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Unveiling oil-additive/surface hierarchy at real ring-liner contact

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Abstract

Zinc-dialkyldithiophosphate (ZDDP) additive in oil has been extensively reported to form a protective tribofilm between the moving components of engine for preventing wear. In this study, surface and interface characterizations were conducted on real piston ring/cylinder liner contacts, the interacting mechanism between oil-additive and solid surfaces under realistic mechanical and thermal conditions was predicted according to the identification of the chemical composition and structure of the tribofilm. The results demonstrate the interesting laminated hierarchy of tribofilm. This tribofilm is composed mainly of dense carbon precipitation at the top region and a thinner polyphosphate intermediate layer in contact with deformed iron oxide substrate on the cylinder liner. The depletion of polyphosphate compounds and competitive growth of solid carbon in term of lubricant's degradation was speculated. These significant findings help manufacturer to understand possible tribochemical processes occurring in the real tribosystem from the practical view, and in particular inspire researchers to develop the new strategy to improve capability and efficiency of oil-additive at sliding contacts.

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Unveiling oil-additive/surface hierarchy at Real ring-liner contact

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Abstract: Zinc-Dialkyldithiophosphate (ZDDP) additive in oil has been extensively reported to form a protective tribofilm between the moving components of engine for preventing wear. In this study, surface and interface characterizations were conducted on real piston ring/cylinder liner contacts, the interacting mechanism between oil-additive and solid surfaces under realistic mechanical and thermal conditions was predicted according to the identification of the chemical composition and structure of the tribofilm. The results demonstrate the interesting laminated hierarchy of tribofilm. This tribofilm is composed mainly of dense carbon precipitation at the top region and a thinner polyphosphate intermediate layer in contact with deformed iron oxide substrate on the cylinder liner. The depletion of polyphosphate compounds and competitive growth of solid carbon in term of lubricant's degradation was speculated. These significant findings help manufacturer to understand possible tribochemical processes occurring in the real tribosystem from the practical view, and in particular inspire researchers to develop the new strategy to improve capability and efficiency of oil-additive at sliding contacts.

Keywords: Piston ring-cylinder liner assembly, Tribochemistry, Tribofilm, surface/interface, characterization

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1. Introduction

Boundary/mixed film lubrication regimes primarily occurs in the engine components, e.g. cylinder-piston rings and valve train, where very complex interactions are involved between oil-additives and rubbing contacts.[1] For the ferrous metal contacts, the capability of friction reduction and wear mitigation of moving parts is predominantly managed by the boundary tribofilm coming from the tribochemcial interaction of functional additive in oil with the solid contacts.[2] It is well-known that, lubricating oil includes various types of additives which work in synergy to improve the oil performance with regard to wear resistance, friction reduction and corrosion prevention.[3] Among them, ZDDP has been extensively reported to be primarily responsible for wear prevention of the sliding contacts by creating a tribologically adaptive polyphosphate tribofilm, which is a glassy composite film mainly comprising zinc/iron sulphide/polyphosphate.[3, 4, 5] In particular, polyphosphate has different chain length that varies as a function of depth over an intermediate sulphide layer. Martin well proposed the chemistry of ZDDP derived tribofilm regarding the tribochemical reactions between polyphosphate and iron oxides on the basis of the hard and soft acid and bases (HSAB) principle.[6] Although investigations have been conducted to understand the ZDDP/Fe-based surface interactions, researchers have always attempted to get deep insight of the interaction of formulated oil with ZDDP and the rubbing interface that approaches to real mechanical and thermal conditions, and thereby exploit the attributes of existing oil-additives.

Considerable investigations have been conducted using *in-situ* and *ex-situ* techniques,[3-7] to build the correlation of the tribological effects of ZDDP films and tribofilm hierarchy under the defined conditions. The working mechanisms as to the formation of ZDDP tribofilm on rubbing surfaces have been proposed, including thermal degradation,[7] surface adsorption,[8] oxidation by hydroperoxides and radical reactions,[9] hydrolysis,[10] and combinations of the aforementioned.[11] It can be summarized that among these mechanisms, temperature and shearing pressure are two basic factors that affect ZDDP tribofilm formation and depletion.[12, 13] Thus the mechano-chemistry theory is also available for explaining the antiwear capability of ZDDP tribofilm.[14] With there still being some doubts about the tribofilm formation and responsive hierarchy, it is significant to find new knowledge on the interactions of oil-additive with the tribo-system.

Very recently, the growth mechanism of ZDDP was *in-situ* accessed by single-asperity sliding contacts.[15] The tribofilm grows exponentially with either applied pressure or temperature. As to the tribofilm hierarchy, it grows not uniformly on rubbing surface, its thickness is in the range of 50~150nm, and it is dynamically oriented with a laminated construction across the tribofilm. In particular, it adapts to variables of engine components by the smart nature of sacrificial and healing actions from the polyphosphate.[3, 6] Relatively small fraction of sulphides and sulfate, iron and/or zinc oxides preferially locates at the intermediate region over iron oxide, which further makes essential contribution to wear alleviation and friction adaption.[4, 5] These studies on the working mechanics of polyphosphate have been conducted as planned. However, under actual service conditions, engine components are always subjected to various ambiences, the composition and the hierarchical structure of tribofilm on engine components changes with engine running conditions due to the variation of speeds, loads and lubricating oil characteristics, which is not yet considered comprehensively.

Unblocking the formation tribofilm derived from ZDDP have been extensively carried out by characterizing the interaction of oil-additive with Fe-based solid surface under the defined conditions.[5-12, 16, 17] However, the tribofilm composition and structure on the real piston ring/cylinder liner interface is not fully understood when submitted to the variable working conditions. This paper attempts to unveil resultant composition and structure of tribofilm at the real piston ring/cylinder liner after long service life, obtaining the true nature of tribological interface. Scaning electron microscope (SEM), Transmission electron microscope (TEM) and corresponding EDS techniques enable revealing the tribofilm hierarchy in terms of chemical composition and structural orientationin the spatial resolution, predicting relevant working mechanisms.

2. Experimental details

2.1 Materials

The piston ring/cylinder liner assembly were cut from the standard engine of car with the running distance of 600 000 kilometers, without any liquid during the cutting process. The piston ring #1 consists of a low alloyed tempered spheroidal cast iron coated with a chrome layer which acts as the running surface in Figure 1. The thickness and micro-hardness of chromium coating is around 20 μm and 650±50 HV, respectively. The piston ring #2 is affirmed to be nitriding ring, and has a microhardness of 600±50 HV.

Lamellar cast iron has superior tribological characteristics and high damping capacity, which is used as the cylinder liner material in Figure 2. The composition of grey cast iron is C 2.7-4 wt. %, Mn 0.8 wt. %, Si 1.8-3 wt. %, S 0.07 wt. %, P 0.2 wt. %, with Fe the balance. The micro-hardness of grey cast iron is 450±50 HV averaged from the 11 times evaluations.

The piston ring/cylinder liner materials were lubricated by commercially 15W-40 CF-4 engine oil. Engine manufacturers recommend changing the oil every 10000 km, accordingly the lubricating oil was changed 60 times.

2.2 Characterization

The worn morphologies were observed by scanning electron microscopy (SEM). Scanning Transmission Electron Microscope (TEM) with Electron Dispersive Spectroscopy (EDS) were implemented to evaluate the film thickness, visualize the nanostructure, and identify the chemical composition within the tribofilm. The TEM samples were prepared using a Focused Ion Beam (FIB) system with a Ga source and a fine beam current of 100pA to extract a cross-sectional sample within the wear track of the specimen (15 μm × 15 μm). Prior to the FIB lift-out procedure, a thin layer of Pt was sputtered onto the wear track to protect the surface structure. Raman Spectrum was used to track the structural change of carbon species on the surface of the cylinder and the rings, using an Ar^+ laser of 532 nm and a resolution of 1 cm^{-1}.

3. Results and discussion

3.1. Worn morphology on the piston ring/cylinder liner assembly

Figure 3 shows the worn morphology of top piston ring and second ring. The chromium surface of top piston ring (Figure 3a and 3b) demonstrates the characteristics of grooves parallel to the sliding direction, ridging and shearing on the surface. Thus, the wear mechanisms of chromium surface are abrasion and plastic deformation. In contrast, many deep furrows and accumulated debris can be seen clearly on the nitriding iron surface of second piston ring in Figure 3c, deep scratches and damaged regions can be found as well in Figure 3d. This implies a severe occurrence of abrasive wear on the second ring. Such carbon and iron oxides species are identified by the EDS analysis in Figure S1, which indicates either solid carbon particulates or hard particles transferred from the counterpart liner presenting between the contacts. In particular, solid particulates, either the agglomeration of carbon soot or hard particles transferred from the counterpart will behaves as the “third body”,[18-22] thus enable wear worsening to occur on the piston ring/cylinder liner system.

Figure 4 shows the worn morphology of cylinder liner at different regions. At the top dead center (TDC) area, wear debris particles, grooves parallel to the sliding direction and scattered cracking at some locations are distinctly observed in Figure 4a and 4b. Particularly, the EDS analysis affirms those particles composed of carbon and oxygen in Figure S2, which probably originates from carbon soot during combustion or solid carbon due to carbon decomposition. The mid-stroke area displays clear deep furrows and delaminated craters in Figure 4c and 4d, severer wear occurring as comparing with the TDC region. At the bottom dead center (BDC) area, the worn morphology of grey cast surface is as similar as that at TDC, debris build-up, fragmentation and tearing at the cylinder liner surface can be distinguished in Figure 4e and 4f. Thus, abrasion and plastic deformation dominantly occur on the cylinder liner.

From the worn surface analysis, solid particulates on the piston ring and cylinder liner are mainly carbon and iron according to the EDS analysis, while other metallic elements are hardly detected. The variation of worn morphologies in Figure 4 is thus in close association with tribofilm presence and solid carbon precipitations at different regions of the cylinder surface. However, SEM/EDS analysis only can detect the constituents from reactive ZDDP and other additives in engine oil from the top view. Further TEM-EDS analysis are applied to identify the tribofilm composition and structural orientation at the cylinder liner interface from the cross-sectional view. Besides carbon species, even zinc (Zn), calcium (Ca), phosphorus (P) and sulfur (S) elements are detectable at the minimum level as shown in Figure S2. Whether a continuous carbon precipitation or a thin polyphosphate film presents at the moving interface, or they are integrated together, or laminated/composite oriented structure occurs, can be confirmed by the following Raman and TEM/EDS analysis.

3.2 Raman analysis on the piston ring/cylinder liner assembly

Figure 5 shows Raman spectra at different concentrated areas on the cylinder liner surface. All spectra were obtained from a laser excitation wavelength at 532 nm. Normally, graphitic carbon materials present the so-called D band at 1350 cm^{-1}, and the G band at 1620 cm^{-1}.[21, 22] Comparing the Raman spectrum for the three selected regions on the cylinder liner, since TDC region always suffers higher temperature and contact pressure, the formation of a more graphite-like carbon with relatively small amount of defects occurs, which is explained by the relatively sharp G peak at approximately 1600cm^{-1}. Meanwhile, amorphous carbon also presents at the mid-stroke region and BDC regions. These results well agrees with the investigation by Obara et al.[23] The Raman results well demonstrate amount of disordered graphitic carbon existing on the worn trace, which is both carbon soot from the combustion chamber and amorphous carbon from oil decomposition. Such carbon precipitation probably retains the necessary lubrication capability to offset the depletion of polyphosphate tribofilm, which is closely dependent on the state of solid carbon.[24, 25] However, the piston ring with chromium surface does not show any Raman characteristics of solid carbon deposit in this study, which indicates no carbon precipitation on the piston rings, as shown in Figure S3. In comparison, the piston ring with nitride surface demonstrates the clear Raman spectroscopy of amorphous carbon existing as shown in Figure S3, which is consistent with above-mentioned SEM/EDS analysis (Figure S1). Since carbon species are probably too retardant to adsorb onto chromium coated piston ring, but elements such as iron, calcium, phosphorus and sulfur can be detected from reactive additives by the EDS analysis in Figure S1.

3.3 TEM analysis of tribofilm at cylinder liner interface

Cross-sectional TEM imaging, EDS chemical analysis and corresponding phase contrast imaging reveals a thin layer closely adhered onto the plastically deformed iron oxide over cast iron as shown in Figure 6-9. Figure 6 demonstrates the tribofilm and deformed region underneath, where the topmost layer is a protective platinum (Pt) layer during the ion-beam sputter-thinning of TEM specimen. The morphology of the tribofilms features as a distinguished laminated construction across the tribofilm in Figure 6c and 6d.

The thickness of tribofilm at TDC region is within the range of 20 nm, but it is continuous and uniform, which is different from the densely packed “islands” of pitch-like tribofilm material separated by valleys as described in a published literature.[6] This is associated with the presence of carbon layer. It generally appears as hard fine particle, under the combinative thermal and shearing pressure conditions it works together with reactive additives in oil, facilitating the film continuity.[7] From the EDS and corresponding phase contrast imaging in Figure 8 and 9, the laminated hierarchy of tribofilm comprises amorphous carbon at the top and non-crystalline polyphosphate composites at the intermediate region, resulting from interaction of oil-additives rather than additive singly. However, the layer consisting of additive compounds like phosphorus, sulfur, and zinc is specifically thin, less than 5nm; the top amorphous carbon is a little bit thick, around 15nm in Figure 7b.

In Figure 10, the continuous tribofilm at the BDC region of cylinder liner displays a similarity with that at TDC area. The thickness of tribofilm is no more than 15nm in Figure 11, the corresponding phase contrast imaging show the main composition within tribofilm are carbon and relevant additive compounds. The EDS analysis further shows the tribofilm primarily includes Ca, O, S, P, Zn and higher fraction of Fe in Figure 10, which reveal the fact that a tribochemical reaction occurred between cast iron’s surface oxide and additives-oil. In the special case of Ca element, it mainly originates from calcium-related detergent. In particular, relatively large volume of carbon precipitates over polyphosphate can be distinguished as well in Figure 12 and 13b, presumably due to either amorphous carbon soot or the contribution from decomposition of oil molecule. Therefore, carbon deposition probably behaves as the lubricious solid carbon, thus retaining a capability of friction reduction. It can be concluded that, the above-mentioned results demonstrate well the tribofilm appearing on real components of engine. The tribofilm is truly laminated, where amorphous carbon located at top region and polyphosphate layer lay over deformed iron oxide, which differs greatly from the published literatures.[9-13,17]

3.4 Discussion

Extensive research has been done as to the antiwear functionality of ZDDP additive at defined conditions, it has been widely accepted that ZDDP additive allows wear prevention and oxidation protection by creating protective polyphosphate glass tribofilm over the rubbing contacts.[3-11] However, resultant ZDDP tribofilm appearing on the piston surfaces especially if it meets with actual variable conditions, is not known. Although previous investigations confirmed that polyphosphate tribofilm definitely formed over the piston ring/cylinder contacts at the defined testing conditions, the tribofilm composition and structural hierarchy of components after the real operation of engine needs to be exploited. This study aims to unblock the chemical composition and structure orientation of tribofilm formed on real piston ring/cylinder liner and to update the knowledge regarding the interacting effect of carbon species and reactive polyphosphate on tribofilm formation after aging service.

As for the origin of carbon species, a relative high fraction of carbon precipitation appears especially under high contacting pressures, where the sliding components are lubricated by base oil. [26] Also, the aged oil preferred to form amorphous carbon-rich tribofilm after the long running duration.[27] Besides carbon soot, this implies amount of solid carbon coming from oil decomposition further contributes to carbon precipitation of tribofilm in this study. The formed carbon-rich tribofilm is more easily sheared as compared to polyphosphate compounds, which features as decreasing friction coefficient and steady-state wear.[28] It is thus thought that solid carbon particulates at right level are tribologically useful.[19, 21]

When the formulated oil with additives [ZDDP, around 1200ppm] presents at the mated parts, tribofilm occurs and both solid contacts display improved capability of wear resistance and anti-oxidation.[29] The surface and interface characterizations well affirm the chemical compositions of current tribofilm on cylinder liner surface, including Zn, S, O and P elements from reactive additives. Also, it is distinguished that phosphates and sulphides layer locates between superficial carbon precipitation and intermediate oxide. The tribofilm thickness is around 10~20 nm, which is thinner than the reported values of polyphosphate film alone.[3-7] It is sensible to be concluded that, a carbon-rich film probably competes with polyphosphate film, if the reactive additives are gradually depleted. However, some researchers claimed that such solid carbon from engine oil will compete with ZDDP-induced tribofilm for creating tribofilm, yielding a negative performance in wear aggregation.[29, 30]

The agglomerated solid carbon in engine oil may behaves as the ‘third-body’ abrasion, causing wear deterioration and friction increment of critical engine components.[21, 26, 27] But actually, different mechanisms are involved simultaneously at engine components in real conditions. A competition mechanism between carbon precipitation and ZDDP tribofiln probably accounts for this case. The abundance of active sites and chemical bonds of solid surface always varies as well as concentration of carbon precipitation.[31-33] If the sliding condition allows a large production of carbon precipitation, such carbon could adsorb oil molecule and reacts with each other to form carbon particulates, the concentration of solid carbon maintains low and uniformly dispersed in engine oil, it is capable of reducing friction and less wear by the roller effect of carbon solids in combination with ZDDP additives.[34, 35] Conversely, carbon solids grow larger as a result of agglomeration and adsorption if higher concentration of carbon particle presents, it will block the entry of oil fluid into the friction pairs, and eventually works as a third body that enables progressive abrasion and friction increment. This is consistent with previous studies showing that the tribological performance of solid carbon depends on their relative concentration and particulate sizes.[29, 30]

Researchers indicated that solid carbon particulates are not abrasive, they preferentially adsorb additives in oil and undermines the tribological function of antiwear additives.[19-27] Precipitated carbon would incorporate inorganic particles from the mechano-chemical reaction between wearing metal and oil additives under high shearing pressure conditions.[19] However, it does not cause a severe abrasion.[27] The possible working mechanism associated with two parts, the formation and depletion of ZDDP tribofilm due to physical adsorption of carbon precipitation on the surface, carbon incorporation causing the changing property of the reactive ZDDP tribofilm in terms of physical and mechanical strength, which may provide the complementary effect on the depletion of polyphosphate tribofilm. In this study, more carbon presents over the aged components, which is associated with wear of engine components in Figure 3 and Figure 4.

Above-mentioned surface and interface analysis well demonstrates resultant tribofilm hierarchy that is associated with carbon presenting at rubbing contacts. From the chemical identification, the weak trace of active calcium element presents, typically related to the detergent additives including calcium sulfonates and calcium phenates.[36, 37] Normally, They function as the corrosion inhibitor. As reported, the interaction of calcium based detergents with ZDDP produces the antagonistic effect on quality and effectiveness of boundary lubricating film. A competitive adsorption of ZDDPs and detergents limits effective interaction of ZDDP with metallic surface, retarding the efficacy of ZDDP during friction.[38] In particular, such calcium sulfonates deplete the sulphur within tribofilm and calcium phenates make polyphosphate shortening, which gives rise to poor wear behaviour only if its concentration is in excess of 2 wt.%.[39] Also, they helps to suspend carbon soot, alleviating the deleterious effects of carbon agglomeration and thereby wear decrement. Ratoi et al. further stated that appropriate dispersant facilitates the uniform suspension of soot particulates.[40]

According to this study, the tribological performance of lubricants not only depends solely on additives, solid carbon species itself also contribute significantly to friction and wear behaviours of rubbing contact at boundary lubricating regions, which can be found in this study as shown in Figure 13c.[41] It seems premature and counter-intuitive to assume *in-situ* creation of carbon-rich tribofilm by decomposition of the lubricating oils or carbon soot on rubbing surfaces, in particular, when such solid carbon probably delivers a comparable capability as polyphosphate as to wear prevention and friction reducing. Very recently, Erdemir et al.[42] have reported lubricious carbon-based tribofilm from oil molecules is achievable by developing a catalytically active nitride coating under shearing pressed parts, where nanometre-scale copper crystalline incorporated in nitride layer facilitates the conversion of hydrocarbon fluids into solid carbon. Additional research further justified carbon precipitation derived from base fluids and carbon-containing vapour.[43-46] These conflicting investigations well suggests both positive and negative effects of solid carbon particulates presents, depending on the particle size, morphology, and concentration, etc.

5. Conclusions

This study reveals the tribofilm structure and composition in real engine components after long-term service. Since being subjected to variable lubricated conditions with formulated oil, the tribofilm at aged surface contains the relatively low concentration of reactive additive elements from ZDDP and large amount of solid carbon. A laminated hierarchy of tribofilm occurs on real engine components, a “dense carbon-rich precipitation” lies on a thin polyphosphate layer. A competition between the additive-based tribofilm and growth of carbon-rich film can be predicted from surface and interface analysis. This further inspires us to develop new strategy toward improving efficiency of oil molecules and reducing additive usage.

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Figure captions

Figure 1 (a) SEM observation of piston ring coated with electroplated Cr from the cross-sectional view, (b) the corresponding EDS mapping of electroplated chromium

Figure 2 Graphite morphology of the grey cast iron used for the cast iron flats

Figure 3 SEM image of the worn surface of (a, b) electroplated chromium coated piston ring and (c, d) nitriding piston ring

Figure 4 SEM image of the worn morphology of cast iron cylinder liner surface at different regions, (a, b) Top dead centre (TDC), (c, d) middle-stroke area, and (e, f) Bottom dead centre (BDC).

Figure 5 Raman spectra of different concentrated regions on the cast iron cylinder liner surface

Figure 6 Cross-section TEM images of tribofilm at the TDC region of the cast iron cylinder surface, (a, b) Dark field images of tribofilm continuity and uniformity, (c, d) bright field images of tribofilm laminated hierarchy.

Figure 7 (a) Bright field and (b) Dark field images of tribofilm laminated hierarchy at the TDC region of the cast iron cylinder liner

Figure 8 Cross-section TEM image and corresponding EDS phase contrast images of tribofilm at the TDC region of cast iron cylinder liner

Figure 9 (a) Cross-section TEM image of tribofilm and (b, c) corresponding elemental distribution across the tribofilm at the TDC region of cast iron cylinder liner

Figure 10 Cross-section TEM images of triboflm at the BDC region of cast iron cylinder liner, (a, b) Dark field images of tribofilm discontinuity and non-uniformity, (c, d) Dark field images of tribofilm laminated hierarchy.

Figure 11 (a) Cross-section TEM image of tribofilm laminated hierarchy and (b) corresponding EDS lining of tribofilm at the BDC region of cast iron cylinder liner

Figure 12 Cross-section TEM images and corresponding phase contrast images of tribofilm at the BDC region of cast iron cylinder liner

Figure 13 Cross-section TEM image of tribofilm at the BDC region of cast iron cylinder liner, (b) corresponding elemental distribution across the tribofilm, and (c) Schematic of tribofilm on cast iron cylinder liner surface.