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Real time durability of tribofilms in the piston ring – cylinder liner contact

S. Spiller, C. Lenauer, T. Wopelka, M. Jech*

AC2T research GmbH, Viktor-Kaplan-Straße 2, 2700 Wiener Neustadt, Austria

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ABSTRACT

In boundary lubrication, the ability to form protective tribofilms determines the effectiveness of lubricants regarding friction and wear. In order to be able to control tribofilm formation, even if additives have to be reduced due to environmental regulations, the dynamics of the tribofilm protection of surfaces are investigated. This study investigates the durability of the tribofilm formed on the cylinder liner – piston ring contact and the corresponding wear protection capability in real time. To accomplish this, additivated engine oil was replaced by a non-additivated oil during test runs, after the steady-state wear rate had been reached. For the analysis of the tribofilm durability, the chemical composition of worn surfaces is compared to the dynamic wear and friction behavior.

1. Introduction

Engine oil formulations, beside base oil, contain a wide variety of additives, such as antiwear additives, friction modifiers, detergent and dispersant packages, antioxidants and corrosion inhibitors. Each of these additives may affect the properties of the lubricant itself and the properties of lubricated surfaces. The effect of lubricant additives and their antiwear performance is especially important for components running in boundary and mixed lubrication regimes. In these regimes, where e.g. metal-to-metal contact prevails, the lubricant-related protection of surfaces is mainly provided by surface-active additives, while physical parameters of the oil, such as viscosity, play a secondary role. In boundary lubrication regime, surface protection is provided by tribofilms, which are generated from the lubricant additives by the friction process at the contact interface. The action of antiwear additives, primarily zinc dialkyl dithiophosphates (ZDDPs), has been extensively studied in the past, and several reviews summarizing the research on ZDDPs and their antiwear role can be found in the literature [1,2].

Tribofilms form rapidly once the sliding starts [3], however the chemical pathways of the tribofilm formation are still not clear. Mechanisms governing tribofilm formation include thermal degradation [4,5], surface adsorption [6,7], oxidation by hydroperoxides [2], radical reactions [2], hydrolysis [8], and combinations of the aforementioned mechanisms [2,9]. A model of tribofilm formation that is often proposed, is a combination of thermal and oxidative degradation of ZDDP [10,11] where intermediate ZDDP products are produced and chemically react or adsorb on the friction surfaces.

The chemical composition of ZDDP tribofilms has been studied extensively. They are composed of glassy phosphates, with mostly Zn cations, but with Fe cations increasing in proportion towards the bulk material [12]. Within the tribofilm, presence of sulfides and oxides has also been observed, [13,14]. It is presumed that sulfur is present in the form of a zinc sulfide [15]. Additionally, Martin et al. [12] proposed that the ZnO and ZnS are embedded in the phosphate glass tribofilm. By employing X-ray absorption near edge spectroscopy (XANES) [16], it was found that the films have a layered structure: with short chain phosphates forming close to the bulk material – tribofilm interface, and long chain phosphates forming in the surface tribofilm layer (5–10 nm) [17].

Such tribofilms cover the surfaces in a non-uniform manner, forming pad-like structures separated by "valleys". During sliding, these patches evolve into a more continuous pad-like film, as shown by monitoring the tribofilm morphology during sliding [3]. The thickness of the tribofilms has been estimated using X-ray absorption near edge spectroscopy (XANES) [18], scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) intensity [19,20], X-ray photoelectron spectroscopy (XPS) coupled with Ar^+ ion sputtering [18], atomic emission spectrometry (AES) [12,21], ellipsometry [4], atomic force microscopy (AFM) [22] and spacer-layer interferometry (SLIM) [22,23]. All studies agree that ZDDP forms tribofilms from 50 to 150 nm in thickness. However, the majority of previous research has found no significant correlation between the tribofilm thickness and anti-wear properties of tribofilms [10,24,25]. The durability of tribofilms is determined by their formation and removal rates [23,26,27]. Depending on the contact and lubricant conditions, either the forma-

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* Corresponding author.
E-mail address: jech@ac2t.at (M. Jech).

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tion or the removal process dominates. Usually, tribofilm thickness is used as a measure of tribofilm durability [4,23,24], since tribofilm thickness is a result of the balance of film formation and removal. ZDDP tribofilms have been reported to have extremely stable thickness, even after 24 h of sliding in non-additivated base oil [24].

In the literature, several anti-wear mechanisms of tribofilms have been reported. One of the most accepted anti-wear mechanisms of tribofilms is that they act as a mechanical barrier between two metals, thus preventing adhesion, metal transfer and uncontrolled oxidation or sulfidation [1,28]. It is also proposed that, during the early stages of the running-in process, an iron sulfide layer forms, which prevents localized adhesion and facilitates the formation of a glassy, phosphate layer. As suggested in [28], if the tribofilms have a gradient structure, such that the layers close to the metal substrate act as an elastic solid, and the layers close to the tribofilm surface act as a viscous lubricant, the intermediate layers of tribofilm would exhibit a combination of these two anti-wear actions. Another popular anti-wear mechanism is proposed in [29], where it is suggested that the tribofilm "digests" abrasive iron oxide particles. It has also been proposed, that the ZDDP wear debris re-enter the contact [30], or that the glassy phosphates passivate the surfaces against corrosive wear [27].

Interactions between other surface-active additives and lubricated surfaces cause alterations in the pure ZDDP tribofilm composition and structure. Several studies have investigated the antiwear mechanisms of model oils containing two or three additives in addition to base oil. These additives are mainly ZDDP, friction modifiers based on organomolybdenum compounds and/or Ca-based (sulfonates, salicylates or phenates) detergents [29,31–33]. It is generally agreed that the addition of different additives decreases the anti-wear efficacy of pure ZDDP tribofilms [16,17,21,31,34]. This antagonistic effect can be explained by the competition between the additives, especially dispersants, for adsorption on the metal surfaces [5,16,25]. This can result in thinner tribofilms, when detergents and especially, dispersants are present in the lubricant formulation. The presence of detergent and dispersant additive package in the formulated oils can also lead to a change in the chemical structure of the phosphate tribofilms. These changes include shortening of the phosphate chain lengths and phosphate cation exchange in favor of Ca cations. Additionally, it can result in a lack of supply of unreacted ZDDP present on the tribofilm surfaces, which could otherwise act as a lubrication reserve [17].

Increasingly strict environmental regulations are aimed at reducing the phosphorous levels in oils, increasing the oil drain intervals and reducing the NOx emissions. These oil requirements are generally in conflict with the ability of the lubricant to form effective anti-wear films. In particular, as the oil drain intervals increase, it is important to address the issue of the effect oil oxidation and additive depletion have on wear performance of both gasoline and diesel engine oils. Still, not many studies are published on the anti-wear capabilities of additive-depleted and oxidized engine oils [35–39].

This paper focuses on examining the real-time wear response of tribofilms formed from a commercial fully formulated engine oil in fresh and artificially aged condition, as well as how durable these films are once the additives responsible for forming of these tribofilms are not available anymore.

In this study, durability of tribofilms is defined via the wear response of the tribofilm covered cylinder liners, rather than tribofilm thickness when no additives are present in the lubricant (PAO8 base oil).

The questions investigated in this paper can be summarized as follows:

1. How long will it take until the cylinder liner wear increases once the oil is changed to PAO8?
2. Will there be differences in the durability between the previously formed fresh and aged tribofilms?
3. What is the chemical composition of tribofilm after the oil change at the end of the tests?

Table 1
Physico-chemical properties of the SAE 5W-30 fully formulated engine oil in fresh condition.

Kinematic viscosity (at 40 °C/at 100 °C), [mm^2/s]	56.2/9.84
TAN, [mg KOH/g]	3.6
TBN, [mg KOH/g]	10.5
Antiwear additive	primary ZDDP
Friction modifier	no
Base oil group	mineral group III oil
Chemical elements, [ppm]	
Zn	1190
Ca	3860
Mg	< 10
B	< 10
P	1065
Cl	< 30
S	< 0.55

The durability of tribofilms formed from fully formulated oil both in fresh and artificially aged condition is studied for the first time via wear measurement in real time and this response is then related to the chemical composition of the worn surfaces.

2. Materials and methods

2.1. Lubricants

The lubricant used in all tests is a fully formulated mineral engine oil, SAE grade 5W-30, with the basic physico-chemical properties and the elemental composition shown in Table 1. As can be seen from the Table 1, the fully formulated oil used in these experiments did not contain any Mo-containing additives (e.g. Mo-based friction modifiers).

Since the oil in the passenger car engines is in its fresh condition only for a short time, the fresh engine oil was artificially aged to simulate the situation in common passenger car engines more realistically. The artificial oil aging was performed in order to gain insight into the effect aged oil has on the tribofilm composition and wear protection capability of such tribofilms.

Artificial oil aging was performed in accordance to the standard designed for the testing of the thermal-oxidative stability of the oils, by exposure to dry air and elevated temperatures [40]. In this procedure, the lubricant (engine oil) is placed into a three-neck glass flask. Air is supplied to the engine oil via glass tube, while the gas flow is controlled by a flow controller. The exhaust gases are evacuated through the second neck. The third neck was closed and was used for oil sampling during the aging procedure; samples were taken every 6–18 h, totaling 7 samples before the end of the alteration procedure. The applied aging conditions were: oil bath temperature of 180 °C (kept constant during the aging procedure), air flow at 10 l/h and 300 g of oil in the flask. The oxidation value of the oil was determined by Fourier transform infrared spectroscopy, as described in the DIN 51453 standard [41]. Oxidation (given in absorbance per cm), is calculated at the wavelength of 1710 cm^{-1}, with oxidation (A/cm) = extinction (A) / thickness of cuvette (cm). When the oxidation reaches the value of 12, it can be stated that the oil is deteriorated (Fig. 1), which is why oil aged for 94 h was chosen for the tribometer testing. Visual inspection of the artificially aged sample established that no sludge, particles or deposits formed at any time during the oil aging process. Fig. 2 shows the changes in color due to aging – the oil is already visibly darker after 8 h and very dark and completely opaque after 50 h. The total base number after 96 h aging was 6.8 mg KOH/g (measured according to ASTM D 2896) and the neutralization number 2.3 mg KOH/g (measured according to DIN 51558).