Applied Surface Science 403 (2017) 472–486

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

A new insight into the interfacial mechanisms of the tribofilm formed by zinc dialkyl dithiophosphate

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ARTICLE INFO

Article history:
Received 21 July 2016
Received in revised form 11 January 2017
Accepted 18 January 2017
Available online 22 January 2017

Keywords:
Boundary lubrication
Tribochemistry
Tribofilm durability
ZDDP
XPS

ABSTRACT

Understanding the true interfacial mechanisms involved in the growth of tribofilms generated by Zinc Dialkyl Dithiophosphate (ZDDP) is important because it is the most widely used anti-wear additive and there is legislative pressure to find efficient environmentally-friendly replacements. The main focus of this study is to investigate the durability of the ZDDP tribofilm and correlate it to the chemical and physical properties of the glassy polyphosphates. A novel experimental method has been developed to study the effect of lubricant temperature and contact load on tribofilm growth and durability. Results show that physical parameters such as temperature and pressure significantly influence the tribofilm durability. XPS analyses were carried out before suspending the test and after changing the oil to assess the difference in chemical structure of the tribofilm before and after stopping the test. The chemical analyses suggest that there are different chemical properties across the thickness of the tribofilm and these determine the durability characteristics.

1. Introduction

1.1. Boundary lubrication

The Boundary Lubrication (BL) regime is the regime where the fluid lubricant is not able to sustain the load between surfaces. The surfaces are not wholly separated by a viscous lubricant film and direct asperity-asperity interactions occur. The severity of the contact is high and the probability of adhesion, abrasion and fatigue, and therefore wear, is increased. Frictional heating and rubbing of surfaces induces tribochemical reactions at the interfaces and the result is the formation of a very thin reacted film on the substrate called a tribofilm.

Antiwear additives have been commonly used in oil to reduce the wear of boundary-lubricated contacts by forming a protective layer on the surface which prevents the direct asperity-asperity contact thus reducing wear. There are also different mechanisms in which the additives react with the surface to form the tribofilm [2].

1.2. ZDDP as an anti-wear additive

Zinc Dialkyl Dithiophosphate (ZDDP) is the most commonly used antiwear additive in engine oils. Considering new environmental legislation on reducing the amount of metals, Phosphorous and Sulphur in engine oils, the concentration of ZDDP in lubricant oils is continually decreasing. Alternatives to ZDDP are urgently required. The design of new antiwear chemistries requires an understanding of the principle modes by which ZDDP acts to provide antiwear function.

It is reported that adsorption of the ZDDP molecules on the substrate is necessary prior to the formation of any surface films [3,4]. Surface studies show that ZDDP thermal films are different from tribofilms [5–7]. The tribofilm, unlike thermal films, needs asperity-asperity contact and sliding to be formed on the surface and generally they form at much lower temperatures than the thermal films [3,8–10]. The thickness of the tribofilm is reported to be in the range of 50–150 nm on steel surfaces [9,11,12]. ZDDP tribofilms grow initially on small single patches and with time cover the surface in pad-like structures [13].

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http://dx.doi.org/10.1016/j.apsusc.2017.01.178
0169-4332/

1.3. Mechanical properties and durability of ZDDP tribofilm

Several works have studied the mechanical properties of ZDDP tribofilms formed in boundary lubricated contacts [13–19]. These have demonstrated that the properties of the ZDDP tribofilm layers are dependent on applied load [20,21].

Mosey et al. [20] developed a new theory for the functionality of ZDDP tribofilms at the molecular level. They suggested that pressure-induced cross-linking is the reason for chemically-connected networks and many aspects of experimentally-observed behaviour of ZDDP can be explained by this theory. It was reported that the high pressure at the surface of the film will lead to higher cross-linking and result in longer chain phosphates. The different mechanical properties of long and short chain polyphosphates were simulated and reported in the work. All these studies give good insights of mechanical characteristics of ZDDP tribofilms under severe conditions.

It was suggested by Morina et al. [22] that the durability of tribofilm can be evaluated by the chemistry of the tribofilm formed on the surface. The experiments were based on investigating the formation, stability and removal of the tribofilm by changing the oils during the tests and monitoring the friction coefficient. The concept of tribofilm removal was also reported by Lin et al. [23]. Based on the experimental wear results, they suggested that a comparison between the rate of formation and removal of the tribofilm can characterise wear in boundary lubrication.

1.4. Chemistry of ZDDP tribofilm

The chemical composition of the ZDDP tribofilm in boundary lubrication conditions on steel surfaces has been extensively characterized. The general conditions is that there is a viscous layer of physically –adsorbed additive on the top layer of the tribofilm which can be easily removed by means of solvents and washing. Underneath this viscous layer, there is a chemically adsorbed layer of amorphous zinc and iron polyphosphates with different chain lengths [3,24–26]. The ZDDP tribofilm has a layered structure with different chain lengths at different positions in the layer [24,26]; shorter chain polyphosphate layers are present at the bottom adjacent to the substrate interlinked with the iron oxide. The top layer is reported to be thinner consisting of mainly longer chain polyphosphates. The interfaces is present between the layers are most likely to be gradual changes in the structure of the tribofilm.

Crobu et al. [1,24] characterised the surface chemistry of zinc polyphosphates using XPS and Time-of-Flight Secondary-Ion Mass Spectroscopy (ToF-SIMS) by assessing the intensity ratio of bridging oxygen (P-O-P) and non-bridging oxygen (P=O and P-O-M) and. The chain length of the glassy phosphates in the tribofilm can be identified by a combined use of bridging oxygen/non-bridging oxygen (BO/NBO) intensity ratio and the difference in binding energies between the Zn3s-P2p$_{3/2}$ peaks from XPS and a modified Auger parameter. This combined method allows characterisation of polyphosphate chain composition ranging from zinc orthophosphate to zinc metaphosphate (Fig. 1).

1.5. Growth of ZDDP tribofilm

An important aspect in the study of ZDDP tribofilms is the growth rate and the steady state thickness. The growth of ZDDP tribofilm on contacting surfaces has been subject of several studies [13,19,27–31]. Fujita et al. [32,33] studied the growth of ZDDP tribofilm using a Mini Traction Machine (MTM) and Spacer Layer Interferometry Method (SLIM). The experimental results were then used to extract semi-empirical relationships for the growth of the tribofilm.

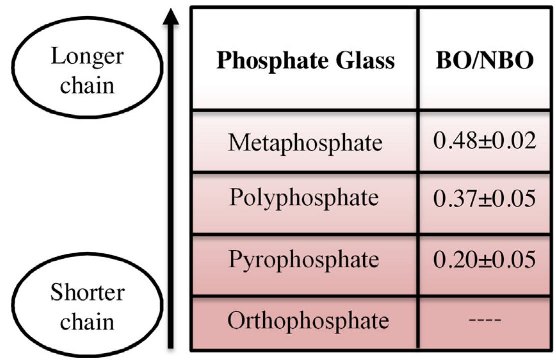

Fig. 1. Identification of different composition of zinc polyphosphates [1].

It was suggested [32,33] that ZDDP tribofilms are very durable when rubbed in base oil once they are formed. A base oil containing dispersant was found to be essential to remove the tribofilm patches. It was shown that secondary ZDDPs reach to a maximum film thickness very rapidly and then a removal of the tribofilm occurs due to different surface phenomena. They suggested that a combined model of formation and removal can explain such a behaviour. It was hypothesized that the removal process only begins after some time of rubbing [32,33]. There was a difference between the growth patterns for primary and secondary ZDDPs. Results revealed that primary ZDDP generally follows a straightforward increase in the thickness while secondary ZDDP grows to a maximum value and then levels out to a steady-state.

Recently Gosvami et al. [34] designed an experiment to monitor the growth of the ZDDP tribofilm in a single asperity contact. They used Atomic Force Microscopy (AFM) to generate the tribofilm and monitor the growth *in-situ*. It was reported that temperature and stress play a significant role in the initiation of the tribochemical reactions.

Authors of the current manuscript recently reported a theoretical model with a hypothesis that formation and removal of the tribofilm happen simultaneously [35]. The hypothesis was based on the experimental observations of removal of the tribofilm and wear of the system even in the presence of fully-formed tribofilms [17,31,36]. The wear hypothesis was then validated against some wear measurements in experiments [37,38] and has shown good agreement. Testing the model in different conditions suggests that the removal of the tribofilm is time dependent [22,32].

The aim of this study is to investigate the effect of different physical parameters such as temperature and load on the durability and chemical characteristics of the ZDDP tribofilm. XPS analyses were carried out to be able to evaluate the tribofilm chemical characteristics. The change in the tribofilm thickness was correlated to the chemistry of the glassy polyphosphates. This study will open new insights into the real mechanisms in which ZDDP acts as antiwear additive by correlating its durability to the chemical structure. This will help to better understand the growth mechanism and the kinetics of the tribochemical reaction. The durability of such films is an important parameter to consider in the design of new lubricants containing antiwear additives.

2. Experimental procedure

2.1. Tribology test rig

A Mini Traction Machine (MTM) is used to sismulate a sliding/rolling contact in boundary lubrication. One of the key points in using MTM is that slide-to-roll ratio (SRR) can be changed in the experiments over the wide range of (0< SRR <5) [39].