

Surface analytical studies of surface-additive interactions, by means of in situ and combinatorial approaches

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Abstract

The influence of tribological conditions on the surface reactions occurring between zinc dialkyldithiophosphate (ZnDTP) and steel surfaces has been studied by means of a combination of X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectroscopy (ToF-SIMS), in situ attenuated total reflection (ATR) infrared spectroscopy, and high-throughput combinatorial approaches. Purely thermal treatment at 150 °C appears to lead to the formation of zinc polyphosphates. However, in the presence of tribological stress, simple phosphates appear to dominate, with some indication that higher load conditions lead to an increase in the surface concentration of both phosphate and, at higher temperatures, polyphosphate.

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1. Introduction

Originally added to lubricating oils as an antioxidant [1], zinc dialkyldithiophosphate (ZnDTP) has become one of the most widespread and heavily investigated antiwear and extreme-pressure additives. Crucial to the functioning of ZnDTP is the formation of a protective film on rubbing surfaces in situations where elastohydrodynamic lubrication has broken down [2]. Despite innumerable studies that have sought to characterize such films, the literature has not, to date, reached a consensus on the chemical pathways involved in this process. One probable reason for this situation, recently expounded by Bec et al. [3], is that ZnDTP functions as a “smart” material, producing films with different chemical and mechanical properties, depending on the prevailing tribological conditions. In other words, since most laboratories have employed different sets of conditions for their investigations, the films that they have been scrutinizing have displayed correspondingly different properties.

In this study, we have employed a combination of imaging surface-analytical approaches: X-ray photoelectron spec-

troscopy (XPS) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS), a recently developed in situ tribometer [4] and a combinatorial, high-throughput screening method [5], in order to determine the effects of temperature and load on the reaction pathways that occur during tribochemical activation of ZnDTP.

2. Experimental

2.1. Materials

A purified commercial secondary ZnDTP (C3+C6, Hitec 7169, Ethyl Petroleum Additives International Ltd., UK. 30, Shell International Trading Company) and a commercial poly- α -olefin (PAO, Durasyn 166, Tunap Industrie GmbH & Co. Germany) were used as lubricant additive and base oil, respectively, unless stated otherwise. The purification of the commercial ZnDTP was carried out by liquid chromatography. 100 g of the additive was eluted from a column of 200 g of column-chromatography-grade silica gel (short column, Silica gel 60, 0.063–0.22, Merck, Switzerland) with hexane and ethyl acetate.

In the ball-on-disk experiments, a 1 wt.% solution of di-isopropyl zinc dithiophosphate (*i*-ZnDTP) in decane was used as a lubricant. To dissolve the additive in the lubricant, the solution was stirred at 60 °C for 30 min.

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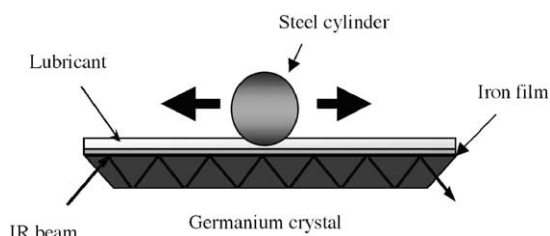


Fig. 1. Schematic diagram of the ATR FTIR tribometer.

2.2. Methods

2.2.1. Attenuated total reflection (ATR) infrared tribometry

ATR spectra were obtained in situ with a Nicolet Magna-IR System 550 Fourier Transform Spectrometer, equipped with a Greasby-Specac advanced overhead (specaflo) 1401 Series ATR System. The ATR spectra were collected in the spectral range $4000\text{--}650\text{ cm}^{-1}$, with a resolution of 2 cm^{-1} . The ATR tribometer is equipped with a crystal holder that is heatable to $200\text{ }^{\circ}\text{C}$, so that both purely thermal reactions and tribochemical reactions can be studied at elevated temperatures (Fig. 1). During sliding, a normal load of 7 N (apparent contact pressure 34 MPa) was applied, the average sliding velocity (sinusoidal) being 24 mm/min . Further details may be found in [4].

2.2.2. X-ray photoelectron spectroscopy

The XPS analyses were performed on a PHI 5700 system with an Omni Focus IV lens system (Physical Electronics, Eden Prairie, MN, USA). The residual pressure in the spectrometer during the data acquisition was always below $5 \times 10^{-7}\text{ Pa}$. The X-ray source was $\text{Al K}\alpha$ (1486.6 eV), run at 350 W . The diameter of the analyzed area was either 400 or $120\text{ }\mu\text{m}$ in the case of the combinatorial approach experiments. The spectrometer was operated in the fixed analyzer transmission (FAT) mode [10,12]. The instrument was calibrated using the spectral lines of $\text{Au}(4f_{7/2})$ and $\text{Cu}(2p_{3/2})$ at 83.98 and 932.67 eV , respectively [316]. $\text{Ag}(3d_{5/2})$, $\text{Cu}(3p)$, $\text{Cu}(\text{LMM})$ and $\text{Ag}(\text{MNN})$ peak energies at 368.26 , 75.14 , 567.96 , 1128.78 eV , respectively, were used to verify the linearity of the binding-energy scale. The accuracy was $\pm 0.05\text{ eV}$.

Spectroscopic maps were acquired using the imaging capabilities of the Omni Focus IV lens system. The analyzed spot is electrostatically rastered over the sample (typically 64×64 pixels, $2\text{ mm} \times 2\text{ mm}$). For each pixel a full spectrum of the selected energy region is acquired. The acquired images were processed with the PHI Multipak (V6.0) software. Spectra can be extracted from the map by selecting a region of interest and can be used to reconstruct "Chemical State Maps" with a linear-least-squares (LLS) routine. The correlation between the extracted spectra and the spectra at each pixel generates a new map, which shows regions having similar chemical states of the given element.

From these maps, areas of interest were determined and analyzed by small-area XPS (SAXPS). For curve fitting, CASA XPS (V2.0) software (CASAXPS Software Ltd., UK) was used. The spectra were resolved into their components after an integrated Shirley background subtraction. Curve-fitting parameters (FWHM and Gaussian/Lorentzian ratio) were determined from reference spectra. The spectra were fitted with Gaussian/Lorentzian peaks, keeping the FWHM and the Gaussian/Lorentzian ratio constant and fitting the energy of the peaks and their heights using a LLS algorithm. Quantitative analysis was carried out correcting the intensities for the inelastic mean free path according to Seah and Dench [6], the photoionization cross-section according to Scofield [8] and the analyzer transmission function [9].

2.2.3. Time-of-flight secondary ion mass spectrometry

The spectra were acquired using a Physical Electronics PHI 7200 ToF-SIMS instrument (Physical Electronics, Eden Prairie, MN, USA), allowing parallel mass registration with high sensitivity and high mass resolution. A gallium liquid-metal ion (LMI) gun at 25 keV beam energy was used for spatially resolved ToF-SIMS analysis. The beam diameter was $0.25\text{ }\mu\text{m}$, the pulse width 100 ns and the TDC bin size 10 ns . A mass resolution ($m/\Delta m$) of 4500 at $m/z = 29$ was obtained.

Images of the same region of the sample were collected in positive and negative SIMS polarity over an area of typically $100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$ using the LMI gun at 25 keV beam energy. The total primary ion dose for each image was about 10^{13} ions/cm^2 . A Sun workstation was used for spectral acquisition and processing using ToF-Pak software.

2.2.4. Tribometer experiments

Flat-on-disk tribological measurements were performed with a CSEM tribometer (CSEM, Neuchâtel, Switzerland) using steel/steel tribo-pairs (AISI 52100). The load was kept constant at 10 N (nominal pressure: 857 Pa) while the velocity was varied stepwise from 1 to $10,000\text{ mm/min}$. During the tribological experiment the pin was maintained at a constant distance from the center of the disc. The steel was mechanically polished and the final roughness (R_a) was $0.01\text{ }\mu\text{m}$ for the flat and less than $0.01\text{ }\mu\text{m}$ for the disk. The steel pair was immersed in the lubricant during the tribological testing, which was carried out in air at $25 \pm 1\text{ }^{\circ}\text{C}$, at a RH of 50% .

Ball-on-disk measurements were carried out with a CETR UMT-2 (CETR, Campbell, CA, USA) tribometer, which allows the programming of load, rotational velocity and duration of the tribotest. The tribometer is equipped with a load cell with a maximum capacity of 5 N and a resolution of $\pm 5\text{ mN}$ in two axes (normal load and friction force). Normal load is applied via a spring, and is constantly monitored and adjusted via a feedback loop. The spring constant was determined to be 2.7 N/mm in the z -direction and 5.7 N/mm in the y -direction (friction force). Normal load, friction force,