Characterization of tribofilms derived from zinc dialkyldithiophosphate and serpentine by X-ray absorption spectroscopy

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\section*{A B S T R A C T}

The tribological performance of serpentine in combination with ZDDP as additive for base oil was investigated by a Plint high frequency friction tester at room temperature and 100 °C. The tribofilms formed by serpentine and ZDDP were analyzed using the scanning electron microscopy technique equipped with energy dispersive X-ray spectrometry. X-ray absorption spectroscopy at phosphorus K- and L\(_{2,3}\)-edges, sulfur K- and L\(_{2,3}\)-edges, silicon K-edge, magnesium K-edge, oxygen K-edge, and zinc L\(_{2,3}\)-edge were recorded to determine the chemistry of the tribofilms. It is found that a combination of serpentine with ZDDP helps reduce the friction of oil blend and exhibits better antiwear properties than base oil.

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\section*{1. Introduction}

Zinc dialkyldithiophosphate (ZDDP) has been employed as the main multifunctional additive for engines oils for many years [1,2]. ZDDP acts as an antioxidant, corrosion inhibitor and antiwear reagent by forming a protective film at the rubbing surfaces [1]. However, the phosphorus in engine oils is known to cause poisoning and failure of catalytic converters, which are the parts of the car exhaust system [3]. As a matter of fact, it is necessary to reduce the amount of phosphorus/sulfur content in the engine oil. In other words, there is a need to replace partially or totally ZDDP from engine oil formulation [4].

In recent years, the usage of inorganic micro- and nanoparticles as additives in lubricating oil has received more and more attention [5–8], since the addition of solid lubricant particles to engine oil can reduce friction, particularly under boundary lubrication conditions [9–13]. Serpentine, as a member of a group of common rock-forming hydrous magnesium phyllosilicate minerals \(\text{Mg}_6\text{Si}_4\text{O}_{10}\text{(OH)}_8\), has a layered structure. It is reported [14–20] that the addition of serpentine to lubricating oil reduces wear and friction coefficient. As a result, the addition of micro- and nano-particle serpentine as friction modifier to oil blends is beneficial because it might reduce the amount of phosphorus and sulfur containing additives.

In this paper, a pin-on-disc Plint high frequency wear tester was used to study the antiwear and friction-reducing properties of serpentine in combination with ZDDP in base oil (without other additives) at room temperature and 100 °C. The morphologies and the element distributions on the worn surface were detected by the SEM equipped with energy dispersive X-ray detector (EDX). Chemical changes of the tribofilms were measured by X-ray absorption near-edge structure spectroscopy (XANES) [21–26].

\section*{2. Experimental details}

\subsection*{2.1. Sample preparation}

The ultrafine serpentine powder (particle size around 3 \(\mu\)m) was prepared by mechanical crushing and ball-grinding of the natural rock-forming serpentine mineral. The preparation and characterization of serpentine powder used in this paper have been described elsewhere [15,16]. The ZDDP used in this study is a commercial concentrate which is a mixture of neutral and basic forms, consisting of secondary butyl (85%) and n-octyl (15%) groups. An oil solution with ~0.1 wt% phosphorus and ~0.22 wt% sulfur was prepared by mixing 1 wt% ZDDP concentrate in MCT-10 base oil, and stirred by magnetic stirrers at room temperature for about 30 min. MCT-10 is a mineral oil with a maximum sulfur content of 0.25 mass percent and a viscosity of \(30 \times 10^{-6} \text{m}^2\text{s}^{-1}\) at 40 °C [27]. The serpentine concentration in the lubricating oil is 1 wt%. The oil blend containing serpentine was first stirred using a magnetic stirrer and then further mixed in an ultrasonic bath for 10 min, in order to obtain good dispersion of serpentine in the base oil. The constituents of various oil blends are listed in Table 1.
2.2. Friction and wear tests

Antiwear films were formed on 52100 steel using a pin-on-disc Plint high frequency wear tester (Fig. 1). The 52100 steel coupons (thickness 4 mm, diameter 16 mm) were polished with 0.3 μm diamond paste followed by 0.05 μm diamond paste. The 52100 steel consists of 96.9 wt% Fe, 1.04 wt% C, 1.45 wt% Cr, 0.35 wt% Mn and 0.275 wt% Si [28]. The cylindrical pins have a diameter of 6.2 mm and a length of 11 mm. Steel coupons and pins were cleaned using hexane for 10 min in an ultrasonic bath prior to the experiment. Approximately 15 mL oil sample was placed in the Plint high frequency wear tester. For tests performed at 100 °C, the bath temperature was increased gradually to 100 °C in 15 min, and kept at 100 °C during the test. Then the pin was loaded against the coupon in the oil bath under the load of 220 N. The test frequency was increased to 25 Hz and maintained for 1 h. The coefficient of friction was automatically recorded during the test. After the test, excess oil was gently blotted from the surface with tissue paper. The wear scar width of the pin was measured using an optical microscope over 10 random regions along the length of the pin. These values were averaged and used as a measure of wear.

2.3. Data acquisition

X-ray absorption data were collected at the Variable Line Spacing Plane Grating Monochromator (VLS-PGM, 5–250 eV) [29], the High Resolution Spherical Grating Monochromator (SGM, 250–2000 eV) [30,31], and the Soft X-ray Microcharacterization Beamline (SXMB, 1.8–10 keV) [32] beamlines of the Canadian Light Source (CLS), located in the University of Saskatchewan, Saskatoon, Canada. X-ray absorption spectroscopy (XAS), in general, deals with the excitation of electrons from an atomic core level to unoccupied states in gases, liquids and solids. In the general, TEY and FY detection modes measure the total number of electrons and fluorescence photons per incident photon flux, respectively, as a function of photon energy [33]. In this work, both TEY and FY techniques were used to measure surface and bulk of the film, respectively.

3. Results and discussion

3.1. Tribological performance

The friction coefficient was detected during each experiment. In a previous study [15], the tribological effects of serpentine in base oil were reported. Here in Fig. 2a, the friction coefficient of base oil containing ZDDP and serpentine is presented. The coefficient is related to the normal load, sliding speed, the contact surfaces and film material’s mechanical properties [34]. It can be seen that the friction is very unstable during the first few minutes; then it becomes relatively stable. However at 100 °C the value increases as reported by others [35]. From Fig. 2a, ZDDP, and ZDDP in combination with serpentine, show similar friction-reducing performances. However, as the rubbing continues, the friction coefficient tends to decrease in the blend containing serpentine. This suggests that serpentine can provide a better friction-reducing properties at prolonged test time [16].

The wear scar width (WSW) measurements of the pin are shown in Fig. 2b. In general, WSW (within errors) is smaller at room temperature than that at 100 °C with the exception of the blend containing ZDDP and serpentine. The most important finding is that the addition of serpentine into blend containing ZDDP has no adverse effects on wear performance at 100 °C as well as friction reduction both at room temperature and 100 °C. They both have a better tribological performance than base oil.

3.2. Morphology and elemental composition of tribofilms

Typical SEM images, EDX patterns, and elemental maps of the worn surfaces generated from base oil blended with ZDDP, base oil combined with ZDDP and serpentine at 100 °C are shown in Figs. 3 and 4, respectively. One can see that the tribofilms generated from lubricating oil containing ZDDP with and without serpentine exhibit noticeable differences. The low magnification SEM image of the tribofilm shown in Fig. 3 illustrates that the antiwear pads on the surface of the steel substrate are uniformly covered with large pads. For the high magnification image, there

![Fig. 1. A schematic diagram and picture of the Plint high frequency wear tester.](image-url)
are still some areas left uncovered by the film. EDX spectra reveal that the wear surface contains Zn, P, S, O and C originating from ZDDP and Fe from the steel substrate.

**Fig. 4** shows SEM images of tribofilms generated from the oil blend containing ZDDP and serpentine. It is obvious that the surface is different from the surface of base oil with ZDDP alone. The tribofilm does not cover the entire steel surface homogeneously. There are some scratches on the wear surface, which are believed to be due to crushing of the serpentine particle during the wear test. The wear surface has areas covered by glassy pad which are comprised of P, S, O, and Zn. In between the pads, we observe some small serpentine particles (the region of Mg and Si) trapped inside the tribofilm. The elemental distribution maps show that there is a higher concentration of phosphorus, sulfur, zinc, and oxygen on the glassy pads, while in between the pads, magnesium and silicon are present at higher proportion. This suggests that serpentine is partially mixing (reacting) with ZDDP decomposition products and plays an important role in wear and friction reduction.
Tables 2 and 3 show, respectively, the EDX elemental composition of the surface generated by base oil containing ZDDP with and without serpentine at 100 °C. The results show that Mg and Si originating from serpentine were present in the film generated from ZDDP/serpentine blend. There is a small amount of Si in the film derived from ZDDP. This Si originates from the steel substrate.

3.3. XANES characterization of tribofilms

3.3.1. P K- and L2,3-edge spectra

In order to indentify the chemical composition of phosphorus in antiwear film, it is essential to compare the spectra of films with different model compounds in which the local chemical environments of P are known [25]. The P K-edge XANES spectra of tribofilms and model compounds are presented in Fig. 5. The main Peak a' of ZDDP (arising from P 1s to states of p character modulated by the local bonding) has shifted to the position (peak a) characteristic for

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**Table 2**

Elemental composition of the tribofilm generated by ZDDP in base oil.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>O</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Fe</th>
<th>Zn</th>
<th>Totals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt%</td>
<td>7.20</td>
<td>10.65</td>
<td>0.25</td>
<td>8.19</td>
<td>3.59</td>
<td>50.46</td>
<td>19.66</td>
<td>100.00</td>
</tr>
<tr>
<td>At%</td>
<td>21.03</td>
<td>23.34</td>
<td>0.31</td>
<td>9.26</td>
<td>3.93</td>
<td>31.59</td>
<td>10.54</td>
<td>100.00</td>
</tr>
</tbody>
</table>

**Table 3**

Elemental composition of the tribofilm generated by base oil with ZDDP and serpentine.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>O</th>
<th>Mg</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Fe</th>
<th>Zn</th>
<th>Cr</th>
<th>Totals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt%</td>
<td>4.21</td>
<td>6.68</td>
<td>0.50</td>
<td>0.62</td>
<td>4.84</td>
<td>2.21</td>
<td>65.27</td>
<td>12.51</td>
<td>3.16</td>
<td>100.00</td>
</tr>
<tr>
<td>At%</td>
<td>14.28</td>
<td>16.99</td>
<td>0.83</td>
<td>0.90</td>
<td>6.37</td>
<td>2.81</td>
<td>47.57</td>
<td>7.79</td>
<td>2.47</td>
<td>100.00</td>
</tr>
</tbody>
</table>

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*Fig. 4.* SEM images, EDX spectra, and corresponding element distribution maps of the tribofilms formed by base oil with ZDDP and serpentine.
phosphates. This is interpreted in terms of the difference in the structure of ZDDP and phosphate. ZDDP has the phosphorus atom coordinated by two oxygen atoms and two sulfur atoms, while the phosphorus atoms in Zn₃(PO₄)₂ are coordinated with four oxygen atoms [27]. The P K-edge spectra of the tribofilms are similar to that of zinc polyphosphate. Peak b of zinc orthophosphate (spectrum B) is not present in the spectra of tribofilms. Thus the primary components of P in tribofilms are zinc polyphosphate derived from the decomposition of the ZDDP under friction. The TEY and FY spectra of the films are identical, indicating that the phosphorus composition of the surface and bulk of the films is very similar.

P L₂,₃-edge XANES spectroscopy (2P₃/2,1/2 to 3d and 4s transitions) is a very powerful technique for chemical characterization of complex compounds containing phosphorus due to very narrow core-hole lifetime broadening and very high spectrometer energy resolution. Thus the spectra are very sensitive to small changes in

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**Fig. 5.** P K-edge XANES spectra of model compounds and tribofilms measured in TEY and FY modes.

**Fig. 6.** P L₂,₃-edge XANES spectra of model compounds and tribofilms measured in TEY and FY modes.

**Fig. 7.** P L₂,₃-edge XANES TEY spectrum of zinc polyphosphate (spectrum C in Fig. 5) fitted to Gaussian lines using an arctangent background.
the chemical environment of the absorbing atom [25]. The P L3,2-edge XANES spectra of tribofilms and some model compounds are shown in Fig. 6. Peak d is characteristic of all phosphates regardless of their structure [36]. In a previous study [37], the phosphate chain length was determined by the ratio of the intensity of pre-edge (peak a) to white line (peak c), i.e. a higher ratio of a/c suggests longer chain polyphosphates.

In order to quantify peak position and intensity of polyphosphates in tribofilms, in Fig. 6, all the TEY spectra were fitted to several Gaussian lines using a least squares program. An arctangent step function representing the transition of ejected photoelectrons to the continuum was also fitted to the spectra [37]. As an example the deconvoluted Zn polyphosphate XANES spectrum is presented in Fig. 7. The peak a/c ratios for tribofilms and Zn polyphosphate were determined from fitted spectra and summarized in Table 4. It is obvious that the ratio of peaks a/c for Zn polyphosphate (spectrum C) has the highest value (0.49) whereas the ratio for Zn orthophosphate (spectrum B) is 0.25. The corresponding value of the tribofilm (spectrum D in Fig. 6) generated from ZDDP at room temperature, is 0.28. After the addition of serpentine to the oil, the value drops to 0.21 (spectrum E). However, when films are formed at 100 °C, the ratios for films

<table>
<thead>
<tr>
<th>Peak</th>
<th>ZDDP RT</th>
<th>SZDDP RT</th>
<th>ZDDP 100</th>
<th>SZDDP 100</th>
<th>Zn Polyphosphate</th>
<th>Zn3(PO4)2</th>
</tr>
</thead>
<tbody>
<tr>
<td>a/c</td>
<td>0.13/0.46=0.28</td>
<td>0.08/0.38=0.21</td>
<td>0.17/0.46=0.37</td>
<td>0.12/0.41=0.29</td>
<td>0.18/0.37=0.49</td>
<td>0.16/0.64=0.25</td>
</tr>
</tbody>
</table>

Fig. 8. S K-edge and L3,2-edge XANES spectra of model compounds and tribofilms measured in TEY and FY modes.
without and with serpentine increase to 0.37 and 0.29, respectively. One has to be careful in interpreting the results at room temperature. Because it is well known that, ZDDP does not decompose completely to polyphosphate at room temperature under rubbing and a residual un-decomposed ZDDP remains in the tribofilm [38]. As a result, the ZDDP peaks interfere with the intensities of peak a and b of polyphosphate, as can be obviously seen from Fig. 6. We have observed antiwear film consisting of large polyphosphate pads, which has been reported elsewhere [39]. In addition, combining ZDDP with serpentine does not disturb the polyphosphate formation substantially and as a result we obtained good antiwear properties for the blend as was shown in Fig. 2.

The most important result emerges from this study is that serpentine can partially replace ZDDP as an antiwear additive. More research is required to optimize the system.

3.3.2. S K-edge and L3,2-edge spectra

Fig. 8 shows S K-edge and L3,2-edge XANES spectra of model compounds and tribofilms measured in TEY and FY modes. The sulfate K-edge XANES showed a single distinctive peak at around 2482 eV which is different from the sulfides. S K-edge XANES spectra of tribofilms in TEY and FY mode, are almost identical to that of spectrum of ZnS. This indicates that the S in tribofilms exists mainly as $S^{2-}$ and is not oxidized to $S^{6+}$ during the friction, even in the presence of serpentine. The same results are obtained with the S L3,2-edge spectra. The presence of peaks a and b represent the existence of sulfide, while the sulfate has the distinctive peaks e, f, g and i. The S L3,2-edge spectra probe the surface (S L3,2-edge is in the VUV-soft X-ray region and has very short penetration depth) whereas S K-edge measures the bulk of the film. Thus it can be concluded that there is no sulfate present in the tribofilms with or without serpentine.

Fig. 9. Si K-edge XANES spectra of model compounds and tribofilms measured in TEY and FY modes.

Fig. 10. Mg K-edge XANES spectra of model compounds and tribofilms measured in TEY and FY modes.
3.3.3. Si K-edge spectra

Fig. 9 shows the Si K-edge spectra of the tribofilms and model compounds recorded in TEY and FY mode. Spectrum (B) is the Si XANES spectrum of raw serpentine powder while spectrum (C) is for serpentine which was heat treated at 810 °C for 1 h (serpentine810). After heat treatment, serpentine turns to a new phase which is known as forsterite (Mg2SiO4) [19,40]. There are some minor differences in the intensities of the post-edge features b, c and d of spectra C compared to B, which are related to the phase transformation. However, the position of peak (a) which is related to the chemical environment of Si, remains unchanged.

The TEY spectra of films (E) and (D) produced by the base oil containing ZDDP and serpentine at 100 °C and room temperature, respectively, are similar to the spectrum of serpentine (B). This indicates that serpentine is physically present in the film but does not react with the ZDDP decomposition products. The FY spectra are rather noisy, indicating that serpentine is mostly present on the surface of the film.

3.3.4. Mg K-edge spectra

Fig. 10 presents the Mg K-edge spectra of the model compounds and tribofilms measured in TEY and FY modes. The forsterite structure (Mg2SiO4) is an orthosilicate where the Mg octahedrons share edges and corners to other [MgO6] octahedrons and [SiO4] tetrahedrons. In forsterite, Mg is located in two six-fold sites, called M1 and M2, with identical multiplicities [41]. In serpentine (Mg6Si4O10(OH)8), the environment of Mg is the same with coordination number 6. From Fig. 10 we can see minor differences between serpentine (B) and forsterite (C). Spectra of serpentine and forsterite both have the most intense...
peak b. Peak positions of film (D) generated at room temperature and film (E) at 100 °C are identical to serpentine. This suggests that, as we noticed before, serpentine has not reacted substantially with ZDDP in the friction process. It is also obvious that no MgO is formed.

3.3.5. O K-edge spectra

The O K-edge spectra collected in TEY and FY of the tribofilms and the model compounds are shown in Fig. 11. In previous studies [3,42], it has been shown that Fe compounds have spectral characteristics showing peaks a and a' (hybridization of O 2p with partially unoccupied d orbitals) while Zn compounds with full d bands do not have these features. Thus we can easily differentiate between Fe and Zn compounds from their O K-edge spectra. The TEY spectra of the tribofilms do not show peaks a and a' and thus no Fe compounds is present in the films within the detection limits of XANES technique [33]. Tables 2 and 3 show the presence of Fe in the sample. These results are from EDX measurements, which are bulk sensitive, and probably the bulk substrate of the film. Thus, based on the results of EDX and O K-edge, it is believed that the Fe detected by EDX is from the substrate and not the film. The spectra of the films look similar to the spectra of Zn3(PO4)2. The FY spectra of tribofilms show weak peaks a and a' due to the bulk sensitivity of the FY mode since fluorescence X-rays can penetrate through the film to probe iron oxide on the substrate.

3.3.6. Zn L3,2-edge spectra

Fig. 12 shows the Zn L3,2-edge spectra of the model compounds ZDDP, ZnS, Zn3(PO4)2, and Zn polyphosphate together with spectra of the tribofilms, recorded in TEY and FY modes. All the spectra of the tribofilms look the same and resemble those of Zn3(PO4)2 and Zn polyphosphate with small contribution from that of ZnS [42]. As it was noticed in Tables 2 and 3, the proportion of S in the tribofilm is small compared to Zn and P. Thus films generated at different temperatures have little effects on the chemistry of Zn compounds produced in the tribofilms. It also indicates that, the serpentine added to the oil has no chemical effects on Zn compounds. The Zn3(PO4)2 and Zn polyphosphate formed in the tribofilms originate from the thermal oxidative decomposition of ZDDP [43].

4. Conclusions

The wear performance of serpentine in combination with ZDDP as lubricating oil additive was investigated by the pin-on-disc Plint high frequency wear tester at room temperature and 100 °C. The microstructure and element compositions of the tribofilms were detected by SEM equipped with EDX. The chemical compositions of the tribofilms were analyzed using XANES technique at P K- and L2,3-edge, S K- and L2,3-edge, O K-edge, Si K-edge, Mg K-edge and Zn L2,3-edge, in both surface sensitive TEY and bulk sensitive FY mode. The conclusions are as follows:

1. The lubricating oil containing serpentine presents better friction-reducing properties than ZDDP at room temperature, while the antwear properties are as good as ZDDP (at 100 °C) on its own and much better than base oil (at room temperature and 100 °C), although the films are not as homogeneous as those generated from ZDDP alone.

2. Combining ZDDP with serpentine does not disturb the polyphosphate formation substantially. Polyphosphates are the essential ingredient of tribofilms. This result suggests that serpentine can partially replace ZDDP as an antwear additive.

3. The tribofilms produced by the base oil containing serpentine and ZDDP have a glassy appearances containing serpentine and Zn polyphosphate, ZnS, from the decomposition of ZDDP.

4. The O K-edge XANES spectra clearly show that no iron phosphate is present in the film within the detection limit of XANES technique.

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