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

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ABSTRACT

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 spectroscopy. X-ray absorption spectroscopy at phosphorus K- and $L_{3,2}$-edges, sulfur K- and $L_{3,2}$-edges, silicon K-edge, magnesium K-edge, oxygen K-edge, and zinc $L_{3,2}$-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.

1. Introduction

Zinc dialkyl dithiophosphate (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 nano-particles 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 $Mg_6Si_4O_{10}(OH)_8$, 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].

2. Experimental details

2.1. Sample preparation

The ultrafine serpentine powder (particle size around 3 μm) 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 $30 \times 10^{-6}\ m^2\ s^{-1}$ 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.

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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 (SXRMB, 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 case of solid thin films on a solid substrate, the transmission mode is not feasible, but any process which is linked to the filling of the core holes can be used to measure absorption. The filling or annihilation of the core holes can take place by a two competing processes, the Auger decay or the X-ray fluorescence process. The total electron yield (TEY) detection mode was used to collect all the exited electrons by monitoring the sample current directly in the presence of a voltage bias. A multi-channel plate has been used to measure the fluorescence yield (FY). The 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.

Table 1
The constituents of various oil blends.

Oil blend name	Component	Test temperature
BS RT	Base oil only	Room temperature
SB RT	Base oil plus serpentine	Room temperature
ZDDP RT	Base oil plus ZDDP	Room temperature
S ZDDP RT	Base oil plus serpentine and ZDDP	Room temperature
BS 100	Base oil only	100 °C
SB 100	Base oil plus serpentine	100 °C
ZDDP 100	Base oil plus ZDDP	100 °C
SZDDP 100	Base oil plus serpentine and ZDDP	100 °C

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 films between 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

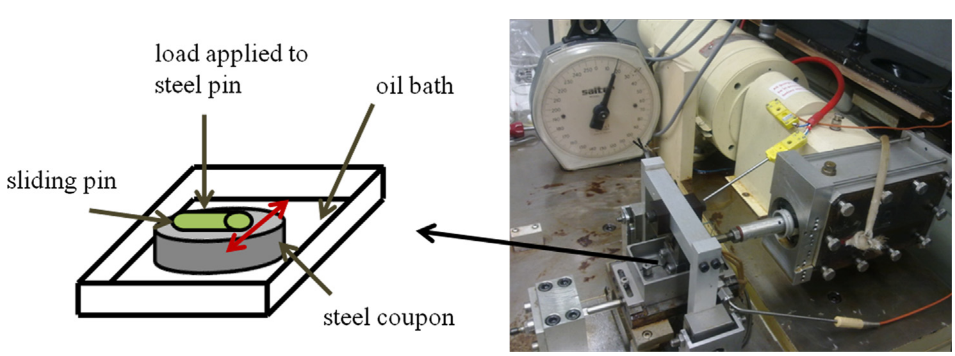

Fig. 1. A schematic diagram and picture of the Plint high frequency wear tester.