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Enhanced DLC Wear Performance by the Presence of Lubricant Additives

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Lubricant additives play significant role for reducing friction and wear of mechanical elements. The additives presented in 5W30 oil were developed for metal surfaces. However, they have been used in engine pieces covered with DLC coatings because they also offer the potential to reduce friction losses and wear in automotive applications. The friction and wear tests were carried out by using a UMT-CETR ball-on-disk tribometer in rotational mode under 5W30 synthetic oil at 100 °C. The X-ray photoelectron spectroscopy (XPS) showed the presence of Mo and S in the wear tracks. These elements are from decomposition of ZDDP and MoDTC additives producing MoS_2 in DLC surface, which offers enhanced durability by low wear rate.

Keywords: *DLC, MoDTC, ZDDP, friction*

1. Introduction

The demand for more compact, efficient and powerful engines has stimulated the undergoing of studies for improvement these technological aspects. Becker (2004) showed that inside the internal combustion engines, 15% of the total fuel energy is mechanically lost as friction[1]. Podgornik et al. (2003) and Taylor (1998) conducted studies to investigate feasible alternatives towards the enhancement of engine efficiency, such as coatings in certain components, in attempt to minimize friction and wear[2,3]. According to Podgornik (2001) the coatings must have high levels of hardness, wear resistant surfaces, good frictional properties, and maintenance of mechanical resistance[4].

DLC (diamond-like carbon) is now becoming an option for such coatings, in transportation industry, because they offer the potential to reduce friction losses and wear in automotive applications[5-7]. Some authors[3,4,8] mention several studies using DLC coatings in internal combustion engine components because of their excellent tribological behavior in severe environments. DLC has also been mentioned as an applicable coating in valve lifters, obtaining good results for friction and wear[9,10].

In recent studies, Kalin et al. (2006 and 2007) showed a decrease in the friction coefficient and wear of DLC coatings under lubricated conditions[11,12]. They measured the influence of two antiwear additives, an amine phosphate and zinc- dialkyl-dithio-phosphate (ZDDP), on the friction and wear of hydrogenated DLC films[11,12]. The tests were carried out in reciprocating mode, sliding contact at temperatures up to 150 °C. They found that both additives reduced wear at temperatures of 80 °C and above but that the additives both increased friction[11]. In addition, is known that friction coefficient decreases significantly when using hydrogenated DLC films[13,14]. Erdemir et al. (2005) also showed the importance of considering the surface and lubricant as a single system[15]. They reported that improvements in both friction and wear occur when materials with high lubricity (solid lubricants) are used in systems operating in the boundary lubrication regime. According to Person (1998), Hutchings (1992) and Bayer (1994), the friction coefficient is proportional to viscosity and velocity and inversely proportional to normal force and hV/W is proportional to the liquid lubricant thickness[16-18]. The relation between friction coefficient and hV/W is showed by Stribeck diagram (Figure 1). The high load bearing capacity and lubricity of solid lubricants in this regime provide a back-up function to lubricants[19]. However, it is not common for the surface and lubricant to purposely be used in partnership to optimize performance. It is known that wear and friction performance in the boundary lubrication regime is controlled mainly from the lubricant additives which form tribofilms in the contacting surfaces. However, surface treatments and coatings have an important role to play in providing an improved performance or they can in fact eliminate the benefits of the additives. Knowing the details of how surfaces and additives react is paramount in understanding how to achieve optimal lubrication in the boundary regimes. So, the lubrication of DLC-coated substrates can be complicated by variations in DLC chemical composition due to the presence of additives that have been optimized for iron surfaces[20]. The iron absence on DLC films prevents the reaction with additives such as ZDDP and its decomposition products. Some studies show that the low friction coefficient under automotive oil is observed in non-hydrogenated amorphous carbon (a-C)[6], as well as the tribofilm formation on DLC surface under poly-alpha-olefin (PAO) lubricant containing a mixture of Mo (Molybdenum) and ZDDP[21, 22]. Haque et al. studied the influence of ZDDP in combination with two types of molybdenum dithio-carbamates (MoDTC) in a reciprocating hydrogenated DLC on cast iron contact[23]. They found that MoDTC-ZDDP reduced friction compared to ZDDP alone and also identified molybdenum disulphide (MoS_2) and molybdenum trioxide (MoO_3) on the rubbed DLC surface using X-ray photoelectron spectroscopy (XPS). Using atomic force microscopy (AFM) they also showed that ZDDP formed very thin (2-nm thick) films, which is consisted of short chain zinc pyro and metaphosphate, on the raised regions of the DLC surface[24].

The main objective of this work is to compare the tribological behavior of 20% hydrogenated DLC films using carbonitride adhesion interface when lubricated and non-lubricated with 5W30 commercial oil at room temperature and at 100 °C in the boundary lubrication regime, as well as, the MoS_2 formation in the wear track of DLC film.

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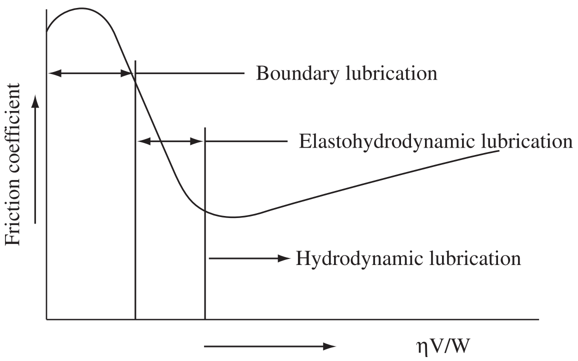

Figure 1. Stribeck diagram.

2. Experimental Procedures

This study focuses on the combined effects of material pair and the nature of the lubricant additives.

2.1. DLC coating preparation

The DLC films with 20% hydrogen concentration were deposited by using pulsed-DC discharge under controlled conditions on 316L stainless steel substrates using carbonitride diffusion process as interlayer[19,25,26]. The 316L stainless steel surface was modified by single diffusion process during one hour at 430 °C using a mixture of N_2, H_2 e CH_4 gases. During the first 30 minutes, the carbonitride process was performed in the proportional of 16:3:1 N_2, H_2 and CH_4 gases and 16:3:4 for the last 30 minutes[27]. This carbonitride interlayer has around 10 GPa of hardness and 10 μm of thickness[27]. For all tests, the disk specimen surfaces were polished to a final finish of about 0.02 μm average roughness (R_a). The ball was not submitted by the polishing process, so that it was used with the original roughness about 1.81 μm R_a. Both of them were cleaned in ultrasonic acetone bath. The substrates were additionally cleaned by argon discharge with 1 sccm gas flow at 11.3 Pa working pressure and a discharge voltage of -700 V for 30 minutes prior to deposition. The DLC film 20% hydrogenated was deposited using methane to a thickness of ~2.0 μm. The deposition was performed using 1 sccm of gas flow, during 2 hours at 11.3 Pa and a discharge voltage of -700 V.

2.2. Sliding test experiments

The tribological tests were performed for 316L pairs. The counter-body and the body (ball and disk, respectively) were coated with DLC film. The 50 mm-diameter disks and the 4 mm-diameter balls were used for the tribological tests. The friction and wear tests were carried out by using a UMT-CETR ball-on-disk tribometer in rotational mode at 120 mm/s linear sliding speed under 2N of applied load during 1000 cycles. The environment during the tests was strictly controlled to keep humidity at 40 ± 2% and temperature at 23 ± 1 °C, as well as, the number of particles in the clean room at 10000. Figure 2 shows the tribometer in the rotational mode and the schematic design of the tribossystem. The tests were repeated three times for each pair combination. A new position on the ball/disk was used for each test, and the friction coefficient was collected from the steady-state region[28]. The initial average Hertzian contact pressure ranged from 0.73 to 1.09 GPa. For the lubricated tests it was used a commercial, Poly-Alpha-Olefin (PAO) synthetic oil (SAE, 5W30 API SL/CF), at room temperature and at 100 ± 5 °C, according to ASTM D445 norm (Standard Test Method for Kinematic Viscosity). Table 1 shows the main oil properties. After the friction measurements, the ball wear rate was measured and calculated automatically through the optical profiler (Veeco NT1100).

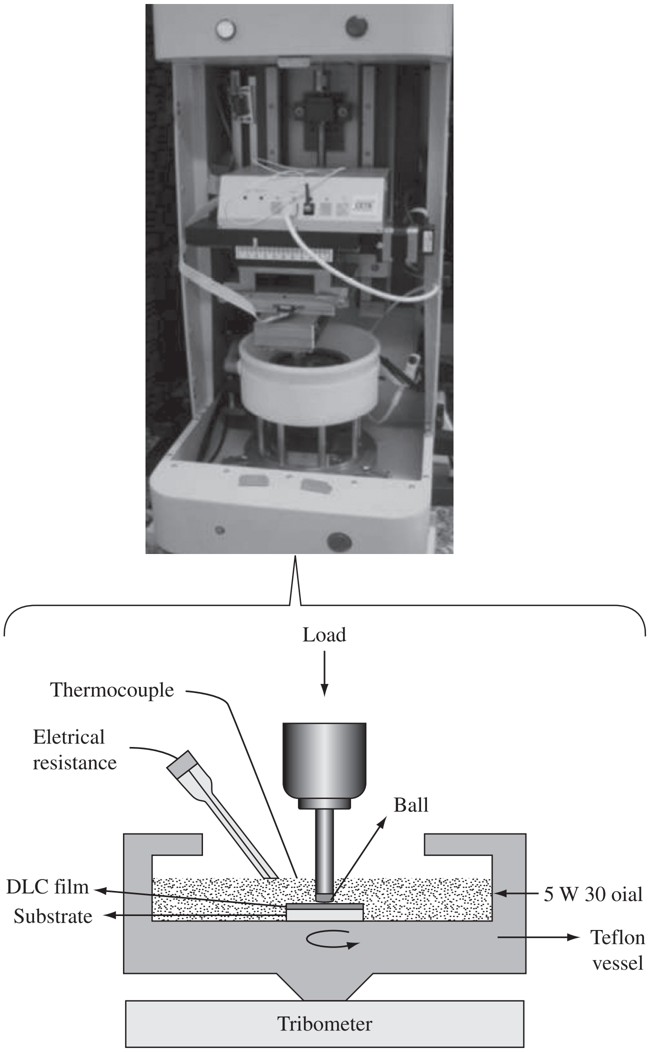

Figure 2. UMT Tribometer in the rotational mode for friction and wear characterizations, as well as, the schematic design of tribossystem used with oil.

Table 1. Oil properties.

Properties	5W30
Density (20 °C) g.cm^{-3}	0.84
Viscosity (100 °C) cSt	11.1

2.3. Surface analyze experiments

2.3.1 X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) analyses were obtained using a VG 220I apparatus. XPS was performed by a non-monochromatized source with dual anode for MgKa/AlKa irradiation. The size of the X-ray probe was set at 100 × 100 μm^2. The thickness probed in XPS was about 3-4 nm with exponential decay.

2.3.2 X-ray Fluorescence (XRF)

The X-ray Fluorescence (XRF) analysis were performed in order to identify the presence (or absence) of one or more analytes in 5W30 oil, such as, zinc, phosphorous and less commonly copper that are used in antiwear additives. Sulfur, phosphorous and molybdenum are common components of extreme-pressure additives; and calcium, barium and magnesium are components of detergent additive packages used in engine oils. This technique was based on the detector system's capability to determine the energy of the photons.

3. Results and Discussion

3.1. Friction and Wear

Figure 3 shows the friction and wear of DLC/DLC and 316L/DLC pairs in air conditions, under 5W30 oil at room temperature and under 5W30 at 100 °C. For the DLC/DLC pair in air conditions, the friction was around 0.09, Figure 3a. High contact temperature results in the tribofilm layer formation, graphitization of DLC. The tribofilm is formed due to interstitial diffusion process of hydrogen atoms forward to DLC bulk, increasing C-H bonds and conversions of sp^3-hybridized C sites to sp^2-hybridized (disordered clusters of sp^2 sites). It provides high wear of DLC coating and low friction[29,30]. The 316L/DLC pair in air condition presented a friction coefficient around 0.18, while the wear rate decreased 20% compared to DLC/DLC pair in the same condition.

It is interesting to note that, when 5W30 oil at room temperature was added on DLC/DLC pair, it did not affect the friction coefficient and the wear rate. Jisheng et al. (1997) also noted this and attributed it to the oil ability to form a layer of carboxylic acid on the DLC surface preventing the tribofilm formation[31]. However, for 316L/DLC pair, it caused a decrease of 55% in the friction coefficient and 36% in the wear rate compared to DLC/DLC pair in the same condition. It occurred because both DLC-coated surfaces were separated by a thin oil film at the sliding contact[6]. De Barros Bouchet et al. (2007) also observed the same behavior in their experiments. The reduction mechanism of friction on steel parts has been attributed to the effect of long chain polar molecules, amphiphilic, called Self-Assembled Monolayer (SAM). The polar molecules ends are chemically adsorbed on the native oxide layer presented in the steel surface. The amphiphilic molecules promoted the crystalline structure formation, so that the low friction coefficient was attributed by the easy sliding of methyl groups[32].

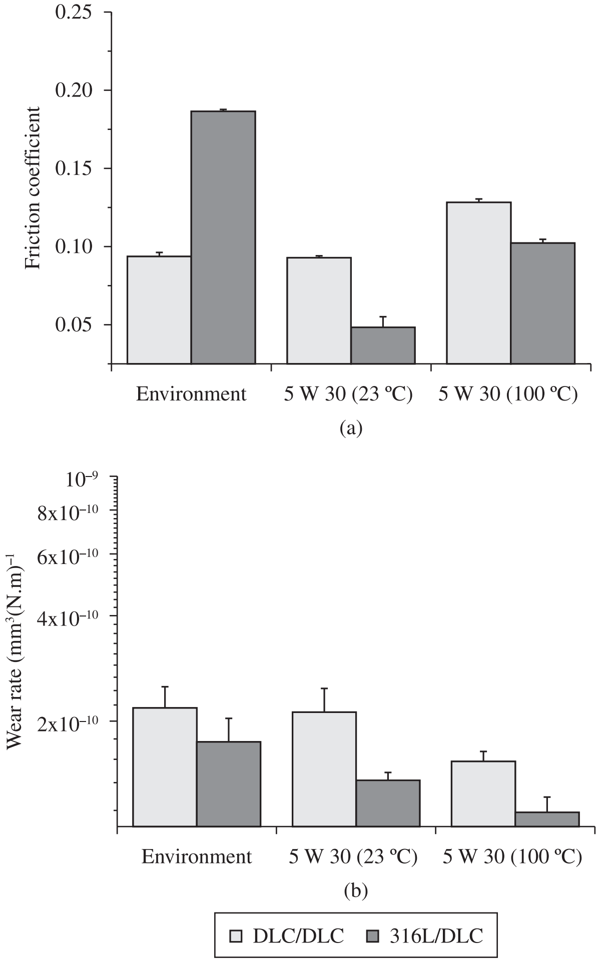

Figure 3. a) Friction coefficient; and b) wear rate of DLC film in environment air, under 5W30 oil at room temperature and at 100 °C.

When the 5W30 oil at 100 °C was added on the DLC/DLC and 316L/DLC pairs, the friction coefficient increased to 33 and 150%, respectively, compared to the same pairs with oil at room temperature. This behavior is related to a reduction of fluid viscosity due to the effects of high temperature. When a substantial reduction in fluid viscosity occurs, it promotes asperity contacts (mechanical rubbing) and an increase in the friction coefficient temperature[33]. It occurred by tribochemical interactions of oil additives in DLC surface[6]. On the other hand, DLC/DLC and 316L/DLC pairs showed a particular behavior, the wear rate was decreasing with the increase of temperature. At 100 °C the DLC/DLC and 316L/DLC pairs showed a decrease of 27 and 20% in the wear rate compared to the same pairs with oil at room temperature. According to the literature, with increasing temperature the formation of graphitic layer (tribofilm) occurs due to a transformation of sp^2 to sp^3 phase of DLC coatings in dry sliding conditions[34]. When the oil is added among surfaces in contact, they are separated by a thin layer of carboxylic acid preventing the formation of tribofilm, as well as, reduce the contact temperature and contribute to interactions between oil additives and DLC surface[6,10].

3.2. XPS analyses

In order to understand the role of oil additives on the durability of the DLC coatings, chemical analysis of the tribofilm formed inside of the wear track were performed using XPS. The XPS spectra of the DLC before tests and the tribofilm formed by 5W30 oil are given in Figure 4a and b respectively.

The XPS spectra obtained before friction tests show elements of DLC surface, Table 2. After friction tests, it shows elements coming from additives, as well as, interacting materials of the DLC film.

It is interesting to note that Mo 3d peak was found in the top layer of tribofilms formed by 5W30 oil, indicating the presence of a compound derived from lubricants. The binding energies of XPS peak of the tribofilm inside of the wear scar and DLC coatings are given in Table 3.

In 5W30 oil, the MoDTC (molybdenum dithio-carbamates) additive decomposed into MoS$_2$ and Mo-oxide, see Figure 4c. MoS$_2$ sheets having very low shear strength provide low friction while the crystalline structure of Mo-oxide provides high friction[35,36].

However, the formation of molybdenum disulphide, after friction at high temperature promotes the reduction of wear rate due to the formation of lamellar structure with relatively low surface energy. The low presence of water contained in 5W30 oil, Table 4, promotes little hydrogen bonding between the crystallites, decreasing the adhesion between them, which leads to the low wear[37].

In the case of ZDDP, derived Zn (Zinc) was found in the tribofilm formed inside of wear scar with binding energies of Zn 2p, and O 1s indicating the formation of ZnO/Zn-metaphosphate antiwear compounds[38,39]. It is interesting to note that the formation of MoS$_2$ (molybdenum disulphide) and ZnO (zinc oxide)/ZnS (zinc blende

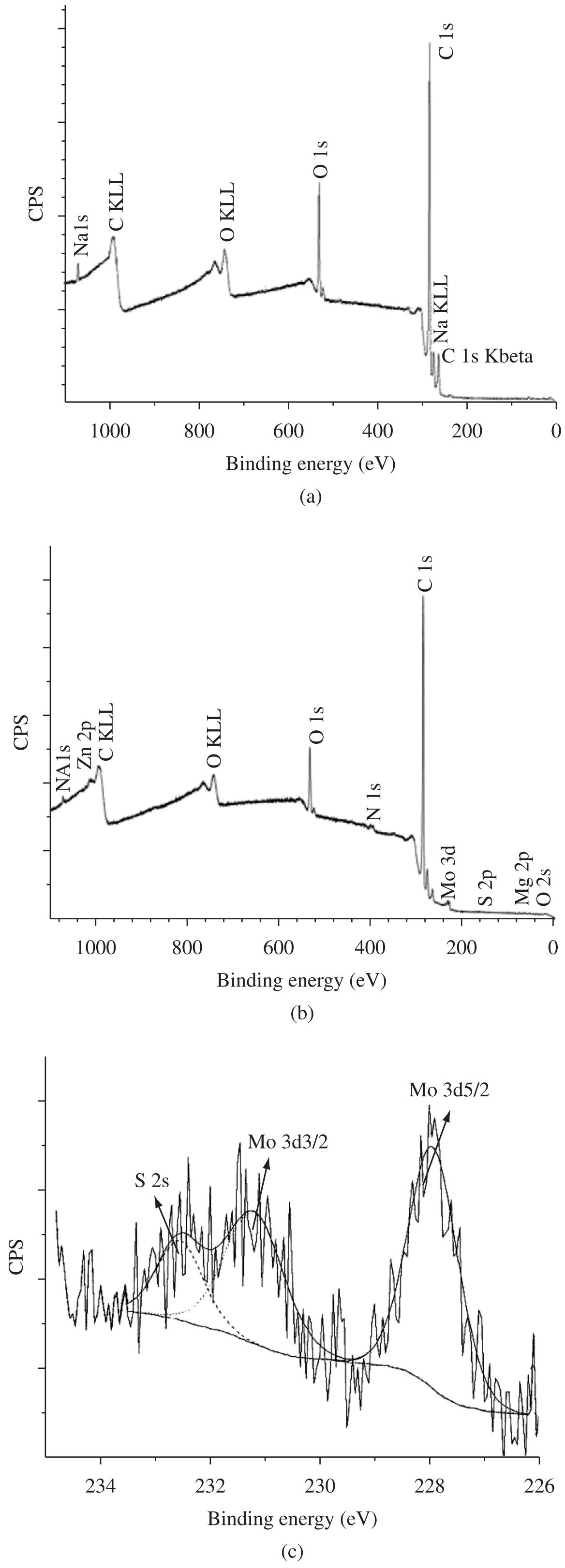

Figure 4. XPS spectra of DLC film a) before friction tests; b) after friction test under 5W30 oil at 100 °C; and c) after friction test under 5W30 oil at 100 °C showing the presence of Molybdenum between 234 and 226 eV.

Table 2. Elements in DLC surface before friction tests.

Elements	Binding energy	At%
C 1s	285.35	87.61
O 1s	532.60	11.52
Na 1s	1071.60	0.59

Table 3. Elements in DLC surface after friction tests under 5W30 oil at 100 °C.

Elements	Blinding energy	At%
C 1s	285.15	89.90
O 1s	532.40	8.60
N 1s	399.65	0.47
Na 1s	1070.65	0.23
Mg 2p	51.65	0.50
S 2p	161.90	0.21
Zn 2p	1021.15	0.04
Mo 3d	227.90	0.05

Table 4. Water content of 5W30 oil.

Oil	H_2O (ppm)
5W30	952.4

Table 5. Compound concentration of additives elements in 5W30 oil.

Quantification of sample 5W30 oil
Compound Conc. (%)
P 0.230
S 0.788
Ca 2.330
Zn 2.584
Mo 0.634

or sphalerite) compounds in the DLC surface inside of the wear scar was caused by shearing and contact of the asperities, so the friction is needed to produce these speciation's[40].

3.3. X-Ray Fluorescence

In order to evaluate the additives contained in 5W30 oil, X-Ray Fluorescence analyses was performed. The chemical compositions of additives are summarized in Table 5 by elements as percent of total mass of the oils. Zn (Zinc), P (Phosphorus), Ca (Calcium), S (Sulphur) and Mo (Molybdenum) were the predominant elements in the 5W30 oil. It is in agreement with elements that were showed by XPS analyses inside of wear scar at high temperature.

4. Conclusions

The 20% hydrogenated DLC film showed compatibility with the oil, reaching low friction coefficient and wear rate values. Also, the DLC film responded differently to changes in temperature of the 5W30 oil. The tribofilm was identified in the DLC surface, as well as, it graphitization after friction tests. The increase of temperature to 100 °C promotes the formation of a tribofilm composed by sulfides and oxides of molybdenum and Zinc. In general, the best results were obtained for the 316L/DLC pair (when only one surface was coated with DLC film).

In addition, from this study it is possible to conclude that:

1. The MoS_2, ZnO and ZnS compounds formation in the DLC track surface is derived from MoDTC and ZDDP decomposition.
2. The increase of friction coefficient at high temperature is attributed to the reduction of 5W30 viscosity, which leads to increasing contact asperities.
3. The wear rate decreased inversely proportional to the increase of temperature for DLC/DLC and 316L/DLC pairs.

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