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Friction reduction efficiency of organic Mo-containing FM additives associated to ZDDP for steel and carbon-based contacts

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ABSTRACT

The lubricating properties of two different organomolybdenum additives combined with ZDDP were evaluated for different tribopairs involving carbon-based coatings, hydrogenated DLC and nanocrystalline diamond NCD. Their performances were investigated using reciprocating linear tribometer and compared with the traditional additivation MoDTC/ZDDP. The highly sulfurised moly-trimer additive and organic molybdate ester additive displayed good friction reducing properties in comparison with traditional additivation MoDTC for all tribopairs tested, especially organic molybdate ester. XPS and ToF-SIMS surface analyses performed on the tribofilms formed with these different organomolybdenum additives showed the formation of $MoS_2/MoS_{2-x}O_x$ species exhibiting a solid lubricant character, but preferentially on steel surfaces. HRTEM/EDS analyses confirmed the presence of $MoS_2/MoS_{2-x}O_x$ sheets embedded inside an oxygen-rich amorphous matrix. This is different from the traditional additivation that leads to the polyphosphate/phosphate glass matrix. Organic molybdate ester is a sulfur- and phosphorus-free additive that appears particularly interesting for achieving low friction while minimizing the S content of the lubricant.

1. Introduction

Due to the depletion of energy reserves and high demand of low gas emission to preserve the environment and people's health, friction reduction of machine parts is increasingly required. Liquid lubricants formulated with friction modifier and anti-wear additives are commonly used to achieve this goal. Under low and moderate contact pressures, polar molecules like carboxylic acids, esters and fatty acids, adsorb onto metallic surfaces building a low-shear molecular tail that avoids asperity contact and makes easier the sliding motion. As the contact conditions become more severe, a higher number of asperities come into contact and, under such boundary lubrication conditions, stronger protection is needed. This is commonly achieved by more adherent chemically-formed organometallic films that limit friction and wear [1–6].

Molybdenum-based FM additives have been widely studied during the last decades due to their well-known friction reducing properties related to their capacity to form MoS_2 lamellar structure providing low-shearing under high contact pressure [7–11]. The most widely investigated soluble molybdenum-based molecules are dithiocarbamates (MoDTC) and dithiophosphates (MoDTP), used alone or synergistically combined with well-known anti-wear and antioxidant additive dialkyldithiophosphates (ZDDP) [12–14]. Despite really interesting friction reduction properties for steel-based surfaces, Mo-based molecules suffer from non-complete sulfuration process leading to the formation of molybdenum oxides (MoO_x) and oxisulfides ($MoS_{2-x}O_x$) species [14,15]. They also suffer from rapid thermal decomposition and/or ageing effect in the oils shortening their durability and friction reduction efficiency [16–18].

On the other hand, other tribological materials such as diamond-like carbon (DLC) coatings have been recently proposed to go further in friction reducing level under different lubrication regimes, and more specifically mixed and boundary conditions. MoDTC performance has then been investigated on different types of DLCs and results showed that this kind of coatings can improve the friction reduction and wear-resistance for DLC/DLC tribo-pairs but it is not always the case for DLC/steel contacts due to the severe chemical wear that can occur with that configuration [19–24].

In this overall context, it is not surprising that recent investigations were made on different soluble friction modifying Mo-based compounds for tribological applications. Hu et al. [25] synthesized recently sulfur and phosphorous-free organic molybdate esters more stable in temperature and they reported good anti-wear and friction-reduction performances for steel/steel

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contact when it was synergistically associated with ZDDP. Other authors have also reported the interesting anti-wear abilities of such S and P-free compounds at different loads, especially at high loads [26,27]. On the other hand, highly sulfurised molybdenum dithiocarbamates (without oxygen atoms) were produced like moly-trimer $Mo_3S_7(DTC)_3$. It is interesting to evaluate their friction and wear reducing properties in different tribological contacts involving carbon-based materials. For these highly sulfurised compounds, the formation of abrasive Mo-oxides is not expected and production of lamellar MoS_2 species is certainly favorized [28,29]. These oxides being often suspected to be involved of the strong wear of DLC coatings [19–22,30], a strong benefit can then be expected with this moly-trimer.

In this work, we investigated the lubricating mechanism of two different friction modifying molybdenum-based compounds coupled to the traditional anti-wear additive ZDDP for three different friction pairs. The first one is a highly sulfurised moly-trimer and the second one is a more environmentally friendly S-and P-free organic molybdate ester. The well-known MoDTC friction modifier is also studied as a reference.

To better understand the tribochemical mechanisms of these soluble Mo-containing molecules in the presence of ZDDP, we analyzed the chemistry of these compounds in the liquid phase by X-ray Photoelectron Spectroscopy (XPS), first alone and in the binary mixtures with ZDDP. The chemistry of tribofilms formed in the presence of these binary mixtures on different sliding contacts was investigated by XPS and complementary information was obtained from ToF-SIMS analysis. The structure of these tribofilms and their interface with the substrate were revealed by TEM coupled to EDS using cross-sections nanomachined by the FIB technique. The originality of this study lies also in the fact that tribofilms were generated with three different friction pairs, namely steel/steel, hydrogenated DLC (a-C:H/steel) and steel/nano-crystalline diamond (NCD). These carbon-based coatings can be used in different contact pressure applications such as valve-train lifters, piston rings or bearings.

2. Experimental details

2.1. Additives and lubricants

Two base oils (a synthetic PAO4 and a mineral GrIII of similar dynamic viscosity 4.9×10^{-3} Pa s at 353 K) and the different additives considered in this work were supplied by TOTAL M&S. It should be noted that the representations of the additive molecules given in Fig. 1 are only schematic. The production processes of these molecules give raw materials with variable chain lengths and partial sulfuration do not guarantee very high purity according to the supplier.

The high sulfurized moly-trimer additive developed by Infineum [31] is called « Mo-tri-nuclear » in the following, its chemical formula is shown in Fig. 1a. This additive is promising because it contains an amount of sulfur greater than that in the well-known moly-dimer MoDTC and it is theoretically free of oxygen. The second organic molybdate ester additive free of S and P developed by Vanderbilt [32] is called « Mo-organic » in the following, the chemical schematic formula of which is shown in Fig. 1b. This additive is sulfur free allowing the decrease of the overall sulfur concentration in a binary with ZDDP antiwear additive, when compared to binary mixtures with MoDTC or Mo tri-nuclear. Considering that in lubricant formulations, concentration of molybdenum for both systems is constant (400 ppm), the use of Mo-organic compound reduces the overall sulfur content by about 20%.

Binary mixtures composed of 400 ppm of Mo-based additive plus 1wt% of ZDDP (II) (synthetized from 1-3-dimethyl buthyl and isopropyl and contained about 10% of Zn) were obtained by stirring and heating to 60 °C for 20 min. Similar binary mixture was performed with traditional MoDTC additive shown in the Fig. 1c.

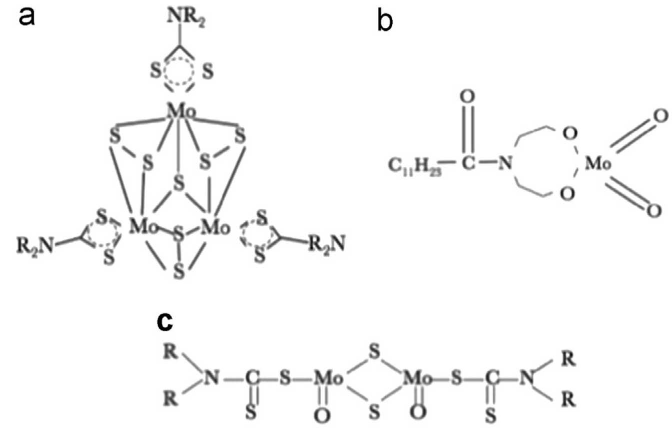

Fig. 1. (a) Chemical formula of the moly-trimer (Mo tri-nuclear). (b) Chemical formula of the organic molybdate ester (Mo-organic) (c) Chemical formula of the moly-dimer (MoDTC).

2.2. Carbon-based materials

In house NCD coatings were deposited on a Ti–6Al–4V flat substrate thanks to the PECVD process at moderate temperature, equal to or lower than 600 °C. from CH_4/CO_2 species [33]. Among the various NCD coatings that can be elaborated [34], a fairly good NCD coating combining high diamond purity, low surface roughness and excellent mechanical properties was selected for this work (see Table 1). Due to the high wear resistance of this kind of coating, its thickness was fixed to about 1.4 μm as estimated from FIB/TEM.

Industrial DLC coating containing hydrogen, a-C:H was also investigated in this work in order to observe the influence of amorphous carbon matrix and sp^3/sp^2 carbon ratio on the lubricated tribological behavior. It was deposited on AISI 52100 bearing steel (96.9 wt% Fe, 1.04 wt% C, 1.45 wt% Cr, 0.35 wt% Mn and 0.27 wt% Si) using a PECVD process and provided by IREIS Company. In that case, the a-C:H coating was deposited on a steel ball with a thickness of about 4.5 μm as indicated in Table 1 that compares the properties of amorphous and NCD carbon-based coatings.

2.3. Tribological experiments

A linear reciprocating friction tribometer with a ball-on-flat configuration was used to generate tribofilms in mild/severe tribological conditions (sinusoidal motion). Three friction configurations were selected, (i) steel/steel, (ii) DLC-coated ball/steel and (iii) steel/NCD-coated flat. Symmetric coated-contact configuration was not tested because this situation is not present in real engine parts. The friction tests were performed at 353 K (80 °C) with a maximum sliding speed of about 0.1 m s^{-1} for one-hour duration, no run-in period prior to the sliding experiment is performed. The maximum initial contact pressure was about 500 MPa that corresponds to the maximal contact pressure between ring and cylinder in engine. In these sliding conditions, the thickness of the lubricant film, at the maximum speed, is equal to about 15 nm corresponding to a λ ratio of about 1. Prior to the experiment, both ball and flat specimens were cleaned in ultrasonic heptane bath in order to remove surface contaminants. An average friction coefficient for each sliding cycle was calculated from one thousand measurements of instantaneous friction coefficients recorded