated from water solutions of additives and model compounds

	S K-edge (eV)				P K-edge (eV)	
Sample	*a*	*b*	*c*	*d*	*a*	*b*
DAPA, 40 °C	–	2473.4	–	2482.1	2150.0	2152.4
DAPA, 60 °C	–	2473.4	2477.0	2482.1	–	2152.4
DAPA, 80 °C	2470.0	–	2476.9	–	2150.2	2152.2
$FeSO_4$	–	–	–	2481.7	–	–
Na_2SO_3	–	–	2477.2	–	–	–
FeS	2470.0	–	–	–	–	–
$Fe_2P_2O_7$	–	–	–	–	–	2152.6
$FePO_4$	–	–	–	–	–	2152.9
DAPA	2469.9	–	2477.4	–	2150.2	–

The P *K*-edge XANES spectra of the thermal films is shown in Fig. 7(b). Peaks *a* and *b* situated at 2150.0 and 2152.4 eV correspond to the adsorbed additive and tribochemical reactant (phosphate or polyphosphate), respectively. There is hardly any pre-edge feature at approximately 2148.0 eV, and it indicates that the cation in the films is mainly Fe(II) and not Fe(III). At 40 and 60 °C, the intensity of peak *b* is obviously higher than that of peak *a*, but it is lower at 80 °C. This indicates that the proportion of phosphate is higher than the adsorbed molecule in the thermal films at 40 and 60 °C, but it is the other way round at 80 °C. This phenomenon may be due to the competition of the different adsorbing modes *versus* chemical reaction at different temperatures. At low temperatures, physical adsorption is the main adsorbing mode, but the chemical adsorption dominates the adsorbing mode at higher temperatures on the metal surface, and the ratio of reacting molecules at higher temperatures is lower than at low temperatures. Another reason may be due to the disposal method of the balls after the tribology test, because ethanol and tissue paper could remove some physically adsorbed molecules from the metal surface, but could not remove the chemically adsorbed molecules and chemical reaction products.

It can be seen from the analysis of the thermal films that the additive would be adsorbed and react with the metal surface at the thermal condition, and different temperatures may result in different components of the thermal films.

Mechanism of the film formation

Based on the results described above, the following mechanisms are proposed to the different durations and temperatures.

At different durations

At beginning of friction, a simple adsorption of the additive molecule takes place on the iron and iron oxide surface. Then, some of the adsorbed molecules would react with iron under the condition of friction and triboheat, which could produce some tribochemical reactant. The tribochemical reactant, mixed with some adsorbed molecules and oxides on the metal surface, will form the tribofilms. The formed films will change with time and would be destroyed at last, and a 'fresh surface' would be exposed to the solution, and the process will cycle again. There are two main factors of the tribofilms that could affect the tribological properties. On one hand, different durations will result in different tribochemical reactants in the tribofilms, and these compounds could lead to different tribological properties. For example, S in the molecule will be converted to sulfide, sulfite and sulfate, and P will be converted to phosphate. With time, some of the sulfide and sulfite will be converted to sulfate by the oxygen in the solution. On the other hand, different proportions of the compounds in the films also have significant influences on the antiwear and friction-reducing properties. That is, the mixtures of the adsorbed additive, polyphosphate, sulfide, sulfite and sulfate can result in good antifriction properties, but the reduction of sulfide and sulfate in the tribofilms will result in higher friction coefficients.

At different temperatures

Temperature also has some influence on the tribofilms formation. With increasing temperature, S in the tribofilms mainly exists as sulfate, with traces of sulfide and sulfite, and the proportion of the adsorbed molecules is high first, then decreases and then becomes high again. Similar results were found on the existence of P in the tribofilms. At low temperatures, the adsorbed additive and phosphate are the main existent forms, but the proportion of phosphate in the tribofilms will increase with the temperature, and the friction coefficient will decrease accordingly. These S- and P-containing compounds, mixed with adsorbed additive molecules, could form the tribofilms in the whole friction process. These tribofilms have significant influence in the antiwear and friction-reduction processes.

Conclusions

From the above results, the following conclusions can be drawn.

1. In the lubricating process of water-based lubricant, the tribofilms mainly consist of an adsorbed layer and a tribochemical layer.
2. Friction duration has very important influence on the components of tribofilms. Different friction durations will result in different compositions of the tribofilm. The mixtures of adsorbed additive, polyphosphate, sulfide, sulfite and sulfate can result in better tribological properties.
3. Temperature plays an important role in the whole lubricating process. Different from the results obtained at room temperature, fewer adsorbed molecules in the tribofilms will produce better tribological properties at higher temperatures. It indicates that the properties of tribofilms generated at higher temperatures are different from those generated at room temperature, and the corresponding tribological properties are different accordingly.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (Grant No. 20872092; No. 10775150), MOST (2007CB607600), and Foundation of Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences (No. BSRF SR06033).

References

[1] M. Ii, H. Eda, T. Imai, M. Nishimura, T. Kawasaki, J. Shimizu, T. Yamamoto, L. Zhou, *Precis. Eng.-J. Int. Soc. Precis. Eng. Nanotechnol.* **2000**, *24*, 231.
[2] C. R. Rasp, *J. Synth. Lubr.* **1989**, *6*, 233.
[3] S. Watanabe, *Int. J. Mater. Prod. Technol.* **2007**, *30*, 309.
[4] S. Watanabe, T. Fujita, T. Yoneshiba, *J. Am. Oil. Chem. Soc.* **1985**, *62*, 125.
[5] S. Plaza, L. Margielewski, G. Celichowski, R. W. Wesolowski, R. S. Taneck, *Wear* **2001**, *249*, 1077.
[6] F. Lin, M. Zhou, Y. Hu, W. Zhang, D. Tao, *Lubr. Sci.* **2000**, *12*, 277.
[7] S. Yamamoto, H. Tomoda, S. Watanabe, *J. Oleo. Sci.* **2007**, *56*, 463.
[8] Y. R. Li, G. Pereira, A. Lachenwitzer, M. Kasrai, P. R. Norton, *Tribol. Lett.* **2008**, *29*, 11.
[9] M. Fuller, Z. Yin, M. Kasrai, G. M. Bancroft, E. S. Yamaguchi, P. R. Ryason, P. A. Willermet, K. H. Tan, *Tribol. Int.* **1997**, *30*, 305.
[10] M. D. Pauli, T. S. Rufael, J. K. Weinert, M. Mowlem, D. K. Saldin, W. T. Tysoe, *Tribol. Int.* **2005**, *38*, 195.
[11] M. N. Najman, M. Kasrai, G. M. Bancroft, *Wear* **2004**, *257*(1–2), 32.
[12] T. W. Mastin, G. R. Norman, E. A. Weilmuenster, *J. Am. Chem. Soc.* **1945**, *67*, 1662.
[13] V. Wystrach, E. Hook, G. L. Christpoher, *J. Org. Chem.* **1956**, *21*, 705.
[14] E. D. Price, A. W. Lees, M. I. Friswell, *Proc. Inst. Mech. Eng. Part J-J. Eng. Tribol.* **2005**, *219*, 85.
[15] M. Kaneta, T. Irie, H. Nishikawa, K. Matsuda, *Proc. Inst. Mech. Eng. Part J-J. Eng. Tribol.* **2006**, *220*, 307.
[16] H. L. Yi, X. Q. Zeng, Y. Cao, T. H. Ren, M. Kasrai, G. M. Bancroft, *Chin. Sci. Bull.* **2006**, *51*, 2710.
[17] H. B. Ma, J. Li, Y. Yu, G. Z. Zuo, T. H. Ren, *Acta. Phys. -Chim. Sin.* **2008**, *24*, 799.
[18] M. N. Najman, M. Kasrai, G. M. Bancroft, *Tribol. Lett.* **2002**, *13*, 209.
[19] M. N. Najman, M. Kasrai, G. M. Bancroft, *Tribol. Lett.* **2004**, *17*, 217.
[20] C. M. Allen, E. Drauglis, *Wear* **1969**, *14*(5), 363.
[21] M. L. Suominen Fuller, L. Rodriguez Fernandez, G. R. Massoumi, W. N. Lennard, M. Kasrai, G. M. Bancroft, *Tribol. Lett.* **2000**, *8*(1), 187.
[22] M. Kasrai, W. N. Lennard, R. W. Brunner, G. M. Bancroft, J. A. Bardwell, K. H. Tan, *Appl. Surf. Sci.* **1996**, *99*(4), 303.
[23] M. Ratoi, V. Anghel, C. Bovington, H. A. Spikes, *Tribol. Int.* **2000**, *33*(3–4), 241.
[24] R. Heuberger, A. Rossia, N. D. Spencer, *Tribol. Lett.* **2007**, *25*, 185.
[25] K. Varlot, M. Kasrai, J. M. Martin, B. Vacher, G. M. Bancroft, E. S. Yamaguchi, P. R. Ryason, *Tribol. Lett.* **2000**, *8*, 9.
[26] V. N. Bakunina, M. Kasrai, G. N. Kuzmina, G. M. Bancroft, O. P. Parenago, *Tribol. Lett.* **2007**, *26*, 33.
[27] M. N. Najman, M. Kasrai, G. M. Bancroft, B. H. Frazer, G. D. Stasio, *Tribol. Lett.* **2004**, *17*, 811.
[28] Z. Zhang, M. Najman, M. Kasrai, G. M. Bancroft, E. S. Yamaguchi, *Tribol. Lett.* **2005**, *18*, 43.