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Electrochemical effect on boundary lubrication of ZDDP additive blended in propylene carbonate / diethyl succinate

Hui Cao, Yonggang Meng*

State Key Laboratory of Tribology, Tsinghua University, Beijing, 100084, China

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ABSTRACT

The objective of this study is to find appropriate surface potentials under which the ZDDP tribofim formation can be promoted efficiently with low ZDDP concentrations. Firstly, the boundary lubrication performance of ZrO_2 ball and AISI 52100 steel plate in propylene carbonate (PC)/diethyl succinate (DES) blended with different ZDDP concentrations was investigated. With increase of ZDDP concentrations, the coefficient of friction and wear volume decreased and the tribofilm covered wider regions within the wear scars. Secondly, the boundary lubrication performance of the same tribo-system under different surface potentials was studied with a relative low ZDDP concentration. The coefficient of friction and wear decreased and the tribofilm-covered area increased along with the elevation of surface potentials, which is similar to the above mentioned concentration test results. Thirdly, the difference of ZDDP tribofilm chemical structures under different surface potentials were characterized by TEM, EDS and XPS. Finally, the mechanism of electrochemical effect on ZDDP tribofilm formation was discussed. It was considered that the effects of applied potentials on the adsorption of ZDDP additive and on activation energy of electrochemical reactions on the steel surface are the reasons for the observed electro-tribochemical experiment results.

1. Introduction

Boundary lubrication is a lubrication regime inevitably and widely existing in most of machine operation conditions. The coefficient of friction (COF) under boundary lubrication is usually higher than those in mixed and fluid film lubrication regimes as indicated in Stribeck curves [1]. Meanwhile, wear always takes place in boundary lubrication. Subsequently, the reliability and lifetime of many mechanical components under lubricated contacts is often determined by their tribological performance under boundary lubrication. To improve boundary lubrication performance, alkyl thiophosphates are often ingredient as additives in formulated lubrication oils [2–4], and they are recognized as irreplaceable lubricant additives for automotive transmissions and engines.

Zinc dialkyldithiophosphates (ZDDP) is a type of multi-functional lubricant additive playing the roles of dispersion, anti-oxidation, anti-wear and friction modification [5–7]. The extensively accepted anti-wear mechanism of ZDDP is that a layer of tribofilm with low hardness and elastic modulus is generated on the contacted substrate surfaces of friction pairs during sliding process [8]. This tribofilm is capable of preventing the harder substrate metallic surfaces from direct contact, and hence results in mild wear [9]. In recent decades, great effort has been devoted to the explorations of formation process and chemical structure of ZDDP tribofilms. It has been found that ZDDP tribofilm is formed in three steps. Firstly, ZDDP molecules enter into the contacting region, where the contact pressure, shear rate and surface flash temperature are very high. Secondly, ZDDP molecules degrade into short activated groups under high stress and high temperature [10]. Thirdly, these activated groups react with substrate metallic compositions or oxygen dissolved in the lubricants. The reaction products deposit on the rubbing surfaces and form a layer of tribofilm. Usually, the pattern of ZDDP tribofim is not continuous but pad-like, because the rate of chemical reactions is not uniform over the whole contacting region [11].

As for the chemical structures of ZDDP tribofilm, there have been numerous analysis techniques used and results reported. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) were used to detect the chemical elements and their valence bonds of ZDDP tribofilm. The results indicated that sulfur, phosphorus and zinc were specified as the characteristic elements of ZDDP tribofilms [12]. A more sensitive technique, time-of-flying secondary ion mass spectrometry (ToF-SIMS), was used to investigate the chemical components of both top and bulk of ZDDP tribofims, and it was found that cations (Fe, Zn) and anions sulfur-rich and phosphate species such as (PSO_2, PS_2O, PO_2, PO_3) were included in the tribofilm [13]. Moreover, X-ray

* Corresponding author.
E-mail address: mengyg@tsinghua.edu.cn (Y. Meng).

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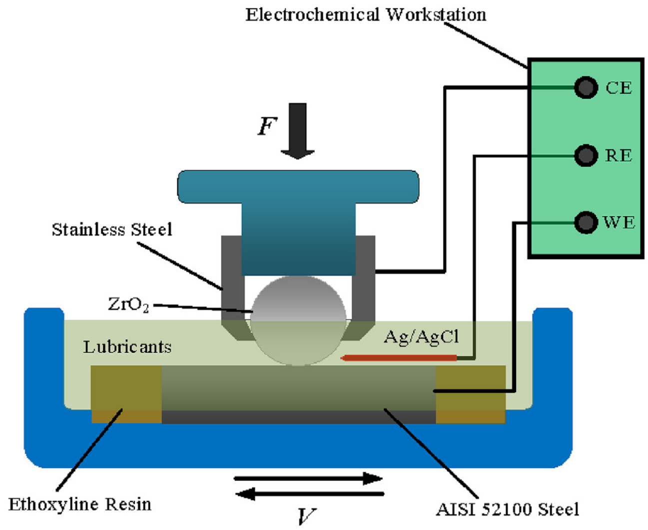

Fig. 1. Schematic of the electrochemical friction test system.

Table 1
Element contents and alkyl-type of the ZDDP additive.

Elements contents				Alkyl-type	
Elements	Zn	S	P	octyl	primary
Mass%	8.6	17.2	8.1	butyl	primary

Table 2
Mechanics of friction pairs.

Materials	Young's modulus (GPa)	Poisson ratio	Hardness (GPa)	Rq(nm)
ZrO_2	210	0.3	13.6	20
AISI 52100 steel	210	0.3	7.8	5

Table 3
Chemical compositions of AISI 52100 steel plate.

Element	Si	Fe	Mn	Cr	C	O
Mass%	0.28	94.51	0.90	1.78	0.99	1.54

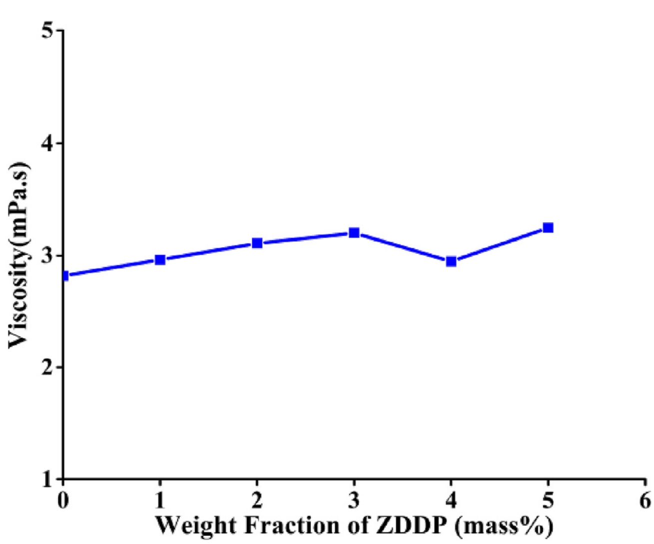

Fig. 2. Viscosity of the model lubricants with different ZDDP weight fractions.

absorption near-edge structure (XANES) analysis also showed that there were Fe/Zn polyphosphates with various chain lengths in ZDDP tribofilms [14]. Recently, the most universally accepted chemical structure of ZDDP tribofilm is the 3–4 layered 'sandwich' structure. At the bottom of the tribofilm, there is usually a thin layer of Fe/Zn sulfide. In the middle there exists a relative thick layer of glassy Fe/Zn phosphate, which is the essential part of ZDDP tribofilms. On the extremely top, there is usually a thin absorbed layer of organic polyphosphates or ZDDP molecules [11].

However, ZDDP additive has a drawback because of its high content of sulfur and phosphorous elements, both of which poison catalytic converters in automotive engines, and thus are harmful to the environment. In recent decades, a lot of researches have been done to find new effective sulfur-and phosphorous-free lubricant additives, such as alkyl-cyclens [15] and ionic liquids [16]. An alternative approach to reduce the harmful effect of ZDDP additive is to cut the ZDDP concentration as low as possible. This requires an effective technique to enhance boundary lubrication at low ZDDP concentrations. In 1989 and 1991, Wang and Tung proposed an electrochemical method to promote the formation of tribofilms of zinc organodithiophosphate (ZDP) additives on cast iron surfaces in mineral base oils [17–19]. Because of the high electrical resistance of the mineral base oils, electro-charging was slow, and the positive effect of electrochemical reactions appeared after sliding for several hours. In 2002 and 2007, Xu and Spikes [20,21] applied the similar idea to the blend of ZDDP additive and an ester lubricant base fluid, diethylhexyl sebacate (DEHS), which is much more conductive than mineral oils. To increase electrical conductivity of the blend, a supporting electrolyte, tetradecylammonium tetrakis-(4-fluorophenyl)-borate (TDATPhFB), was also added at 0.03 M concentration. Their friction and wear experiments showed that the reduction of friction and wear by ZDDP was accelerated by electrochemical activation, the running-in period was shorten from tens of minutes at open circuit potential to a few minutes at 1.5 V controlled potential. With the propylene carbonate (PC), a polar aprotic solvent, as the base fluid, in 2014, Yang and Meng [22,23] demonstrated that boundary lubrication of sodium dodecyl sulfate (SDS) and ionic liquid additives could be controlled remarkably and reversibly with the electrochemical technique. Unlike ZDDP additives, the change of boundary lubrication performance of SDS and ionic liquids additives under electric potentials is attributed to the electrostatic interactions between the polar molecules and the charged friction surfaces, which affects the adsorption and desorption of boundary films, rather than the tribo-electrochemical reactions.

Recently, hybrid ceramic ball bearings become more and more widely serving for industry, especially in high speed and high temperature applications, such as in jet engines and high speed motorized spindles. Although the ceramic ball bearing has self-lubricating capability, early severe wear is not uncommonly existed under these harsh working conditions. To reduce these early failures and modify the wear states of hybrid ceramic ball bearings, it is necessary to study the friction/wear performance of ceramic ball on bearing steel disc. Furthermore, it is desirous that if one layer of anti-wear tribofilm could formed rapidly by putting the bearings into subjecting a running-in period at room temperature in lubricants blended with ZDDP additives before assembled on the machines. ZDDP tribofilm formation between ceramic/steel friction pairs was not as easy as steel-steel friction pairs because of most abrasive wear taking place and the decrease in Fe supply in tribo-chemical reaction. Therefore, it is necessary to find methods to promote ZDDP tribofilm formation efficiently.

In this study, the ZrO_2 ball/AISI 52100 steel disc friction pair was taken as research carrier to systematically investigate the electrochemical effect on the boundary lubrication of ZDDP propylene carbonate/diethyl succinate blended with ZDDP additives. The main contents of the article are as follows: firstly, friction and wear behaviors