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Investigation of the interaction between diamond-like carbon coatings and lubricant additives

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Investigation of the Interaction between Diamond-Like Carbon Coatings and Lubricant Additives

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Doctor of Sciences

presented by
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Abstract

Environmental considerations are leading to the substitution of the widely used oil additive zinc dialkyl dithiophosphate (ZnDTP) by zinc-free, low-phosphorus and low-sulfur additives. Many studies are now being performed to find a replacement for this highly effective additive, ZnDTP, with more environmentally friendly alternatives. The increasing use of diamond-like carbon (DLC) coatings in oil-lubricated, mechanical systems has led to a great deal of interest in optimizing the interactions between lubricant additives and coatings.

In the present work, the ability of ashless anti-wear additives to form protective tribofilms on DLC and steel surfaces was investigated and compared to the reactions of ZnDTP. Reciprocating sliding tests were performed under mild tribological conditions for steel/steel and DLC/DLC contacts to avoid wearing through the DLC coating. A temperature of 80°C was used for all oil-lubricated experiments as this is a standard operating temperature in engines and is too low for thermal decomposition of the additives. DLC self-mated tribocontacts were used to analyze the behavior of the additives in absence of iron. A comparison of the friction behavior of ZnDTP with two ashless additives, a butylated triphenyl phosphorothionate (b-TPPT) and an amine phosphate (AP), indicated that the latter additive behaved in a different manner of the first two. b-TPPT showed the lowest friction coefficient for DLC/DLC contacts whereas the AP gave the lowest friction coefficient for steel sliding against steel. b-TPPT was selected as a typical metal-free additive and AP, as an additive that is both metal-free and sulfur-free.

Atomic force microscopy and environmental scanning electron microscopy were performed to analyze the rubbing tracks and compare the tribofilms formed from the different additives. ZnDTP and b-TPPT showed a similar tribological behavior for steel/steel and DLC/DLC contacts. Both built up pad-like structure on steel and a tribofilm was also formed on DLC coatings from the two additives, with a larger film thickness on steel. Ex-situ scratch tests showed the weaker adhesion of the ZnDTP tribofilm built up on DLC compared with that built up on steel. No AP film was detected on DLC with AFM.

Chemical analyses of the tribofilms and thermal films built up by these three additives on steel and on DLC surfaces were performed with x-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry. ZnDTP built up a tribofilm on steel made of a
mixture of short chain poly(thio)phosphates with a higher presence of zinc phosphate on top and iron phosphates further down. Short chain zinc poly(thio)phosphates were formed on DLC even in the absence of iron. Iron poly(thio)phosphates were also formed on steel from b-TPPT, while the polymerization reaction of the additive was more difficult on DLC in the absence of metallic counter-ions. Polyphosphates were also present in the tribofilm built up from AP on steel. Although no tribofilm from AP was detected with AFM on DLC, products from tribochemical reactions were detected in the rubbing track. Mainly orthophosphates were detected and, additionally, significant concentrations of protonated alkylamines were detected.

Further experiments were performed to characterize the oxidation of sulfur-containing compounds on steel and DLC surfaces. Although it is well-known that thiols are oxidized by iron oxide, it was more surprising that the thiols were also oxidized on DLC. Dialkylamines were also found to react on DLC during tribological experiments.
Résumé

Des préoccupations environnementales conduisent actuellement au remplacement du très largement répandu additif pour lubrifiant moteur, le dialkyl dithiophosphate de zinc (ZnDTP), par des additifs ne contenant pas de zinc et uniquement de basses concentrations en phosphore et en soufre. De nombreuses études sont actuellement menées afin de permettre le remplacement de ce très efficace additif, le ZnDTP, par des additifs ayant un impact environnemental plus favorable. L'utilisation croissante de couches de carbone amorphe hydrogéné (DLC) dans des systèmes mécaniques lubrifiés à l'aide d'huile provoque un grand intérêt afin d'optimiser les interactions entre les additifs pour lubrifiants et les couches minces.

Dans ce travail, la capacité des additifs anti-usure sans teneur en cendre à former un tribofilm protecteur à la surface d'une couche DLC ou à la surface d'un élément en acier fut étudiée et comparée aux réactions obtenues avec le ZnDTP. Des tests de friction à mouvement alternatif ont été effectués sous des conditions tribologiques modérées dans les cas de contacts acier/acier et DLC/DLC. Ces conditions modérées ont permis d'éviter l'usure complète de la couche DLC. Les tests tribologiques ont été effectués à une température de 80°C qui est une température typique de fonction et qui se situe en-dessous du seuil de décomposition thermique des additifs. Des tribococontacts DLC/DLC ont été utilisés afin d'analyser le comportement des additifs sans interaction avec du fer. Une comparaison du comportement en friction du ZnDTP fut effectuée avec deux additifs sans teneur en cendre: un triphénylphosphorothionate butylé (b-TPPT) et un phosphate d'amine (AP). Le b-TPPT a montré le coefficient de friction le plus bas pour les contacts DLC/DLC alors que l'AP a obtenu le coefficient de friction le plus bas lors de contacts acier/acier. Le b-TPPT a été choisi car il ne contient pas de métal alors que l'AP ne contient ni métaux ni soufre.

La microscopie à force atomique et la microscopie électronique à balayage environnementale ont été utilisées afin d'analyser les traces de friction et de comparer les tribofilms formés par les différents additifs. Le ZnDTP et le b-TPPT ont montré un comportement tribologique semblable pour les contacts acier/acier d'une part, ou DLC/DLC d'autre part. Les deux additifs ont formé sur l'acier une structure composée d'îlots. Un tribofilm a aussi été formé par les deux additifs sur la couche DLC, mais avec une épaisseur moins importante. Des tests de rayure ex-situ ont montré une plus faible adhésion du tribofilm de ZnDTP formé sur une
couche DLC que sur une surface d'acier. Aucun film d'AP n'a été détecté par AFM sur une couche DLC. 

Des analyses chimiques des tribofilms et des films thermiques formés par ces trois additifs sur des surfaces métalliques ou DLC ont été réalisées par spectroscopie de photoélectrons (XPS) et par spectroscopie d'ions secondaires avec détecteur de masse à temps de vol (ToF-SIMS). Le tribofilm de ZnDTP formé sur l'acier est composé d'un mélange de poly(thio)phosphates à chaîne courte avec une présence plus importante de zinc en surface et de phosphate de fer endessous. Des poly(thio)phosphates de zinc ont aussi été formés sur la couche DLC, même en l'absence de fer. Des poly(thio)phosphates de fer ont aussi été formés à la surface d'un acier à partir de b-TPPT, alors que la réaction de polymérisation sur une surface DLC en l'absence de contre-ion était plus difficile. Des polyphosphates étaient aussi présents dans le tribofilm formé à partir d'AP sur l'acier. Même si aucun tribofilm d'AP n'a été détecté par AFM sur une surface DLC, des produits de réactions tribochimiques ont été détectés dans les traces de frottement. Des orthophosphates ont principalement été détectés avec, de plus, une concentration significative d'alkylamines protonées.

Des expériences supplémentaires ont été réalisées afin de caractériser l'oxydation de composés contenant du soufre sur des surfaces DLC ou en acier. Bien qu'il soit reconnu que les thiols sont oxydés par l'oxyde de fer, il a été plus étonnant que des thiols sont oxydés sur des surfaces DLC. Des réactions de dialkylamines ont aussi été observées sur des surfaces DLC lors de tests tribologiques.
1. Introduction

1.1. Motivation

In the automotive and machinery industry, there is a great deal of interest in improving environmental friendliness, reliability, durability and energetic efficiency. Developing new technological solutions, such as using of lightweight materials, less harmful fuels, controlled fuel combustion processes or more efficient exhaust gas after-treatment, are possible ways to reduce the environmental impact of vehicles and machines. The reduction of wear and friction is a key element in decreasing the energy losses, particularly in engines and drive trains. Surface treatments and coatings contribute to a better lubrication with oils and can participate significantly in achieving these goals. A study ordered by the American Environmental Protection Agency, including both industry and governmental institutes, was carried out to evaluate the emissions of diesel engines for passenger cars, light- and heavy-duty vehicles, particularly to determine the relationship between harmful elements present in oil and emission gases [1]. It focused especially on the role of lubricant consumption on the emission before and after the catalyst and particles filter. It showed, among other results, a correlation between the phosphorus content of the lubricant and the amount of phosphorus deposited on the catalyst, independently of the type of calcium detergent used. It underlined the need for oils containing less harmful additives, for example, by replacing the widely used anti-wear additive zinc dialkyl dithiophosphate (ZnDTP) with alternatives additives.

Among protective coatings, the class of carbon-based materials shows interesting properties, combining low friction with a good wear resistance. For these reasons, they are increasingly being used as protective films for moving parts such as diesel injection needles, valve train parts, piston pins, tappets or gears [2]. The use of such non-metallic surfaces with new additives leads to investigations into the interaction between these protective overlayers and the additives with two kinds of approaches. The first one is to test operative systems or operative-like systems that allow the real operating conditions to be studied and the second one, which was the aim of this work, is a more fundamental approach, studying the behavior of single oil additives in a controlled environment using simple tribological systems. This approach allowed a focus on the adsorption of the additive onto the surface and the eventual formation of an additive protective layer, called a tribofilm, on carbon-based coatings. Topographical analytical methods, such as scanning electron microscopy (SEM) and atomic
force microscopy (AFM), and surface chemical analysis techniques, for example, x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS), were used to study the mechanisms of the reactions of additives with carbon-based surfaces and were compared with a steel sliding against steel contact system. The thermal film and tribofilm formation with ZnDTP was compared to a butylated triphenyl phosphorothionate (b-TPPT), which is free of zinc, and an amine phosphate (AP), which is both free of zinc and sulfur. The main tribological test performed here allowed the reactions of the additives to be analyzed under typical operating condition avoiding harsh test settings that would lead to accelerated wear. Thus, failure of the coating or a thermal solution degradation of the additive, which could interfere with the initial thermal film or tribofilm formation, could be avoided.

1.2. Tribology

The term "tribology" was introduced in 1966 by Jost [3]. He defined tribology as "the science and technology of interacting surfaces in relative motion and of the practices related thereto". Tribology covers aspects such as friction, wear and lubrication phenomena. Friction is the dissipation of energy between two sliding parts. The fundamental empirical laws of friction of solid bodies were formulated by Coulomb in 1875 from earlier works of Leonardo da Vinci and Amontons [4]:

- Static friction may be greater than kinetic (or dynamic) friction.
- Friction is independent of sliding velocity.
- Friction force is proportional to applied load.
- Friction force is independent of the apparent contact area.

The first characteristic parameter in tribology is the coefficient of friction ($\mu$). It is defined as the ratio between the friction force $F$ and the normal load $N$:

$$\mu = \frac{F}{N} \quad \text{(Eq. 1.1)}$$
The friction between two surfaces usually induces wear. A research group of the OECD defined wear in 1969 as "the progressive loss of substances from the operating surface of a body occurring as a result of relative motion at the surface" [5]. Abrasion, erosion, corrosion, adhesion, cavitation, fretting and fatigue are phenomena contributing to wear with different importance depending on the tribological system. Most of the time, several wear mechanisms occur simultaneously, making a clear distinction difficult. To evaluate wear, Archard postulated that the wear volume $V$ ($m^3$) was proportional to real contact area $A$ ($m^2$) and to the distance of sliding $L$ (m):

$$V = K A L = K L \frac{W}{H} \quad (Eq. \ 1.2)$$

The proportionality coefficient $K$ is called the Archard wear coefficient. $W$ is the load (N) and $H$ is the hardness of the softer surface (Pa).

### 1.3. Lubrication regimes

Three different lubrication regimes can be distinguished for two surfaces sliding against each other in a fluid-lubricated system:

1) Boundary lubrication: the two solids are in direct contact without separation by any fluid. The major contribution to friction is the adhesion between the asperities of the two bodies. Both elastic and plastic deformations occur, provoking heating and wear.

2) In mixed lubrication, a lubricant film is present between the contact surfaces, but some asperities are still in contact.

3) In hydrodynamic lubrication, the lubricant film is thick enough to avoid contacts between the two bodies. The physical properties of the lubricant play the dominating role. In this regime, there is a low friction and low wear rate behavior.
Figure 1.1 Schematic Stribeck curve representing the coefficient of friction versus the Stribeck number, $\eta V / P$ ($\eta$: viscosity; $V$: velocity; $W$: load). The three lubrication regimes are distinguished: boundary lubrication regime (1), mixed lubrication regime (2) and hydrodynamic lubrication regime (3).

**Elastohydrodynamic lubrication (EHL)**

Elastohydrodynamic lubrication (EHL) is defined as a mode of fluid-film lubrication involving an elastic deformation of the two contacting bodies and a variation of the viscosity due to the high local pressure. The loading area is enlarged, allowing the fluid to support the load. Hamrock and Dowson proposed formulae applicable to any contact, elliptical or linear, and valid for most materials [6]. They proposed a calculation of the minimum film thickness, $h_0$ (Fig. 1.2), as:

$$h_0 = 3.63 \left( \frac{U \eta_0}{E' R} \right)^{0.68} \left( \alpha E' \right)^{0.49} \left( \frac{W}{E' R^2} \right)^{-0.073} \left( 1 - e^{-0.68k} \right)$$  \hspace{1cm} (Eq. 1.3)

where:

- $U$ is the entraining surface velocity (m/s) where $U = (U_a + U_b)/2$
- $\eta_0$, dynamic viscosity of the lubricant at atmospheric pressure (Pa s)
- $E'$, reduced elastic modulus (Pa)
- $R'$, reduced radius of curvature (m)
- $\alpha$, pressure-viscosity coefficient (m$^2$/N)
W, contact load (N)

k, ellipticity parameter where k = a / b (a, axis perpendicular to the sliding direction; b, axis parallel to the motion direction).

The equation 1.3 gives the EHL film thickness in the case of perfect surfaces without asperities. Tallian introduced a parameter, $\lambda$, to compare the EHL film thickness with the surface roughness of the two contact surfaces:

$$\lambda = \frac{h_0}{\left(\sigma_1^2 + \sigma_2^2\right)^{1/2}} \quad \text{(Eq. 1.4)}$$

where $h_0$ is the minimum EHL film thickness in the contact area and $\sigma_1$ and $\sigma_2$ are the root-mean-square roughness of the contact surfaces [7]. It is possible to distinguish several domains with different contact and damage characteristics. When $\lambda < 1$, smearing or surface deformation with wear can occur and spalling is possible. For $1 < \lambda < 1.5$, spalling and glazing can appear. Between 1.5 and 3, some glazing may occur and when $\lambda > 4$, the two surfaces are well separated [7, 8].

Figure 1.2 Contact region and film pressure distribution in an elastohydrodynamic contact ($h_c$: central film thickness; $h_0$: minimum film thickness).
1.4. Surface coatings

1.4.1. Wear resistant coatings

Depending on the tribological requirements, many different techniques exist to improve the wear resistance or the friction between metallic components. Thermal surface treatments, such as localized hardening by laser processing or diffusion processes like carburizing or nitriding, can improve the wear resistance of steel. It implies a superficial modification of the microstructure and/or of the composition of the component itself. Another possibility is the deposition of a different material as coating. The deposition techniques can be divided into four categories:

− solid state processes (e.g. lamination, sintered coating or detonation spraying)

− molten or semi-molten state processes (e.g. thermal spraying, welding or laser surface treatment)

− solution state processes (e.g. chemical solution deposition, electrochemical deposition or sol gel processing)

− gaseous state processes (e.g. chemical vapor deposition, physical vapor deposition, ion beam assisted deposition or ion implantation)

Diamond-like carbon coatings (DLC) belong to the last category and the following sections will emphasize the properties and the state-of-the-art of this class of coatings.

1.4.2. Overview of DLC coatings

Diamond-like carbon (DLC) coatings build a material class, rather than a single material. The DLC term describes metastable amorphous carbon coatings containing a fraction of sp$^3$ bonds. It includes hydrogen-free amorphous carbon coatings (a-C), hydrogenated amorphous carbon coating (a-C:H), tetrahedral amorphous coatings (ta-C) and hydrogenated tetrahedral amorphous coatings (ta-C:H). These different types of coatings can be represented on a ternary phase diagram [9, 10]. It is also possible to dope DLC coatings with nitrogen, silicon or metals. This allows the as-named DLC coatings to cover a wide range of hardness (between 3 and 80 GPa) and electrical conductivity (from insulator to semi-conductor).
A large number of techniques exist to deposit DLC coatings. Ion beam deposition, sputtering, cathodic arc, pulsed laser deposition and plasma enhanced chemical vapor deposition (PECVD). Sputtering is widely used for industrial application while PECVD is preferred for laboratory work. Depositions processes are described in several review papers [10, 11] and a-C:H deposited by PECVD is described more in details in the experimental chapter (section 2.1.1).

Figure 1.3 Ternary phase diagram of bonding in hydrogen-containing amorphous carbon coating [10]

The strong interest in DLC coatings is due to an exceptional combination of chemical, physical and mechanical properties. The DLC coatings are chemically inert to organic solvents and inorganic acids. For example, such coatings are not attacked by a solution of three parts H$_2$SO$_4$ to one part HNO$_3$ at 80°C (concentrated acids), which dissolves all hydrocarbon polymers and graphitic carbon materials, but does not attack diamond [12].

DLC coatings are also bio- and haemo-compatible and are promising for orthopedic and other coated implants, like heart valves, stents and drug delivery devices [13-17]. These films can act as a good diffusion barrier against oxygen for PET bottle or medical solutions [18, 19].

1.4.3. Tribological properties of DLC coatings without fluid lubrication

Low friction, low wear behavior and high hardness make DLC coatings interesting for tribological systems. The hardness of DLC coatings is distributed between less than 10 GPa for soft a-C:H coatings up to 90 GPa for some ta-C coatings [10, 11]. DLC coatings generally
have low friction coefficients sliding against a large range of materials; however, this is dependant on the testing conditions.

Anderson et al. showed that ta-C films have different friction behavior depending on the environment [20]. In high vacuum, a ta-C coating gave a friction coefficient as high as 0.65 and a high wear rate. The introduction of low pressure (1300 Pa) gases into the chamber led to a decrease in the friction coefficient to approximately 0.25, 0.15 and 0.07 for oxygen, hydrogen and water, respectively. Moreover, wear was significantly reduced. They repeated the same experimental procedure with a-C:H coatings and found different effects. The friction coefficients in all environments were lower than 0.05. After a longer test in high vacuum, a friction coefficient of 0.007 was achieved with an a-C:H film. The high friction coefficient of ta-C films in vacuum was explained by a lack of adsorbed molecules at the DLC surface, especially during sliding. Thus, dangling bonds at the surface can form covalent bonds with the other sliding surface. The influence of this phenomenon decreases in the presence of adsorbable gas, allowing lower friction coefficients to be reached. In a-C:H coatings, most of the carbon atoms are bound with hydrogen, decreasing the number of free $\sigma$ bonds at the surface, therefore, the friction coefficient is lower, particularly in vacuum.

Ronkainen et al. tested tetrahedral amorphous coatings with different hydrogen concentration sliding against steel in dry air (0% RH) [21]. In this case, the friction coefficient dropped from 0.71 for hydrogen-free ta-C films to 0.28 for a coating containing 16 at. %. During other tests at room temperature with 50% relative humidity, a-C:H and ta-C sliding against a steel or alumina ball were compared. The lowest friction coefficient in the case of a-C:H was around 0.02, in comparison to 0.1 for ta-C films. However, the wear resistance of the ta-C coating was better due to the higher sp$^3$ bonding proportion that makes the coatings harder and denser. With micro-Raman analyses, they observed evidence of graphitization of the surfaces, but with a lower intensity for ta-C than for a-C:H.

A crucial factor in determining the friction behavior of hydrogenated DLC is humidity. For a-C:H sliding against a-C:H, Eryilmaz et al. observed an increase of the friction coefficient from 0.006 in dry nitrogen to 0.065 in humid nitrogen (100% RH) [22]. Li et al. also found an increase of the friction coefficient from 0.035 in dry nitrogen to about 0.2 in humid nitrogen (100% RH) for a steel ball sliding against a-C:H [23]. A carbon-rich transfer layer was observed on the steel ball tested in dry nitrogen, as has also been reported in other studies [24,
This graphitic layer helps to reduce both friction and wear, but loss of adhesion of the transfer layer with the substrate may make the friction coefficient unstable [26, 27].

1.4.4. Alloyed DLC coatings

Certain properties of DLC coatings can be improved by alloying with other elements. For example, the friction in high humidity conditions can be reduced by doping the a-C:H with silicone or fluorine [28, 29]. Many studies have reported the influence of metal addition on the tribological properties of DLC coatings, for example W [30], Cr [31], Cu [32], Ag [33] or TiAl [34]. The incorporation of metals can also increase hardness. Zehnder et al. increased the hardness by alloying the a-C:H with titanium, forming a nanocomposite of TiC crystallites in an a-C:H matrix [35]. The maximum hardness was found when the ratio between crystalline and amorphous phases was near 80 %. It corresponded to a crystallite size of 4-5 nm giving a hardness of 35 GPa. Ti-doping can also decrease the internal stress from about -9 GPa to -1.5 GPa for 10 at.% Ti [36]. By incorporating silicone, Ban and Hasegawa reduced the residual stress of a-C:H coatings from 2.5 GPa to 1.0 GPa for 32 at.% silicone, while the nanoindentation hardness was kept almost constant between 13 GPa and 15 GPa [37]. Molybdenum is also able to decrease the internal stress, but this is accompanied by a reduction in hardness [38].

As well as the formation of nanocomposites of carbides in an amorphous matrix, reduction of the internal stress is possible by producing multilayers [39-41]. Multilayers allow a better wear resistance, but the friction behavior is not always influenced in the same way depending on the dopants and on the testing environment. The surface energy and wettability of the coating can also be changed using dopants. Grischke et al. studied the influence of oxygen during the deposition of fluorine- or silicone-containing DLC [42]. The surface energy decreased from 41 mN/m for a pure DLC to 20 mN/m for fluorinated DLC. Kwok et al. doped a DLC coating produced by plasma immersion ion implantation and deposition with phosphorus and obtained excellent coating wettability [15].
1.5. Lubricants and oil additives

1.5.1. Overview [43, 44]

Hydrocarbon base oils can be classified in two groups: mineral and synthetic oils. Mineral oils are manufactured directly from crude oil. Their composition is very complex and consists of hydrocarbons, including more than a hundred aliphatic and aromatic compounds. It also contains impurities and sulfur is present even after refining in varying quantities, depending on the type of crude oil. The lubrication properties and oxidation stability vary with the composition. Mineral oils are the most commonly used because of their low price in comparison to synthetic oils. However, synthetic oils are being increasingly used due to their better oxidation stability, enhanced durability, higher purity and superior viscosity at high temperature. Synthetic oils are produced using low weight hydrocarbons from the cracking process of crude oil and, therefore, contain a smaller range of molecules. Synthetic hydrocarbon lubricants can be divided into several categories: polyalpha-olefins, esters, cyclo-aliphatics and polyglycols. Additives are added to the base oil to produce fully-formulated lubricants able to fulfill the user requirements. These additives can be classified according to their function and some examples of these classes that are related tribological properties are:

- Friction modifiers adsorb onto surfaces, reducing wear and friction. They are mostly efficient at low temperature and are composed of a polar group with an unbranched aliphatic tail. They are often used to prevent stick-slip phenomena.

- Anti-wear additives (AW) protect rubbing surfaces at higher temperature than friction modifiers. They react chemically with the surfaces to form a protective film.

- Extreme-pressure additives (EP) react with metallic surfaces under harsh tribological conditions like high contact pressure at slow speed and fluid-film failure at high speed. The differentiation between these and anti-wear additives is not always clear.

- Viscosity improvers lower the oil viscosity at low temperature.
1.5.2. Zinc dialkyl dithiophosphates

ZnDTP is the most commonly used anti-wear/extreme pressure additive in oil since the Second World War. It was first used because of its good anti-oxidant properties, but was then found to be a good antiwear and mild extreme-pressure additive. The presence of zinc, phosphorus and sulfur in ZnDTP is leading to its replacement by alternative anti-wear additives.

Habeeb and Stover found aryl ZnDTPs to have the highest thermal stability and secondary ZnDTPs, with branched alkyl chains, to have the lowest [45]. However, secondary ZnDTPs are the best antioxidants and aryl ZnDTPs are the poorest antioxidant [43]. ZnDTPs can react with hydroperoxides and peroxy radicals, stopping the autooxidation cycle that is responsible for oxidation of the hydrocarbon chains in the base oil [46].

In the absence of hydroperoxides and peroxy radicals, a thermal degradation of ZnDTP occurs at temperatures between 130°C and 230°C, depending on the alkyl groups of the molecule [47]. Using 31-P NMR spectroscopy, Fuller et al. did not detect a thermal degradation of ZnDTP in solution at 100°C, but they did for a solution heated to 150°C [48]. After heating the oil for 48 hours at 100°C, 99% of ZnDTP in solution remained unreacted. However, at 100°C, a thermal film was found on a steel surface with XANES. This film contained some phosphate and another intermediate species derived from ZnDTP. Further, Bovington and Dacre found that, at low temperature, ZnDTP adsorbed reversibly on steel. But at temperatures higher than 60°C, the additive reacted irreversibly [49].

In a first step, the ZnDTP alkyl groups are exchanged from the sulfur to the oxygen atoms, as Coy and Jones observed using 31P-NMR spectroscopy [50]. In a further step, Spikes proposed the following polymerization reaction of the dithiophosphate [47]:

As only a small sulfur concentration is generally detected in the film, thionyl groups could be hydrolyzed by water or a network of ultraphosphate could be initially built up that needs the release of the second thionyl group bound to the phosphorus atom, followed by the reaction of...
the polyphosphate with iron oxide at the steel surface to form linear polyphosphate chains [47].

The tribofilm derived from ZnDTP has been the subject of many studies. Under boundary conditions, ZnDTP reacts on iron oxide to build up an antiwear film with a pad-like structure, consisting mainly of (poly)phosphates. The film thickness varies with the tribological conditions from a few nanometers [51, 52] to approximately 100 nm [53-56]. Martin et al. found the tribofilm to have a two-layer structure with a 10 nm thick long chain zinc poly(thio)phosphate on top of a mixed iron and zinc short chain polyphosphate layer [55]. They did not observe any sulfide/oxide layer at the interface between steel and tribofilm.

The hardness of ZnDTP-derived tribofilm was found to be within the range of polymeric glass materials. Bec et al. characterized, with nanoindentation, a solvent-cleaned tribofilm composed of a polyphosphate layer on top of a sulfide/oxide layer covering the steel substrate. They measured a hardness of 2 GPa and a reduced modulus of 30-40 GPa for the polyphosphates layer and 4.7GPa and 90 GPa, respectively, for the sulfide/oxide layer [53]. Aktary et al. investigated variations in the nanomechanical properties with the rubbing time [57]. Although morphology changed with time, similar hardnesses and elastic moduli were measured after testing for 5 minutes and 2 hours. The reduced modulus was around 90 GPa and the hardness between 2.3 and 5.0 GPa.

Pereira et al. analyzed the antiwear film with XANES spectroscopy [58]. They found that most of the sulfur was present as zinc sulfide with a small amount of unreacted ZnDTP, but iron sulfide was absent. Phosphorus K-edge XANES spectroscopy confirmed that the main component was a polyphosphate.

1.5.3. Ashless phosphorus-containing additives

Among metal-free, phosphorus-containing additives, several kinds of compounds are of particular interest due to their anti-wear properties. They act in a similar way to ZnDTP, i.e. by chemisorption onto the metallic surfaces and the formation of a protective film. The main classes are neutral and acid phosphates, phosphites, phosphonates and amine salts [43, 59].

Schumacher and Zinke studied the antiwear behavior of several compounds based on the atomic structure of dithiophosphates, replacing the sulfur atoms by oxygen and varying the alkyl groups [60]. Similar wear and friction properties for both monothiophosphates and
dithiophosphates were observed and a clear correlation was observed between the presence of phosphorus in the antiwear film and a lower wear regime. On the other hand, there was no correlation with the sulphur content. They also established that an increased thermal stability of the phosphorous-containing compounds maintained good additive performance at higher temperature, although some thermal instability is required to allow the compound to react.

Najman et al. studied the tribofilms built up by a diaryl and a triaryl phosphate in steel against steel tribological contacts with XANES spectroscopy [61]. A short-chain iron (II) polyphosphate was generated from both after only one minute of sliding. An amine phosphate was also investigated. The antiwear film was also composed of an iron (II) polyphosphate, but with an ammonium phosphate layer above. The presence of an ammonium cation was thought to contribute to the growth of the phosphate film. In another investigation, Najman et al. studied the behavior of thiophosphates under similar tribological conditions [62, 63]. These additives also built up iron (II) polyphosphates film during the rubbing test. In contrast with ZnDTP, sulfur reacted to form iron sulfates after a certain time and the formation of oxidized and reduced intermediate sulfur species was observed for reduced rubbing time.

Heuberger et al. studied the reactivity of several alkylated phosphorothionates on steel with XPS [64]. They were found to be less efficient than ZnDTP for protection against wear. The tribofilm built up during tests performed at 30°C contained only pyro- or orthophosphates while the chain length increased at a test temperature of 150°C. The sulfur peak was assigned to sulfates, confirming the analysis performed by Najman et al. The tribofilms were thinner with increasing length of the alkyl chains bound on the phenyl group of the phosphorothionates. This was related to decreasing solubility with longer alkyl chains.

Minami et al. proposed hydroxyalkyl phosphates and phosphonates as anti-wear additives for polar synthetic esters oils, where conventional antiwear additives are inefficient [65, 66]. The additives with saturated alkyl and aryl groups showed good antiwear properties while molecules with allylic groups were not beneficial. The authors explained this phenomenon by a preferential oxidation of the allylic groups compared to the saturated ones.
1.6. Interaction between DLC and oil additives

As diamond-like carbon coatings are increasingly being used as an additional protection in oil-lubricated systems, investigations into the interactions with oil additives are becoming increasingly important. Interactions of dialkyl dithiophosphate with a-C:H surfaces were observed by Kalin et al. [67], reducing the wear and avoiding graphitization at high temperature (150°C). However, a chemical reaction between DLC and amine phosphate was not observed with AES, XPS or Raman techniques, despite a reduction in wear. Using DLC coatings doped with silicon, titanium or tungsten, both of the aforementioned additives had a beneficial effect on the wear rate of doped DLC for self-mated contacts [68].

Podgornik et al. compared the influence of anti-wear and extreme-pressure additives in steel/steel, DLC/steel and DLC/DLC contacts, using a WC doped hydrogenated DLC coating with a multilayer structure [69-72]. They found the combination DLC/steel to have the best tribological behavior during both running-in and steady-state friction regimes [70]. A sulfur-based extreme-pressure additive combined with DLC had a beneficial tribological effect, but due to the harsh test conditions (maximum Hertzian pressure between 2.4 and 5.6 GPa), the coatings were worn through during the tests [71]. No tribofilm was observed on DLC following sliding on DLC, but tribofilms were built up for the steel/DLC contact and on worn DLC surfaces. These tribofilms allowed a low friction of about 0.055 to be reached and was made up of material from the coating as well as additive-derived, sulfur-containing products. With XPS analysis, the authors observed FeS, FeS$_2$ and WS$_2$ in the tribofilm [69]. Studying the tribological behavior of formulated oil for DLC/steel contacts, Podgornik et al. found pure a-C:H to have the lower wear rates and WC doped DLC to give the lowest friction coefficient [73].

Boundary lubrication of ZnDTP coupled with molybdenum dithiocarbamate (MoDTC) was studied using different kinds of DLC coatings, i.e. a-C:H, a-C and Ti-C:H [74]. These additives appeared to react on DLC surfaces and XPS analysis showed similar tribofilm composition on both steel and DLC. The main role of ZnDTP was to improve the formation of a molybdenum disulfide film. The presence of hydrogen in the carbon-based coating also seemed to act beneficially on the additive reaction.
Literature


Introduction


Introduction


2. Materials and methods

2.1. DLC coatings

2.1.1. Coating procedure

Amorphous hydrogenated carbon coatings were prepared using a plasma enhanced chemical vapor deposition technique (PECVD). The sample holder was connected with a radio-frequency power supply (13.56 MHz) to generate a plasma. The other electrode that includes the walls of the chamber was grounded. The possibility existed to perform alternatively or simultaneously, a physical vapor deposition process thanks to a magnetron placed on the upper part of the deposition chamber (Fig. 2.1).

Before introduction into the chamber, the substrates were cleaned in an ultrasonic bath with ethanol and acetone. The chamber was evacuated with a turbopump until a pressure lower than $5 \times 10^{-7}$ mbar was achieved. The substrates were etched with argon with a -600V bias voltage to remove the oxide layer, directly followed by the deposition of an adhesion-promoting interlayer of Si-a-C:H from tetramethylsilane (TMS). Then, a-C:H was deposited with acetylene gas at a pressure of 2 Pa and a -400V selfbias. The deposition of a standard pure a-C:H coating used for tribological tests lasted 2 hours to deposit $2 \pm 0.2$ µm. The deposition parameters for this standard coating deposition are shown in table 2.1. If needed, it was possible to alloy the DLC coating with a metal using the magnetron. The steel used as substrate was an AISI 52100 bearing steel with a hardness of 700 Hv. The steel composition is shown in table 2.5.

The deposition process shown in table 2.1 was punctually monitored with a differentially pumped mass spectrometer unit SPM200 (Pfeiffer Vacuum, Aßlar, Germany). The analyzed mass range was between 1 and 100, each cycle lasting 20s. The detection limit was in argon at $10^{-2}$ mbar lower than 500 ppb for water vapor, lower than 100 ppb for oxygen, nitrogen or carbon dioxide.
Table 2.1 Deposition parameters for the standard DLC coating used in most of the tribological experiments. The oxide layer was removed during step 1, the adhesion-promoting interlayer was built up during step 2 and DLC deposition occurred during step 3.

<table>
<thead>
<tr>
<th>Step</th>
<th>Gas</th>
<th>Gas flow</th>
<th>Pressure</th>
<th>Selfbias voltage</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ar</td>
<td>24.0 sccm</td>
<td>2.4·10⁻² mbar</td>
<td>-600 V</td>
<td>40 min</td>
</tr>
<tr>
<td>2</td>
<td>TMS</td>
<td>9.6 sccm</td>
<td>1.6·10⁻² mbar</td>
<td>-600 V</td>
<td>2 min</td>
</tr>
<tr>
<td>3</td>
<td>C₂H₂</td>
<td>7.2 sccm</td>
<td>2.0·10⁻² mbar</td>
<td>-400 V</td>
<td>120 min</td>
</tr>
</tbody>
</table>
2.1.2. Coating characterization

The hardness and the Young's modulus of the DLC coatings were determined by nanoin indentation with a Berkovich diamond tip. The instrument used is a Nano Indentation Tester (CSM Instruments SA, Peseux, Switzerland). The measurements were performed in controlled-load mode with constant load rates. The load resolution is 40 nN for a maximum load of 500 mN and the depth resolution is 0.04 nm. The hardneses and elastic moduli were calculated with the method proposed by Oliver and Pharr [1-3]. The calibration procedure was performed with a fused silica sample (E = 71.7 GPa). The reduced modulus $E_r$, which includes both deformations of the material and of the diamond tip, was calculated as follows:

$$\frac{1}{E_r} = \frac{1 - \nu_{\text{specimen}}^2}{E_{\text{specimen}}} + \frac{1 - \nu_{\text{tip}}^2}{E_{\text{tip}}}$$  \hspace{1cm} (2.1)$$

where $E_{\text{specimen}}$ and $\nu_{\text{specimen}}$ are the Young's modulus and the Poisson's coefficient of the sample and $E_{\text{tip}} = 1140$GPa and $\nu_{\text{tip}} = 0.07$ are the typical values for a diamond tip. For an ideal Berkovich tip, the contact area $A(h)$ is equal to $24.5 \cdot h_c^2$, where $h_c$ is the contact depth. As the real tip apex has a certain radius due to tip imperfection and to wear, the real contact area is determined with the following formula:

$$A(h_c) = 24.5 \cdot h_c^2 + \sum_{i=0}^\infty a_i h_c^{1/2}$$  \hspace{1cm} (2.2)$$

where the coefficients $a_i$ are determined with measurements on the reference sample. As the contact depth $h_c$ differs from displacement into the surface due to sinking-in or piling-up of the material, the contact depth is calculated as follows:

$$h_c = h - \epsilon \frac{P}{S}$$  \hspace{1cm} (2.3)$$

$\epsilon$ is a constant depending of the tip geometry ($\epsilon = 0.75$ for a Berkovich tip), $P$ is the applied load and $S$ is the measured stiffness at the unloading point (in N/m).

For all tested coatings, the nanoindents were performed with a loading and unloading rate of 10 mN/min with a maximum load of 5 mN. This represents an indentation depth between 120 and 160 nm for a 2.0 ± 0.2 μm thick coating. A multiple cycle measurement was performed to determine the hardness in function of the depth.
To determine the adhesion of the coatings with the steel substrates, scratch tests were performed on the DLC coatings with a Micro Scratch Tester (CSM Instruments SA, Peseux, Switzerland). The instrument had a normal load resolution of 100 μN, a tangential force resolution of 0.3 mN and a depth resolution of 0.3 nm. The diamond Rockwell indenter used had a radius of 100 μm. Four scratches were performed for each tested sample. The load was linearly increased between 30 mN and 30 N to make 3 mm long scratches with a speed of 6 mm/min. To characterize the scratches, four different critical loads (Lc) were determined: the first crack, the first coating chipping, the first coating spalling and finally the beginning of the continuous total pull out of the coating. An example of these four typical stages to a total delamination of the coating is shown in Figure 2.2.

![Figure 2.2 Examples of the four critical load stages for a pure a-C:H coating. (a) Lc1: first crack, (b) Lc2: first chip, (c) Lc3: first coating spallation and (d) Lc4: the coating is continuously broken through.](image-url)
To ensure constant structural quality of the pure a-C:H coatings over time, Raman spectroscopy was periodically performed on freshly produced coatings with a Renishaw NIR 780 TF instrument (Renishaw plc, Wotton-under-Edge, Gloucestershire, England) coupled to a Leica microscope with a 50x objective. Raman spectra were acquired at $\lambda = 633$ nm with a He-Ne laser. Raman shifts were measured over a wave number range from 500 to 2400 cm$^{-1}$. Two well-known contributions are present in such Raman spectra, the G and D peaks. Both are due to sp$^2$ sites only. The G peak around 1560 cm$^{-1}$ corresponds to the bond stretching of all pairs of sp$^2$ atoms, whether in chains or aromatic rings. The D peak at around 1360 cm$^{-1}$ corresponds to the breathing mode of the sp$^2$ atoms in rings only. Both peaks were fitted with Gaussian curves using a linear background subtraction. Using UV excitation, a T peak would be present at around 1060 cm$^{-1}$, corresponding to the C-C sp$^3$ vibrations [4, 5].

![Raman spectrum example](image)

Figure 2.3 Example of Raman spectrum of a pure a-C:H coating.

### 2.2. Materials

#### 2.2.1. Additives and lubricant

The base lubricant used was a fully synthetic polyalpha-olefin (PAO6, e-ion, Belgium) called simply PAO in this dissertation. Three extreme pressure/anti-wear additives were used: zinc dialkyl dithiophosphate (ZnDTP), an ashless butylated triphenyl phosphorothionate (b-TPPT) and an amine phosphate mixture (AP). A friction modifier (FM) was also used in the case of the study of mixed zinc-free additives. The additives investigated in this work were all commercially available and were provided by Ciba Specialty Chemicals (Switzerland). Their
molecular structures and commercial names are shown table 2.3. Typically, the tribological tests were performed in PAO with 1 wt% additive. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used to measure the content of zinc, phosphorus and sulfur of the different oils tested. These results are shown in table 2.2. Further tribological tests were performed with AP and a sulfur containing compound. This additional compounds were 1-propanesulfonic acid (Sigma-Aldrich AG, Switzerland) and 1-octanethiol (Sigma-Aldrich AG, Switzerland). Both oils contained 1 wt% AP and the sulfur compounds were added to give a ratio of P/S equal to 1. Tribological experiments in PAO and 1 wt.% didodecylamine (Sigma-Aldrich AG, Switzerland) were also performed in the absence of any sulfur- or phosphorus-containing compounds.

Table 2.2 Zn, P and S content of the oils used to performed tribological tests, measured with ICP-AES analysis.

<table>
<thead>
<tr>
<th>Oil</th>
<th>Zn (mg/kg)</th>
<th>P (mg/kg)</th>
<th>S (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt.% ZnDTP, PAO</td>
<td>440</td>
<td>832</td>
<td>1970</td>
</tr>
<tr>
<td>1 wt.% b-TPPT, PAO</td>
<td>&lt;1</td>
<td>741</td>
<td>832</td>
</tr>
<tr>
<td>1 wt.% AP, PAO</td>
<td>&lt;1</td>
<td>470</td>
<td>&lt;1</td>
</tr>
<tr>
<td>1 wt.% FM, PAO</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>
Materials and methods

Table 2.3 Molecular structure of the additives used for this study with their commercial names in brackets.

\[
\begin{align*}
\text{ZnDTP (Hitec® 7169)} & : \\
\text{AP (Irgalube®349)} & : \\
\text{b-TPPT (Irgalube®232)} & \\
\text{Friction modifier (Irgalube®F10A)} & 
\end{align*}
\]
Further chemical analyses were performed on b-TPPT. For carbon and nitrogen determination, the additive was first burnt in a combustion furnace at around 1000°C under an oxygen gas flow. Then the carbon concentration was determined as carbon dioxide by means of an infrared detector and nitrogen as N\textsubscript{2}, with a thermal conductivity detector. The results are reported in the table 2.4 in weight percent and also in atomic ratio by normalizing the phosphorus content to 1.

### Table 2.4. Quantitative analysis of the additive b-TPPT.

<table>
<thead>
<tr>
<th></th>
<th>Mass g/100g (%)</th>
<th>Normalized atomic concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>8.4 ± 0.1</td>
<td>1</td>
</tr>
<tr>
<td>S</td>
<td>8.6 ± 0.1</td>
<td>0.99</td>
</tr>
<tr>
<td>Zn</td>
<td>&lt; 0.01</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>65.9 ± 0.5</td>
<td>20.2</td>
</tr>
<tr>
<td>N</td>
<td>&lt; 0.1</td>
<td>-</td>
</tr>
</tbody>
</table>

Additionally, the b-TPPT additive was analyzed with electrospray ionization mass spectrometry (ESI-MS) with a Finnigan LCQ instrument (Thermo Fisher Scientific, Waltham, MA, USA). Compounds with masses of interest were further analyzed with tandem MS-MS. Gas chromatography-mass spectrometry (GC-MS) analysis was also performed on b-TPPT using a Finnigan PolarisQ instrument (Thermo Fisher Scientific, Waltham, MA, USA) with a Restek RTX-1MS column (15m, 0.25µm film thickness; Restek Corp. Bellefonte, PA, USA). Helium was used as carrier gas and a volume of 1 µl was injected at 280°C in splitless mode. A 4-steps temperature program was applied: 3 min at 90°C, heating to 205°C at 20°C/min, heating to 280°C at 1.5°C/min and finally 10 min at 280°C. Mass spectra were taken in a m/z range between 100 and 750. The b-TPPT additive was diluted 10'000 times in heptane for GC-MS analyses and in CH\textsubscript{3}CN / H\textsubscript{2}O / CH\textsubscript{3}COOH (50/50/0.1) for the ESI-MS analyses.
2.2.2. Tribological specimens

The steel used for tribological tests with steel/steel contact or as DLC substrate was always the bearing steel AISI 52100. The steel was solution treated at a temperature of 850°C followed by oil quenching and tempering at 220°C to reach a hardness of 700 Hv. The plates were first ground with silicon carbide papers (granularity 220, 600 and 1000). Then the samples were polished with a diamond suspension of 6 μm, 3 μm and finally 1 μm (Presi, Grenoble, France) to reach a roughness R_a of 9 ± 1 nm. The same procedure was used to prepare DLC substrates and steel plates for tribological tests. The counter-parts were ball segments wire-cut from bearing joints with a 50 mm external diameter (FLURO-Gelenklager Gmbh, Rosenfeld, Germany) or 6mm diameter AISI 52100 balls (PCS Instruments, London, England). Both counter-parts had a standard ball-bearing surface finish quality.

Table 2.5 Composition of the AISI 52100 bearing steel.

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>C</th>
<th>Cr</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>97 %</td>
<td>0.98-1.1 %</td>
<td>1.45 %</td>
<td>0.35 %</td>
<td>0.23 %</td>
<td>&lt; 0.025 %</td>
<td>&lt; 0.025 %</td>
</tr>
</tbody>
</table>

Figure 2.4 Scheme of the HFRR tribological system with a ball-bearing segment (diameter: 50mm) immersed in oil.
2.3. Tribological measurements

2.3.1. Pin-on-disc

Tribological experiments were performed at room temperature in air or in pure PAO to observe the effect of oil lubrication. The instrument used was a ball-on-disc tester from CSM Instruments SA (Peseux, Switzerland). DLC sliding against DLC experiments were performed using the 50 mm diameter ball segments with a 5 N constant load in pure PAO and in air with 30 and 70 % relative humidity.

2.3.2. High Frequency Reciprocating Rig

The tribological measurements were mainly carried out with a High Frequency Reciprocating Rig (HFRR; PCS Instruments, London, England). 100Cr6 (AISI 52100) plates, uncoated or DLC-coated, were tested against uncoated or DLC-coated 100Cr6 ball segments (50mm diameter), respectively. After preliminary tests, standard conditions to perform comparative tests were chosen and are presented in table 2.6. These settings gave both boundary and mixed lubrication regimes. Each test was carried out with 4 mL oil. Before the experiments, the tribological pairs were cleaned in an ultrasonic bath with heptane and ethanol (Sigma-Aldrich AG, Switzerland). After the tests, the samples were washed by pouring cyclohexane (Sigma-Aldrich AG, Switzerland) over the surface without using an ultrasonic bath. Experiments without lubricant were also carried out for DLC sliding against DLC contacts at room temperature with 30 and 70 % relative humidity.

<table>
<thead>
<tr>
<th>Table 2.6 Standard condition used for HFRR tests.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Load</td>
</tr>
<tr>
<td>Track length</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Frequency</td>
</tr>
<tr>
<td>Duration</td>
</tr>
</tbody>
</table>
Materials and methods

The elastic deformation of mating parts can be calculated with the Hertzian equation. The contact area radius $a$, maximum pressure $p_{\text{max}}$, and reduced modulus $E_r$ for a ball-on-flat contact are given by the equations 2.4, 2.5 and 2.6, respectively:

\[
a = \left( \frac{3Wr}{4E_r} \right)^{1/3} \quad (2.4)
\]

\[
p_{\text{max}} = \frac{3W}{2\pi a^2} \quad (2.5)
\]

\[
E_r = \frac{(1-\nu_1^2)}{E_1} + \frac{(1-\nu_2^2)}{E_2} \quad (2.6)
\]

Where $W$ is the normal load, $r$ is the ball radius and $E_r$ is the reduced modulus calculated with the Young's modulus $E_{1,2}$ and the Poisson's coefficient $\nu_{1,2}$ of the two contact body (for steel, $E_1 = E_2 = 210$ GPa and $\nu_1 = \nu_2 = 0.3$). For the ball segments (diameter: 50 mm), this gave a contact radius of 93 $\mu$m for a maximum pressure of 274 MPa.

2.3.3. Mechanical tests on tribofilms

After HFRR tests in PAO containing 1 wt.% ZnDTP, ex-situ scratch tests on the tribofilms formed on steel and on DLC were carried out with a Basalt®-Must tribometer (Tetra Gmbh, Ilmenau, Germany). A sapphire ball indenter with a diameter of 3 mm was used with a constant load of 100 mN and a sliding speed of 2 mm/s. Following the scratch tests, the surfaces and tribofilms were examined with environmental SEM.

2.4. X-ray photoelectron spectroscopy

2.4.1. Principles of x-ray photoelectron spectroscopy analysis

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), is an ultra-high vacuum method based on the measurement of the binding energy of the electrons by the photoelectric effect. The sample surface is irradiated with a monoenergetic beam of x-rays, usually from an aluminum or magnesium anode. The characteristic energies and widths of the main radiations are, respectively, 1486.6 eV and 0.85
eV for the Al Kα line and 1253.6 eV and 0.70 eV for the Mg Kα line. The use of a monochromator can reduce the width of the Al Kα line below 0.3 eV. At the same time, it also removes other radiation lines from the anode and reduces the Bremsstrahlung radiation, decreasing the level of the background.

During the photoemission process (Fig. 2.5a), an x-ray photon is absorbed by an electron. If the energy is high enough, the photoelectron is ejected. Applying the principle of energy conservation, the kinetic energy of the electron $E_{\text{kin}}$ is:

$$E_{\text{kin}} = h\nu - E_b - \Phi_s \quad (2.7)$$

$h\nu$ corresponds to the energy of the incident photon, $\Phi_s$ is the working function of the spectrometer and $E_b$ is the binding energy of the emitted photoelectron. The non-scattered electrons give a peak at a binding energy characteristic of an element and also of a chemical state. Inelastically scattered electrons contribute to the background of the spectra.

![Figure 2.5 Mechanism of emission of (a) a photoelectron and (b) an Auger electron](image)

In addition to the photoelectric process, an Auger electron may be emitted due to the relaxation of the excited atom after the emission of the photoelectron (Fig. 2.5b). The emission of a fluorescent x-ray photon is an alternative relaxation process to the release of an Auger electron. The kinetic energy of the Auger electron is independent of the energy of the excitation source. Often, the photoionization process leads to the emission of both a photoelectron and an Auger electron. The sum of the kinetic energy of the two electrons cannot exceed the energy of the incident x-ray photon.
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2.4.2. Instrumentation and experimental settings

XPS analyses were performed with a Quantum 2000 photoelectron spectrometer (Physical Electronics, Chanhassen, MN, USA). The x-ray source is monochromatic Al Kα radiation. Scanning of the sample is achieved with a deflection system that deflects the electron beam striking the anode. The x-ray beam is then focused on the sample by a monochromator. Beam sizes between 7 and 200 µm can be obtained. Charge compensation is achieved by exposing the insulating surfaces simultaneously to low-energy electrons and low-energy argon ions during the analysis. Emitted photoelectrons are guided into an electrostatic hemispherical analyzer. Then, the photoelectrons are multiplied by a channel plate and detected with a 16-channel position sensitive detector. Both emission angle \( \theta \) and source-to-analyzer angle \( \gamma \) are 45° (Fig 2.6). Additionally, depth profiling is possible using an argon ion gun with acceleration voltage between 1 and 4 kV.

![Figure 2.6 Geometrical scheme of the angles between the sample, the incident x-ray beam and the detector direction. \( \theta \) is called the emission angle and \( \gamma \) is the source-to-analyzer angle.](image)

The analyses were performed in fixed analyzer transmission mode. Typically, the pass energy and the step size were 117.4 eV and 0.5 eV for survey spectra or 58.7 eV and 0.125 eV for high-resolution analyses. If not stated otherwise, the beam size was 100 µm. Element mapping was also carried out by scanning the sample with a 20 µm beam size, a pass energy of 58.7 eV and a step size of 0.5 eV.
All binding energy values presented in this work were corrected for an eventual sample charging with the aliphatic carbon C1s peak set at 285.0 eV. Taking a sputter-cleaned metallic silver sample and measuring with the standard high-resolution settings, the full-width at half-maximum height (FWHM) of the Ag 3d$_{5/2}$ peak was 0.7 eV (Fig. 2.7). Furthermore, the position and linearity of the binding energy scale was calibrated with the peaks Au 4f$_{7/2}$, Ag 3d$_{5/2}$ and Cu 2p$_{3/2}$ at 83.98 eV, 368.26 eV and 932.67 eV [6], respectively.

Figure 2.7 High-resolution spectrum of a sputter-cleaned metallic silver sample for a pass energy of 58.7 eV and a step size of 0.125 eV. This measurement was performed with the Quantum 2000 photoelectron spectrometer. The full-width at half-maximum (FWHM) of the Ag 3d$_{5/2}$ peak was 0.7 eV.

Curve fitting of the XPS peaks taken in high-resolution mode was performed with the CasaXPS software (version 2.3.13; Casa Software Ltd, Teignmouth, Devon, UK). In all cases, an itinerated Shirley background was applied. It assumes that the background level is caused entirely by inelastic electron scattering. The peaks were fitted with the sum of a Gaussian and of a Lorentzian function, noted GL(m), where the mixing parameter m is the ratio of the Lorentzian function in the product. For the fitting of a peak from a metallic sample, the Gauss-Lorentz line shape is corrected by multiplying with an asymmetric tail function [7].

Gaussian function:

$$G(x;E,F,m) = \exp \left[ -\ln 2 \left( 1 - \frac{m}{100} \right) \left( \frac{x-E}{F} \right)^2 \right] \quad (2.8)$$
Materials and methods

Lorentzian function:
\[
L(x; E, F, m) = \frac{1}{1 + 4 \cdot \frac{m}{100} \cdot \frac{(x-E)^2}{F^2}}
\]  

(2.9)

Tail modifier:
\[
T(x; s, k, E, F) = \begin{cases} 
\exp \left[ -k \frac{E - E_0}{FWHM} \right] & \text{for } E \leq E_0 \\
1 & \text{for } E > E_0
\end{cases}
\]  

(2.10)

2.4.3. Quantitative analysis

In addition to the chemical state information, quantitative analyses were performed when possible using a first-principles model. The fundamental equation for laterally homogeneous samples includes parameters from the instrument and from the sample [8]:

\[
I_A = J_0(x, y) \cdot \int_{z=0}^{\infty} N_A(x, y, z) \cdot \exp \left[ -\frac{z}{\lambda(E_A) \cos \theta} \right] dz \cdot \sigma_A(h\nu) \cdot L_A(\gamma) \ldots
\]  

(2.11)

In the relation (2.11), the intensity of the signal from element A, \( I_A \) (in CPS·eV), depends on incident x-ray energy \( h\nu \) and on the kinetic energy of the photoelectron \( E_A \). \( J_0(x, y) \) is the flux of x-ray at point \( (x, y) \), \( N_A(x, y, z) \) is the atom density of the A atoms. \( \lambda \) is the inelastic mean free path (IMFP) with the emission angle \( \theta \). \( \sigma_A(h\nu) \) is the photoionization cross-section and their values calculated by Scofield were used [9]. It corresponds to the probability of an incident photon traversing a gas or a solid to produce an ionizing collision. \( L_A(\gamma) \) is the angular asymmetry function and \( \gamma \) is the source-to-analyzer angle. \( L_A(\gamma) \) describes the intensity distribution of the emitted photoelectron:

\[
L_A(\gamma) = 1 + 0.5 \beta_\Lambda (1.5 \sin^2 \gamma - 1)
\]  

(2.12)

where \( \beta_\Lambda \) is the asymmetry factor calculated by Reilman et al. [10] using Hartree-Slater wave functions. \( \beta_\Lambda \) is a constant depending on the subshells of the atom, on the element, and on the x-ray photon energy. For the s-subshells of all elements, \( \beta_\Lambda \) is equal to 2 and for the other subshells, it varies between -1 and 2. \( A_{\text{analyzed}} \) is the analyzed area, \( D(E_A) \) is the detector efficiency and \( T(E_A) \) is the analyzer transmission function. \( T(E_A) \) gives the energy and pass
energy dependence of photoelectron intensity. The product of $T(E_A)$ with the analyzed area and the detector efficiency is known as the étendue. It can be approximated well with:

$$\frac{I}{E_p} = \left( \frac{a^2}{a^2 + RR^2} \right)^b$$

(2.13)

where $I$ is the peak intensity and $E_p$ is the pass energy. The retard ratio $RR$ is given by $E_{\text{kin}}/E_p$. The coefficient, $a$ and $b$, are generally different for each beam size and lens aperture settings. As the Quantum 2000 has only one lens mode, a single calibration is sufficient. The transmission function coefficients were calculated on the basis of measurements on a copper sample at different pass energies and for the different beam sizes. Then, the values were determined by least-square fitting. The peaks used for this calculation are the Cu $2p_{3/2}$ (at 932.6), Cu $3p$ (at 75.1 eV) and Cu LMM (at 567.9) with pass energies varying between 11.75 eV and 117.4 eV. The values of $a$ and $b$ are shown in table 2.7 for spot sizes of 20, 50 and 100 µm.

Table 2.7 Values of the transmission function coefficients, $a$ and $b$, for three spot sizes of 20, 50 and 100 µm.

<table>
<thead>
<tr>
<th>Spot size</th>
<th>$a$</th>
<th>$b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 µm</td>
<td>23.2</td>
<td>0.171</td>
</tr>
<tr>
<td>50 µm</td>
<td>24.9</td>
<td>0.165</td>
</tr>
<tr>
<td>100 µm</td>
<td>22.7</td>
<td>0.185</td>
</tr>
</tbody>
</table>

The electron IMFP were calculated according to Seah and Dench [11]:

$$\text{IMFP} = \frac{A}{E_{\text{kin}}^2} + B \cdot \sqrt{E_{\text{kin}}}$$

(2.14)

The factors $A$ and $B$ are different depending on the materials group: 143 and 0.054 for elements, 641 and 0.096 for inorganic compounds, 31 and 0.087 for organic compounds, respectively. As the detector is positioned obliquely to the sample surface, the IMFP value has
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to be multiplied by a factor $\cos \theta$ ($\theta = 45^\circ$ for the Quantum 2000). Table 2.8 contains the values used in this study of ionization cross-section, asymmetry factor and IMFP's.

Table 2.8 Values of interest for Scofield's ionization cross-sections at 1486.6 eV, $\sigma_A(h\nu)$, [9], asymmetry factors, $\beta$, [10] and calculated IMFP [11] for elemental materials ($\lambda_{el}$), inorganic compounds ($\lambda_{inorg}$) and organic compounds ($\lambda_{org}$). As the IMFP are dependant on the electron kinetic energy, the values shown in this table may vary slightly depending on important chemical shifts.

<table>
<thead>
<tr>
<th>Peak</th>
<th>$\sigma_A(h\nu)$</th>
<th>$\beta$</th>
<th>$\lambda_{el}$ (nm)</th>
<th>$\lambda_{inorg}$ (nm)</th>
<th>$\lambda_{org}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P 2p$_{3/2}$</td>
<td>0.789</td>
<td>1.09</td>
<td>1.99</td>
<td>3.53</td>
<td>3.20</td>
</tr>
<tr>
<td>Zn 3s</td>
<td>1.04</td>
<td>2</td>
<td>1.98</td>
<td>3.52</td>
<td>-</td>
</tr>
<tr>
<td>S 2p$_{3/2}$</td>
<td>1.11</td>
<td>1.16</td>
<td>1.96-1.97</td>
<td>3.48-3.49</td>
<td>3.16-3.17</td>
</tr>
<tr>
<td>C 1s</td>
<td>1</td>
<td>2</td>
<td>1.87</td>
<td>3.32-3.33</td>
<td>3.01-3.02</td>
</tr>
<tr>
<td>N 1s</td>
<td>1.80</td>
<td>2</td>
<td>1.78</td>
<td>3.16-3.17</td>
<td>2.87</td>
</tr>
<tr>
<td>O 1s</td>
<td>2.93</td>
<td>2</td>
<td>1.67</td>
<td>2.97</td>
<td>2.69</td>
</tr>
<tr>
<td>Fe 2p$_{3/2}$</td>
<td>10.82</td>
<td>1.42</td>
<td>1.50-1.51</td>
<td>2.67-2.68</td>
<td>-</td>
</tr>
<tr>
<td>Zn 2p$_{3/2}$</td>
<td>18.92</td>
<td>1.40</td>
<td>1.16</td>
<td>2.07</td>
<td>-</td>
</tr>
</tbody>
</table>

For a homogenous sample over the sampling depth, the equation (2.11) becomes:

$$I_A = J_0(x, y) \cdot \sigma_A(h\nu) \cdot L_A(\gamma) \cdot N_A \cdot \lambda \cos \theta \cdot A_{analyzed} \cdot D(E_A) \cdot T(E_A) \quad (2.15)$$

It is possible to group all parameters in one factor depending on the element, compound and spectrometer. This is called the sensitivity factor, $S_A$. Values of $S_A$ used for 100 $\mu$m spot size are shown in table 2.9. Since the aim is to give the relative composition, the atomic concentration, $X_A$ (in at. %), is calculated as corrected intensity ratios:
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\[ X_A = 100 \cdot \left( \frac{N_A}{\Sigma N_i} \right) = 100 \cdot \left\{ \frac{(I_A/S_A)}{\Sigma (I_i/S_i)} \right\} \]  \hspace{1cm} (2.16)

As the x-ray flux and the detector efficiency can be considered as constant, these two factors can be ignored in the further calculations. Thus it gives for homogenous samples:

\[ I_A = N_A \cdot S_A = N_A \cdot \sigma_A(h\nu) \cdot L_A(\gamma) \cdot T(E_A) \cdot \lambda \cos \theta \]  \hspace{1cm} (2.17)

Table 2.9 Fitting parameters and sensitivity factors for relevant elements analyzed in this study. Sensitivity factors for elemental materials (S_{el}), inorganic compounds (S_{inorg}) and organic compounds (S_{org}). The ranges are due to the influence of the variation the different contribution with the binding energy (see equation 2.17).

<table>
<thead>
<tr>
<th>Peak</th>
<th>Line shape</th>
<th>FWHM</th>
<th>S_{el}</th>
<th>S_{inorg}</th>
<th>S_{org}</th>
</tr>
</thead>
<tbody>
<tr>
<td>P 2p3/2</td>
<td>GL(30)</td>
<td>1.7-2.4</td>
<td>0.840</td>
<td>1.493</td>
<td>1.353</td>
</tr>
<tr>
<td>Zn 3s</td>
<td>GL(50)</td>
<td>2.4-2.8</td>
<td>0.960</td>
<td>1.706</td>
<td>-</td>
</tr>
<tr>
<td>S 2p3/2</td>
<td>GL(30)</td>
<td>1.6-1.8</td>
<td>1.159-1.161</td>
<td>2.061-2.065</td>
<td>1.868-1.871</td>
</tr>
<tr>
<td>C 1s</td>
<td>GL(30)</td>
<td>1.4-1.9</td>
<td>0.888-0.889</td>
<td>1.579-1.581</td>
<td>1.431-1.433</td>
</tr>
<tr>
<td>N 1s</td>
<td>GL(10)</td>
<td>2.0-2.6</td>
<td>1.545-1.546</td>
<td>2.748-2.749</td>
<td>2.490-2.491</td>
</tr>
<tr>
<td>O 1s</td>
<td>GL(20)</td>
<td>1.8-1.9</td>
<td>2.401-2.403</td>
<td>4.268-4.273</td>
<td>3.867-3.872</td>
</tr>
<tr>
<td>Fe 2p3/2*</td>
<td>-</td>
<td>-</td>
<td>8.961-8.987</td>
<td>15-935-15.980</td>
<td>-</td>
</tr>
<tr>
<td>Zn 2p3/2</td>
<td>GL(60)</td>
<td>1.7-2.4</td>
<td>12.582</td>
<td>22.387</td>
<td>-</td>
</tr>
</tbody>
</table>

*: The lines shape and FWHM for different iron compounds are presented in detail in section 3.9.2.

Considering a homogenous sample covered by a thin overlayer of thickness t, the intensity of a signal originating from the substrate, \( I_{\text{sub}} \), is attenuated following the Beer-Lambert law:

\[ I_{i, \text{sub}} = I_{i, \text{sub}, 0} \cdot \exp(-t / \lambda_{i, t} \cos \theta) \]  \hspace{1cm} (2.18)

\[ I_{i, t} = I_{i, t, 0} \cdot \{ 1 - \exp(-t / \lambda_{i, t} \cos \theta) \} \]  \hspace{1cm} (2.19)
where $I_{\text{sub},0}$ and $I_{0,0}$ are the intensity values for homogenous semi-infinite compounds from the substrate and from the overlayer compound. Another easily applicable model is the three-layer model \[12, 13\]. It consists, typically, of a substrate with a middle layer of thickness $l$, e.g. an oxide layer, and an overlayer of thickness $t$, e.g. an organic overlayer.

\[
I_{i,\text{sub}} = I_{i,\text{sub},0} \cdot \exp\left(-\frac{t}{\lambda_{i,t} \cos \theta}\right) \cdot \exp\left(-\frac{l}{\lambda_{i,l} \cos \theta}\right) \quad (2.20)
\]

\[
I_{i,l} = I_{i,t,0} \cdot \{1 - \exp\left(-\frac{l}{\lambda_{i,l} \cos \theta}\right)\} \cdot \exp\left(-\frac{t}{\lambda_{i,t} \cos \theta}\right) \quad (2.21)
\]

\[
I_{i,t} = I_{i,t,0} \cdot \{1 - \exp\left(-\frac{t}{\lambda_{i,t} \cos \theta}\right)\} \quad (2.22)
\]

The subscript, $i$, designates an element $i$ present in this layer, $t$, $l$ and $\text{sub}$ correspond to the overlayer, the interlayer and the substrate. The same denomination is used to design the layer thicknesses. A detailed introduction to XPS is given by Briggs and Grant \[14\].

### 2.5. Time-of-flight ion mass spectrometry

Time-of-flight ion mass spectrometry (ToF-SIMS) spectra were recorded using a ToF-SIMS 5 system (ION-TOF GmbH, Münster, Germany). Primary ions were Bi$_3^+$ with an acceleration voltage of 25 kV. The usual mass resolution was approximately $m/\Delta m = 7000$ for either positive or negative spectra. During the data acquisition process, ion doses were kept close to $1.0 \times 10^{12}$ ions/cm$^2$, well below the static SIMS limit. The mass/charge (m/z) range was calibrated using a set of low-mass peaks. Depending on the samples, the areas measured were 100 µm x 100 µm or 200 µm x 200 µm. Data processing was performed with the softwares IonSpec for spectra analyses and IonImage for imaging mode (ION-TOF GmbH, Münster, Germany).

### 2.6. Atomic Force Microscopy

Surface imaging of the tribofilms was performed with a Dimension 3000 SPM (Digital Instrument Inc., Santa Barbara, CA, USA) in contact mode with silicon AFM probes (BS ContAL, NanoAndMore, Germany). These probes had a nominal force constant of 0.2 N/m. The data were analyzed with the WSxM software (Nanotec Electronica S.L., Tres Cantos, Madrid, Spain).
2.7. Scanning electron microscopy

After tribological tests, surface imaging was performed with environmental scanning electron microscopy (ESEM; Philips ESEM-FEG XL30) in conventional high-vacuum mode. Energy dispersive x-ray spectroscopy (EDX) was performed with acceleration voltages between 12 and 15 keV.

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3. Results

3.1 DLC coatings characterization

3.1.1. Deposition process

The deposition of a-C:H with the standard parameters described in section 2.1.1 was monitored with a gas analyzer (Fig 3.1). Detailed single spectra taken during the three steps of the procedure are shown in figure 3.2. The y-axis corresponds to the current measured by the detector in amperes. Before the deposition process, a vacuum below $8 \times 10^{-8}$ mbar was reached. Ar with a pressure of $2.4 \times 10^{-2}$ mbar was introduced two minutes before igniting the plasma, then the etching process (-600 V selfbias) began with Ar and Ar$_2$ as the main species and a residual contamination, C, CH$_2$, H$_2$O, N$_2$, CO, O$_2$ below 1%. During the deposition of the adhesion-promoting interlayer from TMS [1], the main detected species were silicon based with one to four methyl groups (noted Me). Oxygen was still present. Figure 3.2c shows the spectrum after 90 minutes of DLC deposition from pure acetylene. Water and oxygen remained present below 1 %, but the main species were acetylene C$_2$H$_2$ with polymerized species C$_4$H$_2$, C$_6$H$_2$ and C$_8$H$_2$. An important aspect is that the different species were constant during the two hours of a-C:H deposition [2].

![Figure 3.1 Gas analysis performed during the deposition process of pure a-C:H.](image)
Figure 3.2 Gas monitoring spectra (a) during argon sputtering (after $t = 25$ min), (b) during TMS deposition and (c) after 90 min DLC deposition. The deposition procedure follows the description in the table 2.1.
3.1.2. Mechanical tests

The characterization of pure a-C:H coatings by nanoindentation and scratch testing was performed on samples deposited with the same settings as the standard coating used for the tribological experiments. Coatings deposited at different times over the four years of this project were compared to check the reproducibility of the process during the whole test period. Table 3.1 shows the hardness, Young's modulus and the four critical loads from the scratch experiments (Lc1: first crack, Lc2: first chip, Lc3: first coating spallation and Lc4: coating continuously broken through). The Young's modulus, E, was calculated with the equation 2.1 assuming a Poisson's coefficient, $\nu$, of 0.25 for the DLC layers [3, 4]. This assumption for $\nu$ does not have a large influence on the results as it only changes slightly the calculated $E$. For $\nu = 0.25 \pm 0.05$, the uncertainty on $E$, $dE/E$, is only $\pm 3\%$. No significant variation between the mechanical properties of the coatings was observed. Averaging the values of all pure a-C:H coatings gives a hardness of $23.5 \pm 1.0 \text{ GPa}$ and a Young's modulus of $210.5 \pm 4.8 \text{ GPa}$.

The nanoindentation measurements were carried out with a maximum load of 5 mN. Indents were performed at different depths up to 400 nm or 20% of coating depth. Figure 3.3 shows these results including also the measurements at 5 mN with the error bars in grey. Even at a depth of 20 %, the influence of the softer steel substrate was not observed.

Table 3.1 Hardness and Young's modulus of pure a-C:H coatings measured by nanoindentation. Samples stored in a dry chamber were analyzed. The critical loads $L_{Ci}$ in the scratch tests were determined optically.

<table>
<thead>
<tr>
<th>N°</th>
<th>Age</th>
<th>H (GPa)</th>
<th>E (GPa)</th>
<th>$L_{C1}$ (N)</th>
<th>$L_{C2}$ (N)</th>
<th>$L_{C3}$ (N)</th>
<th>$L_{C4}$ (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#2213</td>
<td>fresh</td>
<td>23.4 ± 2.3</td>
<td>203.5 ± 14.9</td>
<td>4.1 ± 0.2</td>
<td>5.6 ± 0.9</td>
<td>8.9 ± 0.5</td>
<td>19.1 ± 0.7</td>
</tr>
<tr>
<td>#2173</td>
<td>10 months</td>
<td>22.9 ± 1.4</td>
<td>214.6 ± 13.2</td>
<td>4.2 ± 0.5</td>
<td>4.7 ± 0.7</td>
<td>6.8 ± 0.3</td>
<td>17.8 ± 1.0</td>
</tr>
<tr>
<td>#2121</td>
<td>20 months</td>
<td>25.0 ± 1.2</td>
<td>211.9 ± 10.3</td>
<td>4.2 ± 0.2</td>
<td>5.1 ± 0.6</td>
<td>7.3 ± 0.6</td>
<td>18.5 ± 0.4</td>
</tr>
<tr>
<td>#2102</td>
<td>30 months</td>
<td>23.0 ± 0.6</td>
<td>212.0 ± 7.2</td>
<td>4.4 ± 0.4</td>
<td>5.5 ± 0.4</td>
<td>7.6 ± 0.6</td>
<td>19.2 ± 0.4</td>
</tr>
</tbody>
</table>
Figure 3.3 a) Hardness and b) Young's modulus as a function of the penetration depth for a deposited a-C:H coating. The grey error bar corresponds to the settings used to characterize all the coatings presented in tables 3.1 and 3.2.

The hardnesses and elasticity moduli of two titanium-alloyed DLC coatings were also determined with the same procedure as for pure a-C:H coatings (Table 3.2). The ratio of titanium to carbon was measured using XPS after an argon-sputtering cleaning procedure (30s at 4 kV). Figure 3.4 shows images following scratch tests of the recently deposited a-C:H coating (Fig. 3.4 a) and of two alloyed Ti-DLC coatings. The Ti-DLC coatings #2086 (Fig 3.4 b) and #2097 (Fig. 3.4 c) contained 1.5 % and 3.5 % Ti, respectively. Ti-containing coatings could carry a higher load before the first crack appeared with higher \( L_{C1} \) values than for pure a-C:H coatings, but here the chipping and spalling appeared immediately after the outbreak of the first crack, contrary to the pure DLC coatings. Finally, total removal of the Ti-containing coatings appeared later. This can be related with a decrease of the internal stress by alloying with titanium [5]. Furthermore, incorporation of titanium led to a decrease of the hardness from 23.5 ± 1.0 GPa for pure a-C:H to 14.0 ± 0.5 GPa and 17.7 ± 0.8 GPa for coatings containing 1.5 % and 3.5 % Ti, respectively.

Table 3.2 Hardness and Young's modulus of Ti-containing DLC coatings measured by nanoindentation. The content of titanium in DLC was determined by XPS. The critical loads \( L_{Ci} \) of the scratch tests were determined optically.

<table>
<thead>
<tr>
<th>Nº</th>
<th>Ti/(C+Ti)</th>
<th>H (GPa)</th>
<th>E (GPa)</th>
<th>( L_{C1} ) (N)</th>
<th>( L_{C2} ) (N)</th>
<th>( L_{C3} ) (N)</th>
<th>( L_{C4} ) (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#2086</td>
<td>1.5 %</td>
<td>14.0 ± 0.5</td>
<td>155.7 ± 5.9</td>
<td>5.1 ± 0.3</td>
<td>5.3 ± 0.3</td>
<td>5.5 ± 0.3</td>
<td>23.3 ± 1.0</td>
</tr>
<tr>
<td>#2097</td>
<td>3.5 %</td>
<td>17.7 ± 0.8</td>
<td>149.2 ± 3.6</td>
<td>5.0 ± 0.5</td>
<td>5.4 ± 0.2</td>
<td>5.8 ± 0.4</td>
<td>27.7 ± 0.7</td>
</tr>
</tbody>
</table>
3.1.3. Topographical effect of argon sputtering

The topography of a freshly polished steel surface was compared with a steel surface after the argon etching process preceding the adhesion-promoting interlayer using AFM (Fig. 3.5). The freshly polished surface had a root-mean-square roughness ($R_q$) of $5.0 \pm 0.5$ nm. After the 40 minutes of etching, the $R_q$ roughness increased to $8.4 \pm 0.8$ nm and decreased after the DLC deposition to $5.7 \pm 0.4$ nm. The rounded structure of steel after the etching process was related to the steel microstructure observed in figure 3.6. The surface energy of the sharp cut grains boundaries was decreased with the formation of rounded boundaries. Deposited DLC replicated this structure.

Figure 3.4 Scratch tests performed on a) a pure a-C:H coating and on two Ti-containing coatings with b) 1.5 % Ti and c) 3.5 % Ti.
Figure 3.5 AFM images in deflection mode with the related height profiles below. a) Polished steel surface, b) argon etched steel surface and c) pure a-C:H coating.

Figure 3.6 AFM images of the argon-etched steel surface in a) height mode and b) deflection mode. It was possible to distinguish the grain microstructure of the steel.
3.1.4. XPS analysis of an as-deposited pure a-C:H coating

Before the tribological experiments, a fresh as-deposited a-C:H surface was analyzed with XPS without sputtering (Fig. 3.7) and after an argon sputtering process used to remove the oxidized DLC overlayer and contamination due to air exposure (Fig. 3.8). Argon sputtering was carried out for 30s at 4 kV. This corresponded to a sputtering depth of 10 ± 1 nm into a reference silicon dioxide sample. The survey of the as-deposited DLC coating shows peaks corresponding to carbon and oxygen. Two peaks were used to fit the O 1s signal at 532.1 ± 0.2 eV and 533.2 ± 0.2 eV with a FWHM of 1.8 eV, using a line shape of GL(20). The peak at lower BE was attributed to carbonyl bonds and the one at higher BE, to C-O bonds [6, 7]. Both C 1s peaks, before and after argon sputtering, were fitted with a single asymmetric peak with GL(30)T(1.55) as line shape. The signal position was found to be 284.6 ± 0.2 eV with a FWHM of 1.2 eV. As it was not possible to take the usual aliphatic C 1s peak as reference, the main C 1s peak from DLC was set at 284.6 eV. This DLC asymmetric peak was used as reference when the main carbon peak originated from the DLC substrate.

![Figure 3.7 XPS spectra of an as-deposited a-C:H coating surface without sputtering.](image)

![Figure 3.8 XPS spectra of an argon-etched a-C:H coating.](image)
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Using literature values, it was possible to fit the C 1s peak with several contributions from C-C and C-H, C-O and C=O bonds [7-9]. A similar fit of the C 1s peak from the figure 3.7 is shown in figure 3.9. As in this project, DLC was the substrate of organic/organometallic overlayers, fitting with a single asymmetric peak was preferred to distinguish the contributions from the DLC coating from an overlayer also containing carbon contributions.
3.2. Tribological measurements without additives

3.2.1. Pin-on-disc experiments

The influence of the base oil on the tribological performance was determined with pin-on-disc measurements in air with 30% and 70% relative humidity, and in pure PAO at room temperature. This was required to characterize the tribological performance of the standard DLC coating used in later experiments. All tests were performed with standard 2 µm thick DLC sliding against DLC. The parameters for the tests in air are presented in table 3.3. The measurement in PAO was performed with a speed of 6 mm/s until coating failure. Using the equation 1.4, this corresponded to a $\lambda$ parameter of 1.2.

<table>
<thead>
<tr>
<th>Nº</th>
<th>Velocity (mm/s)</th>
<th>Radius (mm)</th>
<th>Cycles (tr)</th>
<th>Distance (m)</th>
<th>Total time (h)</th>
<th>RH %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>8</td>
<td>10'000</td>
<td>502.7</td>
<td>23.3</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>5</td>
<td>10'000</td>
<td>314.2</td>
<td>0.9</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>8</td>
<td>400'000</td>
<td>20'106.2</td>
<td>55.9</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>8</td>
<td>10'000</td>
<td>502.7</td>
<td>23.3</td>
<td>70</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>5</td>
<td>10'000</td>
<td>314.2</td>
<td>0.9</td>
<td>70</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>8</td>
<td>400'000</td>
<td>20'106.2</td>
<td>55.9</td>
<td>70</td>
</tr>
</tbody>
</table>

The evolution of the friction coefficient with time is shown in figure 3.10 for the low speed test in air, and in figure 3.11 for the high speed tests in air. The corresponding optical microscopy pictures are also shown. The measurements of wear are presented in figure 3.12. The experiment numbers correspond to those in table 3.3. The wear on the disc was determined with a series of measurements with a contact profilometer. A main factor in the variation shown by the error bars was the presence or absence of counterpart deposits on the track. The wear was expressed as a wear volume per sliding distance rather than the wear coefficient since the contact area measured on the ball would increase the uncertainty. The negative wear rates for the two low speed experiments indicated a deposition of material originating from the counterpart consistent with the larger error bars and the optical microscope observations. These tests were too short to reach a steady-state behavior. After 500 m at low sliding speed, the friction coefficients were $0.063 \pm 0.002$ and $0.050 \pm 0.001$ at
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30% and 70% relative humidity, respectively. After 500 m at high sliding speed, the friction coefficient increased to $0.079 \pm 0.001$ and $0.123 \pm 0.002$ at 30% and 70% relative humidity, respectively. Moreover, as the friction coefficients did not show a clear stabilization even after 20 km of sliding distance, the calculated wear values are only average values including an important contribution from the running-in process, therefore, these results can only be compared with tests under similar conditions. The profilometry measurements showed that the wear track did not exceed a depth of 1 µm indicating that the 2 µm thick DLC coatings were not worn through.

The scar size on the ball segment was measured with an optical microscope and the worn area was assumed to be flat. The wear on the ball segments was expressed as the wear coefficient $K$ from the equation 1.2 (Fig. 3.9). The high wear coefficients for every short test of 10'000 rotations confirmed that the running-in process lasted for more than 500 m. At larger distances, lower wear regime was reached with wear rates more than one order of magnitude smaller. A stable low friction regime ($0.0648 \pm 0.001$) was reached at RH = 30%, although the wear rate of the disc ($153 \pm 32$ µm$^3$/m) was higher than at RH = 70% ($20 \pm 28$ µm$^3$/m). The wear coefficient on the ball segment was smaller at RH = 30% ($2.0 \cdot 10^{-10}$) than at RH = 70% ($5.0 \cdot 10^{-10}$). The contact area in the high speed test after 20 km at RH = 70% (3.14 mm$^2$) was larger than the contact area at RH = 30% of 1.24 mm$^2$.

The coating on the counterface, the ball segments, was expected to be worn through according to the calculation of the calotte height that gave values larger than 3.5 µm. However, this was not the case. An XPS depth profile of the contact area obtained after the 20 km test at 70 % RH was performed, following the concentrations of carbon, oxygen and iron. Sputtering of 350 nm did not result in the detection of the iron substrate, indicating that the surface was still coated with DLC at the end of the experiments.
Results

Figure 3.10 Pin-on-disc tests performed in air at low sliding speed. a) change in coefficient of friction with time and optical images of the track on the disc after the pin-on-disc measurement at b) a relative humidity of 30% and c) RH = 70% (width of image = 1mm).

Figure 3.11 Pin-on-disc tests performed in air at high sliding speed. a) change in coefficient of friction with time and images of the track on the disc after the pin-on-disc measurement at b) a relative humidity of 30% and c) RH = 70% (width of image = 1mm).

Figure 3.12 a) Wear rate of the DLC-coated discs and b) wear coefficient of the DLC-coated ball segments for the pin-on-disc experiments performed in air.
As the pin-on-disc test in PAO was performed until disk coating failure, a calculation of the wear was not meaningful. The evolution of the CoF and an image of the sliding track on the disc are shown in figure 3.13. Deposits of wear debris were observed on both sides of the track, at approximately 500 µm from the scar. Between the sliding distances of 1.5 km and 3 km, a low friction regime was reached with a friction coefficient of approx. 0.01, however, after 3 km the friction coefficient increased to reach values above 0.06 after 5 km. In this case, the worn contact area on the ball segment was of 3.66 mm².

Figure 3.13 a) Pin-on-disc test performed in PAO at low speed. b) Image of the track on the disc (image width = 1mm).

### 3.2.2. HFRR experiments without lubricant

HFRR tests in air with 30% and 70% relative humidity were also performed at room temperature. All tests were performed with DLC sliding against DLC. Table 3.4 presents the experimental settings. The first two tests were performed with the same pressure and velocity as the following oil-lubricated tests, while the two others were performed under milder conditions. The maximum sliding speed of the ball segment was 160 mm/s for the 5N tests and 80 mm/s for the 2N tests.
Table 3.4 Parameters of the HFRR tests for DLC sliding against DLC without lubricant at room temperature.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>RH = 30%</th>
<th>RH = 70%</th>
</tr>
</thead>
<tbody>
<tr>
<td>5N, 20Hz, 2mm, 1h</td>
<td>Test #1.1</td>
<td>Test #2.1</td>
</tr>
<tr>
<td>2N, 20Hz, 1mm, 1h</td>
<td>Test #1.2</td>
<td>Test #2.2</td>
</tr>
</tbody>
</table>

A steady-state friction coefficient of approximately 0.4 was reached during experiments carried out at RH = 70%, while the friction behavior at RH = 30% was unstable with higher values. The friction coefficients were more than twice as high at RH = 30% compared with the same experiments at RH = 70% (Fig. 3.14). Although the ball segments showed flattened contact areas (Fig. 3.15b), with some scratches, no significant line shape differences were observed with Raman microscopy with excitation at 633 nm either on the ball segment or the counterface (Fig. 3.16). As the intensity variation was not sufficient to detect coating depth changes, normalized intensity spectra are shown to allow a comparison with an as-deposited DLC coating. The as-deposited pure DLC coating showed the two typical peaks from the D and G modes at 1315 cm\(^{-1}\) and 1512 cm\(^{-1}\), respectively.
Results

Figure 3.15 a) Wear coefficients of the ball segments for the HFRR tests performed without oil and b) An ESEM image of the scar edge on the ball corresponding to the test #1.1.

Figure 3.16 Raman spectra of a) a-C:H coating fitted with the peaks from the D and G modes. b) The plate tracks and c) the pin scars for all tests are compared with a spectrum of an as-deposited coating.

The Raman spectra did not show evidence of a graphitization process, however, the wear process was quite different from case to case. Using the tribological parameters later used in the oil-lubricated systems (5N with 180 mm/s maximum speed), a partial polishing wear of the rounded DLC surface texture was observed at RH = 30% (Fig. 3.17a), while at RH = 70%, deposits from the ball segment were observed in the low-speed region of the track. Figure 3.18 shows the friction coefficients for individual strokes at the beginning and end of the experiment. The friction coefficient not only increases with time but there is also a change in the friction behavior with changing speed during reciprocating sliding.
Figure 3.17 ESEM images of the HFRR track on the plates for a) the 5N test at RH = 30%, b) the 5N test at RH = 70% and c) 2N test at RH = 70%.

Figure 3.18 Friction coefficients during the reciprocating sliding strokes for the test #2.1 (5N and RH = 70%). The plots illustrate the change in the friction behavior within each stroke between a) the beginning of the test and b) after 60 minutes of test. Negative friction coefficients simply indicate a change in sliding direction.
3.3. Pure polyalpha-olefin

3.3.1. Tribological results

HFRR experiments were performed in pure PAO with the parameters used for all following experiments with additives (80°C, 60min, 2 mm length, 20 Hz and 5 N load). The average friction coefficient for the 10 last minutes of sliding was 0.129 ± 0.016 for steel/steel contacts and 0.014 ± 0.007 for DLC/DLC contacts. Three representative examples are presented for each case (Fig. 3.19). The spikes present in the friction coefficients for the steel/steel contact were correlated with abrasive wear particles production as detected by ESEM (Fig. 3.20). Wear was not observed after DLC/DLC tests as determined by the detection of the rounded structure of the as-deposited coating with AFM (Fig. 3.21).

![Figure 3.19](image)

Figure 3.19 Evolution of the CoF with time for a) steel/steel and b) DLC/DLC contacts. The HFRR tests were performed in pure PAO at 80°C. Three representative examples are shown for each type of contact.
Figure 3.20 ESEM images of the track on the plate of a steel/steel contact after a HFRR test in pure PAO. a) The central part of the track shows wear particles. b) Impingement of hard wear particles was observed in the absence of a protective film. The reciprocating sliding direction is horizontal for both images.

Figure 3.21 a) AFM deflection image and b) corresponding height profile performed on an HFRR track with DLC/DLC contact in PAO. The image shows a central region of the track corresponding to a high sliding speed.

3.3.2. XPS analysis

The HFRR tracks following the tests performed in pure PAO at 80°C were analyzed with XPS for steel/steel and DLC/DLC contacts. Contact regions near the end of the track, called the low-speed region (sliding velocity between 30 and 60 mm/s), and in the central part, called the high speed-region (sliding velocity between 100 and 140 mm/s), were compared with the non-contact area. The maximum speed region, corresponding to a sliding speed of
Results

180 mm/s, was avoided because in the cases of additive-containing PAO, the tribofilm was damaged when the ball segment stopped after the one hour test. The analyzed areas were always chosen on the secondary electron x-ray induced image (SXI) of the track.

In the case of steel sliding against steel (Fig. 3.22), the XPS surveys showed the presence of iron, oxygen and carbon. The carbon signal showed a main peak from aliphatic carbon set at 285.0 eV. At higher binding energies, small contributions at 286.7 ± 0.2 eV and at 288.7 ± 0.2 eV were always present and were assigned to C-O groups and C=O groups [6, 10, 11]. In both analyzed contact regions, a peak at 289.8 ± 0.2 eV was attributed to carbonates [12, 13]. This last peak was absent in spectra from the non-contact areas. Out of the track, it was possible to observe a small peak from carbides at 282.7 ± 0.2 eV [13-16]. All C 1s peaks were fitted with GL(30) line shape with a FWHM of 1.6 eV in the contact regions and 1.7 eV out of the track.

The oxygen O 1s signal showed three contributions at 530.1 ± 0.2 eV, 531.8 ± 0.2 eV and 532.9 ± 0.2 eV corresponding to iron oxide [12, 17], to C=O groups, carbonates and hydroxides [17-19] and to C-O groups [6, 10], respectively. The iron Fe 2p signal was composed of two main peaks, Fe 2p3/2 and 2p1/2, due to spin-orbit splitting. Only the 2p3/2 was fitted. The three important contributions were the iron oxide peaks Fe(+2) at 709.4 ± 0.2 eV and Fe(+3) at 710.5 ± 0.2 eV and, additionally, iron oxy-hydroxide at 711.8 ± 0.2 eV [18, 20-22]. A satellite peak of the Fe(+2) component was found at 5.5 eV higher than the main peak (at 714.9eV) [17, 23]. A possible satellite peak of Fe(+3) would be found about at 8 eV higher energy than the main peak [23]. However, this small signal would overlap with the metallic iron Fe 2p1/2 at around 720 eV and, for this reason, was not considered. The metallic iron signal Fe 2p3/2 at 706.7 ± 0.2 eV was found in the non-contact and low-speed regions. In the high-speed region, the oxide layer was too thick to distinguish the metallic substrate.
Figure 3.22 a) Surveys of the areas shown in b) Pt1 and Pt2, and high resolution spectra of c) C 1s, d) O 1s and e) Fe 2p of a non-contact area, a low-speed, and a high-speed contact area for tribological tests with steel sliding against steel in pure PAO at 80°C. A secondary electron x-ray induced image (SXI image) (b) depicting half of the HFRR track shows the location of the high-speed (pt 1) and low-speed (pt 2) analyzed areas.
Three similar regions, non-contact, low-speed, and high-speed areas, were analyzed with XPS following tribological measurements on DLC sliding against DLC (Fig. 3.23). Only carbon and oxygen were detected in the contact and non-contact regions. The DLC peak was only detected in the non-contact region at 284.6 eV. In all regions, the aliphatic carbon peak at 285.0 eV, the C-O groups at 286.6 ± 0.2 eV and C=O groups at 288.4 ± 0.2 eV were detected [7-10]. In the low-speed region, a small but clearly visible peak was also found at 283.6 ± 0.2 eV. The oxygen O 1s peak showed two contributions at 532.2 ± 0.2 eV and 533.3 ± 0.2 eV, corresponding to C=O and C-O [6, 7], respectively. While the intensity of the two peaks was nearly equal in the contact regions, the C-O group peak was more than twice as intense as the C=O group in the non-contact area.

Figure 3.23 a) Surveys and high resolution spectra of b) C 1s and c) O 1s of a non-contact region, a low-speed and a high-speed contact area for tribological tests with DLC/DLC contact in pure PAO at 80°C.
3.4. Zinc dialkyl dithiophosphate

3.4.1. Tribological results

Series of three HFRR measurements on the same plate were carried out on steel sliding against steel and DLC sliding against DLC in PAO containing 1 wt% ZnDTP, using a new ball segment for each track. The average friction coefficients for the first measurements on each plate were 0.103 ± 0.018 and 0.072 ± 0.027 for steel sliding against steel and DLC sliding against DLC, respectively (Fig. 3.24). Figure 3.24 shows representative graphs of the friction coefficient versus time for these first measurements. The average friction coefficient for three series (nine measurements) for steel sliding against steel was 0.114 ± 0.023 and for DLC sliding against DLC, it was 0.076 ± 0.023.

![Graph a) and b)](image)

Figure 3.24 Evolution of the friction coefficient with the time for a) steel sliding against steel and b) DLC sliding against DLC. These graphs are from the first HFRR measurement on each plate and were performed at 80°C in PAO containing 1 wt% ZnDTP.

3.4.2. Topographical observations

AFM and ESEM were performed on the rubbing tracks to compare the morphology of the tribofilm built up on steel and on DLC (Fig. 3.25 and 3.26). On steel, the tribofilm formed from ZnDTP showed the characteristic pad-like structure already observed in other studies [24-26]. On DLC, small patches were present in the central part of the HFRR track while much of reacted products were pushed out to the boarder of the contact area (Fig. 3.25d).
AFM was performed on the contact areas of the plates in regions corresponding to a sliding speed between 30 and 60 mm/s ($0.5<\lambda<0.9$).

Figure 3.25 ESEM images of the HFRR tracks following measurements performed in PAO containing 1 wt% ZnDTP. a) and b) Tracks on the plate for steel sliding against steel showed the characteristic pad-like structure. For DLC sliding against DLC, c) the end of the track and d) the central part of the track are shown. The reciprocating sliding direction is horizontal for all images.
3.4.3. Ex-situ scratch test of ZnDTP tribofilms

To determine the adhesion of a ZnDTP tribofilm on DLC, ex-situ scratch tests were carried out on the tribofilms built up on steel and on DLC coatings. These tests were performed in air with a sapphire ball (diameter: 3mm) and an applied load of 100 mN. The sapphire ball moved perpendicularly to the HFRR tracks (Fig. 3.27). The tribofilm on steel showed a complete adhesion to the substrate after scratching (Fig. 3.28a), whereas the tribofilm on the DLC coating was removed under the same conditions (Fig. 3.28b). On the thicker film built up on the edge of the HFRR track on DLC coating, further tests were performed with a load of 15 mN. Figure 3.29 shows the abrupt loss of adhesion of this film with the DLC coating.
Figure 3.27 Ex-situ scratch tests of a) ZnDTP tribofilms on steel and b) on DLC performed perpendicularly to the HFRR tracks.

Figure 3.28 ESEM images of the ex-situ scratch test from figure 3.27 for a) tribofilms built up on steel and b) on the DLC coating.
Figure 3.29 Ex-situ scratch test of a ZnDTP tribofilm on DLC performed on the edge of the contact area in parallel of the HFRR track.

3.4.4. XPS analysis

XPS analyses were performed in contact regions for steel sliding against steel and DLC sliding against DLC after HFRR experiments at 80°C performed in PAO containing 1 wt% ZnDTP. Additionally, thermal (non-contact) films were formed by incubating steel and DLC in solutions of ZnDTP in PAO at 80°C. Survey spectra were always performed to ensure that unexpected elements were absent as shown for the steel plate (Fig. 3.30). High resolution spectra of the main peak of all present elements were measured. The signals P 2p, S 2p, Fe 2p and Zn 2p exhibit two contributions, 2p$_{3/2}$ and 2p$_{1/2}$, due to spin-orbit splitting. The area ratio was fixed to 2:1 and the energy difference between the two peaks was fixed to 0.85 eV [6, 13, 18] for phosphorus and to 1.2 eV for sulfur [6, 27]. As the energy differences were about 13 eV and 23 eV for the Fe 2p and Zn 2p peaks, only the 2p$_{3/2}$ contributions were fitted. Complete tables of fitting parameters are shown in the annexe.

Figure 3.30 XPS survey spectra of a) the thermal film and of b) the tribofilm after tribological experiments with steel/steel contact in PAO containing 1 wt% ZnDTP.
Figure 3.31 shows high resolution spectra of a ZnDTP tribofilm and a thermal film that were built up on steel. For the ZnDTP tribofilm on steel, the pass energy was of 29.35 eV with a step size of 0.125 eV. All other analyses were performed, as described in the experimental part, with a pass energy of 58.7 eV and a step size of 0.125 eV. The phosphorus P 2p\textsubscript{3/2} signal showed a shift of 0.6 eV between the non-contact and contact regions, from 133.4 ± 0.2 eV to 134.0 ± 0.2 eV. Peaks for zinc Zn 3s were also fitted at 140.4 ± 0.2 eV and 140.7 ± 0.2 eV for the contact and non-contact regions, respectively. The sulfur 2p signals from the thermal film and tribofilm were detected at 162.2 ± 0.2 eV and 162.6 ± 0.2 eV, respectively. This corresponded to the oxidation state -2 present in sulfides [18, 21], bound thiols [28-30] or thiophosphates [31]. A peak at higher binding energy was only found for the thermal film at 168.6 ± 0.2 eV, corresponding to oxidized sulfur [13]. The carbon main peak from aliphatic chains was set at 285.0 eV. Small intensity peaks were assigned to C-O groups [6, 10] and to C=O groups [6] or carbonates [12] at 286.5 ± 0.2 eV and 288.8 ± 0.2 eV for thermal film and 286.8 ± 0.2 eV and 289.3 ± 0.2 eV for the tribofilm. The oxygen O 1s signal contained three peaks for the thermal film, but only two for the tribofilm. The main peak in the spectrum of the thermal film originated from the oxides, mostly from the steel plate, at 530.2 ± 0.2 eV [17, 23] but this was absent in the spectrum of the tribofilm. A peak at 531.8 ± 0.2 eV was present in both cases and was assigned to non-bridging oxygen (NBO) in (poly)phosphates [32], as well as to sulfates [33], C=O groups [6, 10], carbonates [12] or hydroxides [17, 19]. At higher binding energy, a minor peak was present at 532.9 ± 0.2 eV in the thermal film and could be assigned to C-O-C or C-O-H [6, 10, 31]. On the tribofilm, the peak at 533.4 ± 0.2 eV was assigned to bridging oxygen from polyphosphates [32, 34].

The spectrum of Fe 2p\textsubscript{3/2} from the thermal film was fitted with five contributions. The first peak at 706.7 ± 0.2 eV originated from metallic iron [17, 21]. Fe (+2) was found at 709.1 ± 0.2 eV with a satellite peak 5.5 eV higher [17, 21, 23]. Fe (+3) was detected at 710.8 ± 0.2 eV [22], while a higher energy peak at 712.8 ± 0.2 eV was attributed to iron phosphate [34]. On the tribofilm, only two peaks were found at 710.9 ± 0.2 eV and 713.9 ± 0.2 eV, attributed to Fe (+3) and iron phosphates. Finally the Zn 2p\textsubscript{3/2} peaks were found at 1022.3 ± 0.2 eV and 1022.7 ± 0.2 eV in the thermal film and in the tribofilm, respectively.
Figure 3.31 High resolution spectra of a) Zn 3s and P 2p, b) S 2p, c) C 1s, d) O 1s, e) Fe 2p and f) Zn 2p$_{3/2}$ peaks for thermal films and tribofilms after tribological experiments for the steel/steel contact in PAO containing 1 wt% ZnDTP.
Two regions were analyzed with XPS after HFRR of DLC sliding against DLC in PAO containing 1 wt% ZnDTP: low-speed and high-speed regions corresponding to sliding speed between 30 and 60 mm/s and between 100 and 140 mm/s, respectively. The thermal film was measured on a DLC-coated plate that had been immersed separately in ZnDTP solution at 80°C. Figure 3.32 shows high resolution spectra of all elements detected. The doublet of P 2p had a low intensity in the non-contact, thermal sample with a P 2p$_{3/2}$ peak at 133.4 ± 0.2 eV. In low-speed and high-speed regions, this peak was shifted to 133.7 ± 0.2 eV and 133.8 ± 0.2 eV, respectively. The Zn 3s signal was found in all cases at 140.5 ± 0.2 eV. The main peak of sulfur was present in all three regions at 162.1 ± 0.2 eV and was attributed to sulfides [18, 21], bound thiols [28-30] or thiophosphates [31]. In both contact regions, a second doublet was found 1.6 eV higher with the S 2p$_{3/2}$ peak at 163.7 ± 0.2 eV. It was assigned to unbound thiols [27, 28, 35, 36]. At 169.0 ± 0.2 eV, a small intensity peak was always present but stronger in the thermal film. It was assigned to sulfates [21]. The carbon C 1s peak showed a contribution from the DLC coating set at 284.6 eV in the non-contact sample but also in the high speed region. This peak was masked in the low-speed region due to a thicker overlayer. The three other peaks were present in the three regions: the main peak from aliphatic carbon at 285.0 eV, the peak due to carbon bound to oxygen or sulfur at 286.7 ± 0.2 eV and the carboxylic groups found at 288.8 ± 0.2 eV. The oxygen O 1s peak signal showed two contributions at 532.1 ± 0.2 eV and 533.6 ± 0.2 eV. The first was attributed to non-bridging oxygen (NBO), but also to oxygen bound to carbon and to sulfates. The second peak was assigned to bridging-oxygen (BO) in polyphosphates, but also to the BO oxygen from ester groups [6]. The Zn 2p$_{3/2}$ peak was found at 1022.5 ± 0.2 eV in the thermal film and at 1023.0 ± 0.2 eV in both contact regions.
Figure 3.32 High resolution spectra of a) Zn 3s and P 2p, b) S 2p, c) C 1s, d) O 1s and e) Zn 2p$_{3/2}$ peaks in non-contact regions (thermal film) and the two contact regions after tribological experiments for DLC sliding against DLC.
3.4.5. ToF-SIMS analysis

ToF-SIMS analyses were performed on both contact and non-contact regions. Table 3.5 shows the negative, secondary ions of interest detected after a steel sliding against steel HFRR experiment. Corrected intensities are shown without any normalization, as the thermal film and the tribofilm may be considered as two different materials with different matrix effects. The total intensity is given to assist a comparison. The main species originating from sulfates or phosphates are shown and the peak assigned to PO₃ was the most intense among the inorganic compounds. Polyphosphates, such as P₂O₆H, ZnP₂O₆H, ZnP₂O₇H and ZnP₃O₉, were detected with a higher intensity on the tribofilm. On the other hand, fragments from the unreacted ZnDTP, such as PSO₂, PS₂O, C₆H₁₄PS₂O₂ and C₉H₂₀PS₂O₂, were mostly observed in the non-contact sample. SO and SO₂ were detected for both thermal and tribofilms.

Table 3.5 The most prominent inorganic, negative, secondary ions measured on the thermal film (non-contact region) and on the tribofilm after a tribological test with steel/steel contact in ZnDTP solution. The detector was saturated for peaks marked with asterisk.

<table>
<thead>
<tr>
<th>Ion (charge 1-)</th>
<th>Thermal film</th>
<th>Tribofilm</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>30.972</td>
<td>1962</td>
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<tr>
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<td>31.972</td>
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<td>SO₂</td>
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</tr>
<tr>
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The thermal film and tribofilms built up during a DLC sliding against DLC experiment were also analyzed. The signal intensities for phosphates, such as ZnPSO₃, ZnP₂O₆H, ZnP₂O₇H and ZnP₃O₉, were higher in the HFRR track than in thermal film. Fragments from unreacted ZnDTP at mass higher than 200 were not detected. SOₓ species were detected in both the thermal film and the tribofilm.

Table 3.6 The most prominent inorganic secondary negative ions measured on the thermal film and on the tribofilm after a tribological test with DLC/DLC contact in ZnDTP solution.

<table>
<thead>
<tr>
<th>Ion (charge 1-)</th>
<th>Thermal film</th>
<th>Tribofilm</th>
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3.5. Butylated-triphenyl phosphorothionate

3.5.1. Tribological results

The friction coefficients for tests performed in PAO containing 1 wt% b-TPPT were 0.097 ± 0.017 and 0.030 ± 0.011 for steel sliding against steel and DLC sliding against DLC, respectively (Fig. 3.33). On steel, the running-in showed a different behavior during different tests, but, with time, the friction coefficients evolved in a range between 0.08 and 0.12. Spikes were also observed in the traces of friction vs time. There were two types of behavior. One was a decrease of the friction coefficient during the running-in followed by an increase of the friction coefficient to 0.12 at the end of the one hour test. The second one gave a higher friction coefficient after 2 minutes followed by a decrease and stabilization between 0.08 and 0.1. On DLC, spikes were also present and all tests showed a similar evolution of the friction coefficient, with a rapid decrease to values between 0.02 and 0.05.

![Graph](image)

Figure 3.33 Evolution of the coefficient of friction (CoF) with time for a) steel/steel and b) DLC/DLC contacts. The HFRR tests were performed in PAO containing 1 wt% b-TPPT at 80°C.

3.5.2. Topographical observations

Scratches were observed in the tracks on the steel plates with ESEM (Fig. 3.34a). They were up to 150 nm deep (Fig. 3.37), but the structure formed by polishing was still present in the contact region. AFM images on steel showed a pad structure with lines of tribofilm oriented in the sliding direction (Fig. 3.37). EDX analysis of the scar on the uncoated ball segment correlated the darker region with a higher content in phosphorus from the tribofilm (Fig. 3.37).
Results

3.36). On DLC, some scratches were observed with ESEM but the characteristic rounded structure of the original DLC coating was still present indicating a very low wear (Fig. 3.34b). Some impinged particles were also detected. On the edge of the HFRR track, small particles indicated that the additive tribofilm had been removed from the DLC during sliding. The removed tribofilm debris had a thickness of more than 100 nm (Fig. 3.38c). On the track, a film was observed with AFM on the DLC surface (Fig. 3.38 a and b). Patches were present in the low sliding speed regions corresponding to the end of the tracks with the rounded DLC texture below. In the high speed region (middle of the HFRR track), a continuous layer of tribofilm was observed and where parts of this tribofilm were removed, the rounded DLC surface could be detected (Fig. 3.38b). The thickness of the tribofilm in the high speed region was approximately 50 nm. In the low-speed region, the pads had a thickness about 15 nm.

Figure 3.34 ESEM images of the central part of the track a) on a steel plate and b) on a DLC-coated plate after tests performed in PAO containing 1 wt% b-TPPT.

Figure 3.35 ESEM images on the HFRR track of a DLC-coated plate a) near the inner edge of the contact area and b) slightly outside the track where tribofilm debris were observed.
3.36 a) ESEM image of an uncoated steel pin after an HFRR test performed in PAO containing 1 wt% b-TPPT and b) the related EDX spectrum of the whole shown area.

Figure 3.37 AFM deflection images and corresponding height profiles of b-TPPT tribofilm for a steel/steel contact. a) and b) Images of a high-speed and c) of a low-speed region are shown. In all cases the sliding direction is vertically oriented.
Figure 3.38 AFM deflection images and corresponding height profiles of b-TPPT tribofilm for DLC/DLC contact. Images of a) a low-speed region, b) a high-speed region and c) the debris at the edge of the contact area. In all cases the sliding direction is vertically oriented.

3.5.3. XPS analysis

XPS analyses were performed in non-contact and contact regions for steel sliding against steel and DLC sliding against DLC after HFRR experiments at 80°C performed in PAO containing 1 wt% b-TPPT. High resolution spectra of the main peak of all detected elements are shown in figure 3.39 for steel/steel contact. Analyses were performed in the non-contact region, and in the low-speed and high-speed regions corresponding to sliding velocity between 30 and 60 mm/s and 100 and 140 mm/s, respectively. Complete tables of fitting parameters are shown in the annexes.

On the steel plate, the phosphorus P 2p signal was fitted with two contributions, 2p$_{3/2}$ and 2p$_{1/2}$, separated by 0.85 eV and with an area ratio of 2:1. P 2p$_{3/2}$ showed a shift from 133.5 ± 0.2 eV in the non-contact region to 134.2 ± 0.2 eV for both contact regions. On the thermal film, the phosphorus peak had a low intensity. Sulfur S 2p peak is also a doublet due to spin-orbit splitting. The 2p$_{3/2}$ and 2p$_{1/2}$ peaks were separated by 1.2 eV with an area ratio fixed to 2:1. In the non-contact region, the S 2p$_{3/2}$ signal showed a peak at 162.3 ± 0.2 eV. It was similar to the value of 162.6 ± 0.1 eV for P=S in frozen pure b-TPPT measured by Heuberger.
et al. [37]. The second peak appeared at 169.1 ± 0.2 eV and was attributed to sulfur with an oxidation state +6. For the contact region, sulfur had only one doublet with the $S\, 2p_{3/2}$ peak at 162.9 ± 0.2 eV in the low-speed area and at 163.8 ± 0.3 eV in the high-speed region. Both peaks have an oxidation state -2. The peak at 162.9 ± 0.2 eV may be related to the sulfur of the unreacted b-TPPT molecule or to iron sulfide [21], while the peak at 163.8 ± 0.3 eV was assigned to unbound thiols [27, 28] or organic sulfides [6]. The carbon C 1s signal was composed of three peaks. The main peak from aliphatic chains was set to 285.0 eV. The second peak at 286.5 ± 0.2 eV was attributed to carbon bound to oxygen [6, 10]. The third peak was found at 289.2 ± 0.2 eV, 289.0 ± 0.2 eV and 288.5 ± 0.2 eV in the non-contact area, the high-speed region and the low-speed region respectively. The first two were assigned to carbonates [12] while the third peak may be attributed to carboxylic acid. A contribution of carbon atoms from the phenyl groups of the unreacted b-TPPT around 284.7 eV could not be included in the peak fitting. The oxygen O 1s signal contained three peaks. The metal oxide peak was found at 530.5 ± 0.2 eV in the non-contact region while it was very weak for both areas on the tribofilm. The most intense peak in the three regions was found between 532.0 ± 0.2 eV and 532.2 ± 0.2 eV and was attributed to non-bridging oxygen in phosphates and poly(thio)phosphate [37] with possible contribution from oxidized sulfur species or carbonates. The third peak was found at 533.3 ± 0.2 eV in the non-contact area and at 533.6 ± 0.2 eV in the two areas on the tribofilm. It was assigned to the bridging oxygen of polyphosphates P-O-P or of the unreacted b-TPPT molecule P-O-C [31, 37]. It may also contain a contribution from adsorbed water [17]. The iron Fe 2p$_{3/2}$ peak contained at 707.0 ± 0.2 eV a signal from metallic iron. It was stronger for the non-contact region, but was also detected for the tribofilm with a lower intensity. On the tribofilm, three other peaks were needed for the fitting, at 710.4 ± 0.2 eV, 712.4 ± 0.2 eV and 714.1 ± 0.2 eV. They were assigned to iron (+3), iron oxy-hydroxide and/or iron phosphate (+2) and iron phosphate (+3) [34], respectively. On the non-contact region, these three peaks were also present with the binding energy 710.4 ± 0.2 eV, 711.7 ± 0.2 eV and 714.2 ± 0.2 eV, respectively. Additionally, the contribution from Fe (+2) was present at 709.3 ± 0.2 eV with its satellite peak at 714.8 ± 0.2 eV [17, 23].

N 1s was also detected in the tribofilm at 402.3 ± 0.2 eV and a weaker signal was present in the thermal film at 399.8 ± 0.2 eV. The signal at low binding energy was attributed to free amines while the peak at higher binding energy corresponded to protonated amines [38-40].
Figure 3.39 High resolution spectra of a) P 2p, b) S 2p, c) C 1s, d) O 1s, e) Fe 2p and f) N 1s peaks in non-contact and contact regions after tribological experiments for steel/steel contacts in PAO containing 1 wt% b-TPPT.
Similar XPS analyses were performed after tribological experiments of DLC sliding against DLC in a b-TPPT solution. Detailed spectra of the detected elements are shown in figure 3.40. The phosphorus $P\ 2p_{3/2}$ peak was found at $133.6 \pm 0.2$ eV in the non-contact region and at $133.8 \pm 0.2$ eV in the tribofilm. Sulfur $S\ 2p_{3/2}$ showed two peaks at $163.5 \pm 0.2$ eV and $168.5 \pm 0.2$ eV in the thermal film corresponding to sulfur with oxidation state of (-2) and (+6) respectively. Both peaks had a very low intensity. In both regions of the tribofilm, a much stronger $S\ 2p_{3/2}$ peak was present at $163.6 \pm 0.2$ eV that was assigned to unbound sulfur [27, 41]. The carbon $C\ 1s$ peak was fitted with four contributions at $284.6$ eV, $285.0$ eV, $286.5 \pm 0.2$ eV and $288.4 \pm 0.2$ eV corresponding to the DLC substrate, the aliphatic carbon, C-O group and C=O groups, respectively [6, 8, 10]. A contribution originating from the phenyl groups of the unreacted or partially reacted b-TPPT molecule around $284.7$ eV could not be separated from the signal of the DLC coating. In the three regions, the $O\ 1s$ signal needed to be fit with two peaks. The peak from non-bridging oxygen from phosphates was found at $532.1 \pm 0.2$ eV, $531.7 \pm 0.2$ eV and $531.6 \pm 0.2$ eV for the non-contact, high-speed and low-speed regions, respectively. It also includes a contribution from oxidized sulfur species of the thermal film. The peak found between $533.1 \pm 0.2$ eV and $533.4 \pm 0.2$ eV corresponded to bridging oxygen P-O-P or P-O-C. As in the case of tribological tests on steel, this peak may also contain a contribution from adsorbed water. Nitrogen was detected in smaller quantities than on the steel plates, but this signal was also always present at $399.6 \pm 0.2$ eV in the thermal film and at $401.6 \pm 0.2$ eV in the contact regions. These signals were attributed to free amines and to protonated amines, respectively [38-40].
Figure 3.40 High resolution spectra of a) P 2p, b) S 2p, c) C 1s, d) O 1s, e) N 1s peaks in contact and non-contact regions after tribological experiments for DLC/DLC contacts in PAO containing 1 wt% b-TPPT.
3.5.4. ToF-SIMS

Non-contact and contact regions for steel sliding against steel were analyzed with ToF-SIMS in both positive and negative modes. Corrected intensities are shown without any normalization, as the thermal film and the tribofilm may be considered as two different materials with different matrix effects. Corrected intensities below 300 counts were not taken in account. A large number of iron polyphosphate species containing up to 5 phosphorus atoms were detected in the tribofilm (Table 3.7), but, for the thermal film, these peaks were absent for the high mass ions and weak for fragments containing two or three phosphorus atoms. On the other hand, species from iron oxides, such as FeO$_2$, FeO and FeOH were only detected in non-contact regions. Oxidized sulfur species, especially SO$_3$, gave stronger signals outside the HFRR tracks.

On the DLC plate, negative, secondary ions from polyphosphates containing up to two phosphorus atoms (Table 3.8) were detected for both thermal film and tribofilm. Oxidized sulfur species gave peaks of higher intensity in the HFRR track, but these signals remained weak compared to the most prominent phosphate species.
Table 3.7 The most prominent inorganic negative, secondary ions measured on the thermal film and on the tribofilm after a tribological test with steel/steel contact in b-TPPT solution.

<table>
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**Total Intensity**  
| **Thermal film** | 858447 |  
| **Tribofilm**    | 1204869 |
Table 3.8 The most prominent inorganic negative, secondary ions measured on the thermal film and on the tribofilm after a tribological test with DLC/DLC contact in b-TPPT solution.

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Results

Table 3.9 The positive amine, secondary ions measured on the thermal film and on the tribofilm after a tribological test with steel/steel contact in b-TPPT solution.

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Table 3.10 The positive secondary ions from amines measured on the thermal film and on the tribofilm after a tribological test with DLC/DLC contact in b-TPPT solution.

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<td>C₁₂H₂₄N</td>
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<td><strong>Total intensity</strong></td>
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<td><strong>95546</strong></td>
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3.5.5. Complementary chemical analyzes of the b-TPPT additive

Further investigations were performed to find the source of the amines present in all experiments performed with b-TPPT, as they were still detected following argon sputter-cleaning of the oil bath. The nitrogen concentration of the pure additive was determined by thermal conductivity detection of the gas phase and was found below the detection limit of 0.1 wt%, meaning that, if the amine was a contamination in the additive, the concentration of nitrogen in the b-TPPT/PAO solution was lower than 10 ppm in weight.
Electrospray ionization coupled to mass spectrometry (ESI-MS) was first performed on the pure b-TPPT. Peaks corresponding to protonated triphenyl phosphorothionate with two, one and zero butyl groups attached to the phenyl groups were detected at m/z of 455.33, 399.33 and 343.27, respectively. Weak peaks were also present at lower m/z with a mass difference of 16, indicating that in some of the additive molecules the sulfur atom had been replaced by oxygen to give the corresponding phosphate. Tandem mass spectrometry (MS-MS) was performed for the three main components detected with ESI-MS. The fragments detected at lower masses corresponded to the loss of O\textsubscript{C\textsubscript{6}}H\textsubscript{5} and S\textsubscript{C\textsubscript{6}}H\textsubscript{5} suggesting that the b-TPPT contained phosphorothionate and phosphorothioate. Gas-chromatography coupled to mass spectrometry (GC-MS) allowed the same fragments to be detected and confirmed the presence of both phosphorothionate and phosphorothioate. However, amine was not detected with either ESI-MS or GC-MS.
3.6. Amine phosphate

3.6.1. Tribological results

The friction coefficients for tests performed in PAO containing 1 wt% AP were 0.074 ± 0.022 and 0.092 ± 0.008 for steel/steel and DLC/DLC contacts, respectively (Fig. 3.41). After one hour of test, the friction was still decreasing in all cases for steel sliding against steel. On DLC, the friction coefficients were very different at the beginning, but after 1 hour, the coefficient of friction tended to values between 0.08 and 0.1.

![Figure 3.41 Evolution of the coefficient of friction (CoF) with the time for a) steel/steel and b) DLC/DLC contacts. The HFRR tests were performed in PAO containing 1 wt.% AP at 80°C.](image)

3.6.2. Topographical observations

ESEM was performed on the contact areas after sliding (Fig. 3.42). On the steel pin, EDX identified the darker regions as containing more phosphorus (Fig. 3.43), but this technique was not sensitive enough to detect additive elements on DLC. The tribofilm formed with AP on steel had a structure that was oriented in the sliding direction (Fig. 3.44). Between the lines of tribofilm, the structure of the steel was still visible. The tribofilm thickness, estimated from the AFM images, was approximately 10 nm in the high-speed region and about 40 nm in the low-speed regions. On DLC, the first observable difference between the tests with AP and ZnDTP or b-TPPT was the absence of a rejected-debris layer around the HFRR track. No tribofilm could be detected with AFM on the DLC coating following sliding against DLC. The rounded structure of DLC was still visible, but, additionally, there was some wear of the
more protruding structures (Fig. 3.45). ESEM could also not detect the presence of a reacted layer.

Figure 3.42 ESEM images of the central part of the track a) on a steel plate and b) on a DLC-coated plate after tests performed in PAO containing 1 wt% AP.

3.43 a) ESEM image of an uncoated steel pin after an HFRR test performed in PAO containing 1 wt% AP and b) the EDX spectrum of the darker region.
Figure 3.44 AFM deflection images and corresponding height profiles of the AP tribofilm for a steel/steel contact. Images of a) a high-speed and b) a low-speed region are shown as well as c) the edge of the contact area. In all cases the sliding direction is vertically oriented.

Figure 3.45 AFM deflection images and corresponding height profiles of the DLC surface following sliding in PAO containing AP. Images of a) a high-speed and b) a low-speed region are shown. In all cases the sliding direction is vertically oriented.
3.6.3. XPS analysis

XPS analyses were performed in contact and non-contact regions on the steel and DLC substrates. High resolution spectra of the main peaks of all present elements are shown in figure 3.46. Analyses were performed in the non-contact region, and in the low-speed and high-speed regions corresponding to sliding velocity between 30 and 60 mm/s and 100 and 140 mm/s, respectively.

The phosphorus P 2p$_{3/2}$ peaks were detected at 133.9 ± 0.2 eV in both contact regions and at 133.7 eV in the non-contact region. The carbon C 1s signal was fitted with three peaks at 285.0 eV, 286.7 ± 0.2 eV and 289.2 ± 0.2 eV corresponding to aliphatic carbon, C-O groups and C=O groups or carbonates, respectively [6, 10]. The oxygen O 1s signal showed a contribution from iron oxide at low binding energy, non-bridging oxygen from phosphates and also carbonates, as the main peak, and bridging oxygen, P-O-P and P-O-C, with the possibility of adsorbed water at high binding energy. The binding energy values were 530.3 ± 0.2 eV, 532.0 ± 0.2 eV and 533.3 ± 0.2 eV for the non-contact regions and 530.1 ± 0.2 eV, 531.9 ± 0.2 eV and 533.5 ± 0.2 eV for both contact areas. In all regions, metallic iron was detected at 707.0 ± 0.2 eV, Fe (+2) at 709.6 ± 0.2 eV, Fe (+3) at 710.5 ± 0.2 eV, iron oxy-hydroxide at 712.0 ± 0.2 eV and iron phosphates at 714.3 eV. The satellite peak of Fe (+2) with an intensity of 8 % of the main signal was present at 715.1 ± 0.2 eV.
Figure 3.46 High resolution spectra of a) P 2p, b) C 1s, c) N 1s, d) O 1s and e) Fe 2p peaks in contact and non-contact regions after tribological experiments for steel/steel contacts in PAO containing 1 wt% AP.
XPS analyses were performed on the DLC-coated plates after tribological experiments in AP solution in the non-contact, low-speed and high-speed regions. In the survey spectra, only signals from carbon, oxygen, phosphorus and nitrogen were detected. High-resolution spectra of the main peaks of these elements are shown in figure 3.47. A table of the fitting parameters is shown in the appendix. The phosphorus P 2p signal was fitted with the two peaks 2p_{3/2} and 2p_{1/2} due to spin-orbit splitting that were separated by 0.85 eV. The area ratio was set to 2:1. The P 2p_{3/2} peaks was found at 133.5 ± 0.2 eV in the non-contact region and at 133.2 ± 0.2 eV in the HFRR track. The carbon C 1s peak was fitted with five peaks in the contact areas and four peaks in the non-contact region. The carbon from the overlayer that were present in all regions were found at 285.0 eV, 286.5 ± 0.2 eV and 288.3 ± 0.2 eV and corresponded to aliphatic carbon, C-O or C-N groups and C=O groups, respectively [6, 10]. The C 1s asymmetric peak from DLC, set from reference measurements at 284.6 eV (§ 3.1.4), was found as the main contribution in non-contact area, but had a much lower intensity than aliphatic carbon from the overlayer in the HFRR track. This was due to the presence of a thin adsorbed layer out of the track, consistent with the low intensity of the signals P 2p and N 1s. In both contact regions, an additional peak was found at a low binding energy of 284.0 ± 0.2 eV and was assigned to graphitic carbon originating from the partial degradation of the DLC coating during the tribological experiments (§ 3.9.1). An additional peak was required at low binding energy as the FWHM of the total C1s signal was 1.6 ± 0.1 eV in the non-contact regions and 2.1 ± 0.1 eV in the HFRR track. The N 1s peak was fitted with two peaks at 399.5 ± 0.2 eV and 401.4 ± 0.2 eV in the contact regions, and at 399.7 ± 0.2 eV and 401.6 ± 0.2 eV in non-contact areas. These two peaks were assigned to dialkylamine and cationized dialkylamine, respectively. The oxygen O 1s signal was fitted with two contributions at 532.1 ± 0.2 eV and 533.1 ± 0.2 eV in non-contact regions, and at 531.2 ± 0.2 eV and 532.8 ± 0.2 eV in the tribological tracks. In non-contact regions, the peak at lower binding energy was attributed to non-bridging oxygen of phosphate, while in the HFRR tracks it was attributed to non-bridging oxygen of phosphates [32], to carboxyl groups [10] and, possibly, amides [6]. The peak at higher binding energy corresponded to bridging oxygen P-O-C for all regions.

In both steel/steel and DLC/DLC contacts, the presence of cationized alkylamines increased relatively to unreacted amine.
Figure 3.47 High resolution spectra of a) P 2p, b) C 1s, c) N 1s and d) O 1s peaks in contact and non-contact regions after tribological experiments for DLC/DLC contacts in PAO containing 1 wt% AP.
Results

3.6.4. ToF-SIMS

Contact and non-contact regions were analyzed with ToF-SIMS after steel/steel tribological experiments in AP solution. Table 3.11 shows the most prominent peaks in negative mode for inorganic ions, particularly the polyphosphate species. Iron polyphosphates were found with significantly higher intensities on the HFRR tracks with fragments containing up to 4 phosphorus atoms. In positive mode, amines were the principal compounds detected. Table 3.12 shows a list of the main peaks found for alkylamines. Alkylamines containing up to 26 carbon atoms were identified.

Table 3.11 The most prominent inorganic, negative, secondary ions measured on the thermal film (non-contact region) and on the tribofilm (contact region) after a tribological test with steel/steel contact in AP solution.

<table>
<thead>
<tr>
<th>Ion (charge 1-)</th>
<th>Mass</th>
<th>Corr. Int.</th>
<th>Tribofilm</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>30.973</td>
<td>1126</td>
<td>2714</td>
</tr>
<tr>
<td>NO₂</td>
<td>45.993</td>
<td>3442</td>
<td>2386</td>
</tr>
<tr>
<td>PO</td>
<td>46.968</td>
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<td>NO₃</td>
<td>61.986</td>
<td>3424</td>
<td>3483</td>
</tr>
<tr>
<td>PO₂</td>
<td>62.964</td>
<td>580783</td>
<td>559791</td>
</tr>
<tr>
<td>SO₂</td>
<td>63.967</td>
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<td>SO₃H</td>
<td>80.962</td>
<td>17897</td>
<td>31371</td>
</tr>
<tr>
<td>FeO₂</td>
<td>87.924</td>
<td>18876</td>
<td>2469</td>
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<tr>
<td>PO₄H</td>
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<tr>
<td>FePO₄</td>
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<td>9465</td>
<td>5958</td>
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<td>P₂O₆H</td>
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<td>23645</td>
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<td>FeP₂O₆</td>
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<td>FeP₂O₇H</td>
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<td>Fe₂P₄O₁₃</td>
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Total Intensity 1226059 1402773
Table 3.12 The most prominent secondary positive ions from amines measured on the thermal film and on the tribofilm after a tribological test with steel/steel contact in AP solution.

<table>
<thead>
<tr>
<th></th>
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<td>NH₄</td>
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<td>6677</td>
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<td>31730</td>
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<td>4137</td>
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<td>3455</td>
<td>5914</td>
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<td>C₂₈H₆₆N</td>
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<td>636</td>
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On the DLC plate in negative mode, only fragments containing up to two phosphorus atoms were found (Table 3.13). Polyphosphates of larger masses were not detected. Nevertheless, the intensities of phosphates were significantly higher on the tracks. In positive mode alkylamines containing up to 14 carbons were found with peaks of higher intensity in the track.
Table 3.13 The most prominent inorganic, negative, secondary ions measured on the thermal film and on the tribofilm after a tribological test with DLC/DLC contact in AP solution.

<table>
<thead>
<tr>
<th>Ion (charge 1-)</th>
<th>Mass</th>
<th>Thermal film</th>
<th>Tribofilm</th>
</tr>
</thead>
<tbody>
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<td>P</td>
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<td>-</td>
<td>536</td>
</tr>
<tr>
<td>NO2</td>
<td>45.993</td>
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<td>347600</td>
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<td>SO2</td>
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<td>709</td>
<td>4351</td>
</tr>
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<td>PO3</td>
<td>78.959</td>
<td>48402</td>
<td>256675</td>
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<tr>
<td>PO4H</td>
<td>95.961</td>
<td>4740</td>
<td>67793</td>
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<tr>
<td>P2O3H</td>
<td>158.925</td>
<td>331</td>
<td>10724</td>
</tr>
<tr>
<td>P2H3O7</td>
<td>176.939</td>
<td>-</td>
<td>5684</td>
</tr>
<tr>
<td><strong>Total intensity</strong></td>
<td><strong>68730</strong></td>
<td><strong>698924</strong></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.14 The most prominent positive, secondary ions from amines measured on the thermal film and on the tribofilm after a tribological test with DLC/DLC contact in AP solution.

<table>
<thead>
<tr>
<th>Ion (charge 1+)</th>
<th>Mass</th>
<th>Thermal film</th>
<th>Tribofilm</th>
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<tr>
<td>CH3</td>
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<td>11284</td>
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<tr>
<td>NH4</td>
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<td>19688</td>
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<tr>
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<td>261222</td>
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<td>C2H8N</td>
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<td>269</td>
<td>1884</td>
</tr>
<tr>
<td>PO</td>
<td>46.966</td>
<td>-</td>
<td>2102</td>
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<tr>
<td>C3H12N</td>
<td>86.100</td>
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<td>C6H14N</td>
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<td>C11H26N</td>
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<td>334</td>
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<td>C12H28N</td>
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<td>C12H28N</td>
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<td>C13H30N</td>
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<tr>
<td>C14H30N</td>
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<td>1182</td>
<td>7196</td>
</tr>
<tr>
<td><strong>Total intensity</strong></td>
<td><strong>40897.04</strong></td>
<td><strong>350620.34</strong></td>
<td></td>
</tr>
</tbody>
</table>
3.7 Mixture of zinc-free additives

3.7.1. Tribological results

As ZnDTP tends to be replaced by packages of additives rather than by a single one, HFRR experiments were also carried out in a PAO solution containing 0.3 wt.% AP, 0.3 wt% b-TPPT and 0.3 wt% of a friction modifier shown in table 2.3. The tests were performed under the standard conditions used for the HFRR tests with pure additives (5N, 2mm, 20Hz, 80°C). The evolution of the friction coefficients with time are shown in figure 3.48 for steel sliding against steel and DLC sliding against DLC. With both steel and DLC, a steady-state was not reached during the 1-hour tribological test. In the steel case, a delayed increase of the friction coefficient appeared after 10 minutes of rubbing from 0.10 up to near 0.14. It was followed by a slow continuous decrease of the friction and after one hour a friction coefficient of 0.093 ± 0.012 was measured. In the case of DLC sliding against DLC, the friction coefficient started at 0.12 and decreased continuously to 0.079 ± 0.008 after one hour.

![Figure 3.48 Evolution of the friction coefficient with the time for a) steel/steel and b) DLC/DLC contacts for the additive mixture.](image)

3.7.2. Topographical observations

ESEM (Fig. 3.49) and AFM (Fig. 3.50) were performed on the steel and DLC-coated plates. On steel, a tribofilm was built up with patches of thickness up to 40 nm, measured from the AFM images. On DLC, structures from reacted products were observed with AFM images. This was not worn rounded structures of the coating, as they were thicker than the 10 to 20 nm high structure of the as-deposited coating.
**figure 3.49** ESEM images of the central part of the track on a) a steel plate and b) a DLC-coated plate after tests performed in PAO containing AP, b-TPPT and a friction modifier. The arrows indicate the sliding directions.

**figure 3.50** AFM deflection images and corresponding height profiles taken in the contact areas for a) steel/steel and b) DLC/DLC contact after tribological experiment in a zinc-free additive mixture solution. The sliding direction is oriented vertically.
3.8. Reference measurements

Further tribological measurements were performed, particularly for DLC sliding against DLC, on reference compounds with the same parameters as in the previous experiments. The role of sulfur in the formation of a thermal film and tribofilm was investigated by adding octanethiol or propanesulfonic acid to a solution of PAO containing 1 wt% AP. As smoothing wear was observed on the DLC coating after tests on AP in PAO and a similar behavior was not observed for tests with ZnDTP or b-TPPT, DLC/DLC measurements were also performed in PAO containing 1 wt% didodecylamine in the absence of phosphates. ESEM, AFM and XPS were used to characterize these samples.

3.8.1. Sulfur-containing compounds

Sulfur-containing compounds were added to 1 wt% AP in PAO before carrying out experiments on DLC/DLC contacts. The friction coefficients measured during sliding in solutions of AP with propanesulfonic acid showed a similar behavior over time for three tests, with a friction coefficient at the end of each test of 0.075 ± 0.006 (Fig. 3.51 a). On the other hand, there was a clear decrease in friction coefficient between the first and the third test for sliding in a solution of AP and octanethiol from 0.127 to 0.060 (Fig. 3.51 b). The graphs of coefficient of friction versus time, shown in figure 3.51, are from experiments performed on a single plate with a new pin for each test. The concentration of sulfur-containing compound corresponded to a ratio 1:1 between sulfur and phosphorus.
Results

Figure 3.51 Evolution of the friction coefficient with time for DLC sliding against DLC in a) PAO containing AP and propanesulfonic acid and b) in PAO containing AP and octanethiol. Each series of HFRR tests were performed on a single plate with a new ball segment for each track.

Following sliding of DLC against DLC in the presence of octanethiol or propanesulfonic acid, ESEM and AFM imaging showed the presence of scratches on the DLC-coated plates. However, a significant amount of wear did not occur as the rounded structures of the as-deposited coating were still present even in the region of low sliding speed. The absence of spikes in the friction coefficient graphs for both sulfur-containing compounds confirmed that the production of wear particles was low. The scratches formed in the presence of octanethiol were ca. 30 nm deep (Fig. 3.54), while they were ca. 60 nm deep in presence of propanesulfonic acid (Fig. 3.55).

Figure 3.52 ESEM images on the HFRR track of a DLC-coated plate a) at the end of the HFRR track and b) in the central part after tests in PAO solutions of AP and octanethiol.
Figure 3.53 ESEM images at a) low and b) high resolution of the central part of an HFRR track on a DLC-coated plate after tests in PAO containing AP and propanesulfonic acid.

Figure 3.54 AFM deflection images and corresponding height profiles on tracks for DLC sliding against DLC in PAO containing AP and octanethiol. Images of a) high-speed and b) low-speed regions are shown. In both cases, the sliding direction was vertically oriented.
3.8.2. Didodecylamine

As in the case of the sulfur-containing compounds (section 3.8.1), three tests were performed on the same plate for DLC sliding against DLC in a solution of didodecylamine in PAO. The three tests showed similar low friction values of 0.025 ± 0.004, near the value obtained in pure PAO (0.014 ± 0.004). However, unlike the tests performed with sulfur compounds, the friction coefficient showed instabilities with the time. This was consistent with the polishing wear observed with AFM (Fig. 3.57).
Figure 3.56 Evolution of the friction coefficient with the time for DLC sliding against DLC in solutions of didodecylamine in PAO. The series of HFRR tests was performed on a single plate with a new ball segment for each track.

Figure 3.57 AFM deflection images and corresponding height profiles on tracks for DLC/DLC contact after tests in PAO containing didodecylamine. Images of a) high-speed and b) low-speed regions are shown. In both cases, the sliding direction is vertically oriented.
The HFRR tracks and the non-contact regions were analyzed with XPS. Spectra of the non-contact region, low-speed (sliding velocity between 30 and 60 mm/s) and high-speed (sliding velocity between 100 and 140 mm/s) areas are shown in figure 3.x. In addition to the signal from the DLC substrate, the carbon C 1s was made up of three peaks at 285.0 ± 0.2 eV, 286.7 ± 0.2 eV and 288.4 ± 0.2 eV corresponding to aliphatic carbon, C-O and C=O groups [6, 10]. The DLC peak positioned at 284.6 eV was strong in the non-contact region, but on the HFRR tracks, the signal was weakened due to the thicker tribofilm. The oxygen O 1s could be assigned to two peaks. The first peak was assigned to C=O groups [9, 10] shifted from 532.2 ± 0.2 eV in non-contact region to 531.9 ± 0.2 eV in the low-speed area and, finally, to 531.7 ± 0.2 eV in the high-speed region. The peak assigned to C-O groups shifted in a similar way from 533.3 ± 0.2 eV in the non-contact region to 533.1 ± 0.2 eV in the low-speed region and, finally, to 532.9 ± 0.2 eV in the high-speed region. The nitrogen N 1s peak was made up of two contributions. The first peak at 399.7 ± 0.3 eV was attributed to the secondary amine while the second peak was assigned to cationized amine. This second peak shifted from 402.0 ± 0.2 eV in non-contact region to 401.4 ± 0.2 eV for the low-speed area and to 401.2 ± 0.2 eV in the high-speed region [38-40, 42].
Figure 3.58 a) Survey and high resolution spectra of b) C 1s, c) O 1s and d) N 1s peaks in non-contact, low-speed and high-speed regions after tribological experiments for DLC/DLC contacts in PAO containing didodecylamine.

ToF-SIMS analyses were also performed on HFRR tracks and in non-contact regions. Differences in composition and the presence of amine fragments were examined in both positive and negative modes. With negative polarity, no significant differences were found. In positive mode the most significant observation was of the presence of alkylamines incorporating more carbon atoms than the starting material, NH(C_{12}H_{25})_{2}. Alkylamines with 30 and 32 carbon atoms were clearly present in the HFRR tracks. Tables 3.x shows the main alkylamine species found on the tracks and in non-contact regions.
Table 3.15 The most prominent positive secondary ions from amines in contact and non-contact regions on the DLC-coated plate after sliding in PAO containing didodecylamine.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Mass</th>
<th>Non-contact</th>
<th>HFRR track</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{12}H_{26}N+</td>
<td>184.2049</td>
<td>543</td>
<td>1998</td>
</tr>
<tr>
<td>C_{17}H_{36}N+</td>
<td>254.2825</td>
<td>155</td>
<td>3613</td>
</tr>
<tr>
<td>C_{24}H_{50}N+</td>
<td>352.3859</td>
<td>110</td>
<td>1826</td>
</tr>
<tr>
<td>C_{24}H_{52}N+</td>
<td>354.4023</td>
<td>457</td>
<td>9842</td>
</tr>
<tr>
<td>C_{30}H_{58}N+</td>
<td>432.4422</td>
<td>107</td>
<td>1065</td>
</tr>
<tr>
<td>C_{32}H_{68}N+</td>
<td>466.5446</td>
<td>89</td>
<td>4393</td>
</tr>
</tbody>
</table>
3.9. Reference samples

Reference materials were analyzed with XPS under the same conditions used for thermal films and tribofilms, i.e. a pass energy of 58.7 eV for a step size of 0.125 eV and a beam size of 100 µm, unless otherwise stated. For reference materials, special attention was given to the position of the S 2p$_{3/2}$ and Zn 2p$_{3/2}$ peaks. Argon sputtering of these samples was only performed when necessary to remove a contamination layer in order to distinguish the signal of interest. Degradation of the material due to the ion beam, such as reduction of elements or preferential sputtering, was carefully examined. AISI steel was analyzed after the same treatment as for steel plates used for the tribological experiments.

3.9.1 Highly oriented pyrolytic graphite (HOPG)

An HOPG sample (Advanced Ceramics Corporation, Cleveland, OH, USA) was used as a reference for graphite. The analysis was performed without sputter-cleaning to avoid any degradation of the graphite structure. A fresh graphite layer was created immediately before the introduction of the sample into the XPS instrument. Without sputtering, the intensity ratio between the signals O 1s and C 1s was 0.3%. The main C 1s peak showed an asymmetric shape fitted with GL(80)T(0.9). Its position was 284.0 ±0.1 eV with a FWHM of 0.7 eV. As HOPG is electrically conductive, a charge correction was not applied. At 6.4 eV above the C 1s main peak, a satellite peak was detected, caused by a shake-up process involving the energy transition of Π→Π$^*$ in graphite [13].

![Graphs showing XPS spectra of HOPG](image)

Figure 3.59 a) Survey and high resolution spectra of b) carbon and c) oxygen of a cleaved HOPG surface.
3.9.2. Polished steel substrate

An AISI 52100 steel plate, polished with the procedure described in section 2.2.2, was analyzed with XPS after ultrasonic cleaning in heptane, ethanol and doubly-distilled water. Spectra of the steel surface without presputtering are shown in figure 3.60 and their fitting parameters are given in table 3.16. In the high resolution spectra, the carbon C 1s signal showed four contributions. The most intense peak at 285.0 eV corresponded to aliphatic carbon. At higher binding energy, the peak at 286.5 eV was assigned to C-O groups [6, 19] and the peak at 288.9 eV, to O-C=O groups [6, 19] or to carbonates [12, 21]. A small peak at 282.9 eV was due to carbides [14-16]. The oxygen signal had three contributions at 530.2 eV, 531.7 eV and 532.9 eV that corresponded to iron oxide, hydroxide and adsorbed water [17]. The iron signal Fe 2p3/2 contained four different contributions [17, 18]. The metallic iron peak was at 706.9 eV, the iron oxide Fe(+2) was at 709.3 eV, iron oxide Fe(+3) at 710.7 eV and Fe(+3) from iron oxy-hydroxide had a contribution at 711.7 eV. A shake-up satellite of the Fe(+2) peak was positioned 5.5 eV above at 714.8 eV. A low-intensity signal from chromium was also observed with a Cr 2p3/2 peak at 576.8 eV assigned to oxide [13].
Figure 3.60 a) Survey and high resolution spectra for b) carbon, c) oxygen, d) iron and e) chromium at the surface of polished AISI 52100 steel without presputtering.

Table 3.16 Fitting parameters of the polished AISI 52100 steel surface without presputtering shown in figure 3.60.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Position (eV)</th>
<th>FWHM (eV)</th>
<th>Shape</th>
<th>Area (CPSxeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s (carbide)</td>
<td>282.9 ± 0.1</td>
<td>1.8</td>
<td>GL(30)</td>
<td>172.8</td>
</tr>
<tr>
<td>C 1s (aliphatic)</td>
<td>285.0 ± 0.1</td>
<td>1.8</td>
<td>GL(30)</td>
<td>3816.6</td>
</tr>
<tr>
<td>C 1s (C-O)</td>
<td>286.5 ± 0.1</td>
<td>1.8</td>
<td>GL(30)</td>
<td>1153.4</td>
</tr>
<tr>
<td>C 1s (COOX/CO3)</td>
<td>288.9 ± 0.1</td>
<td>1.8</td>
<td>GL(30)</td>
<td>1590.2</td>
</tr>
<tr>
<td>O 1s (oxide)</td>
<td>530.2 ± 0.1</td>
<td>1.5</td>
<td>GL(20)</td>
<td>19192.6</td>
</tr>
<tr>
<td>O 1s (hydroxide)</td>
<td>531.7 ± 0.1</td>
<td>1.5</td>
<td>GL(20)</td>
<td>10781.8</td>
</tr>
<tr>
<td>O 1s (water)</td>
<td>532.9 ± 0.1</td>
<td>1.5</td>
<td>GL(20)</td>
<td>3429.9</td>
</tr>
<tr>
<td>Fe 2p3/2 (metal)</td>
<td>706.9 ± 0.2</td>
<td>1.2</td>
<td>GL(30)T(0.75)</td>
<td>3237.8</td>
</tr>
<tr>
<td>Fe 2p3/2 (+2; ox)</td>
<td>709.3 ± 0.2</td>
<td>3.5</td>
<td>GL(50)</td>
<td>2928.3</td>
</tr>
<tr>
<td>Fe 2p3/2 (+3; ox)</td>
<td>710.6 ± 0.2</td>
<td>2.8</td>
<td>GL(50)</td>
<td>13551.2</td>
</tr>
<tr>
<td>Fe 2p3/2 (OOH)</td>
<td>711.7 ± 0.2</td>
<td>3.6</td>
<td>GL(50)</td>
<td>12832.3</td>
</tr>
<tr>
<td>Fe 2p3/2 (sat, +2; ox)</td>
<td>714.8 ± 0.2</td>
<td>3.5</td>
<td>GL(50)</td>
<td>234.3</td>
</tr>
</tbody>
</table>
Results

The spectra of an AISI 52100 steel after presputtering at 3kV for 120 s are shown in figure 3.61 with the fitting parameters in table 3.17. The C 1s peak showed only the contribution of carbide at 283.2 eV, while the O 1s peak contained contributions of oxide (at 530.2 eV), hydroxide (at 531.6 eV) and water (at 532.9 eV), but with very low intensity in comparison to the analysis before sputtering. These contributions of oxide and hydroxide were too small to be distinguished in the Fe 2p\textsubscript{3/2} signal that was fitted only with the metallic iron peak at 707.0 eV. Chromium showed a higher intensity than on non-sputtered analysis and the peak Cr 2p\textsubscript{3/2} at 574.4 eV was assigned to the metallic state [13].

Figure 3.61 a) Survey and high resolution spectra of b) carbon, c) oxygen, d) iron, e) chromium and f) argon at the surface of polished AISI 52100 steel after presputtering (3kV, 120s).
Table 3.17 Fitting parameters of the polished AISI 52100 steel surface after an argon-presputtering shown in figure 3.61.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Position (eV)</th>
<th>FWHM (eV)</th>
<th>Shape</th>
<th>Area (CPS eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s (carbide)</td>
<td>283.2 ± 0.1</td>
<td>1.8</td>
<td>GL(30)</td>
<td>832.8</td>
</tr>
<tr>
<td>O 1s (oxide)</td>
<td>530.2 ± 0.1</td>
<td>1.4</td>
<td>GL(20)</td>
<td>1845.3</td>
</tr>
<tr>
<td>O 1s (hydroxide)</td>
<td>531.6 ± 0.1</td>
<td>1.4</td>
<td>GL(20)</td>
<td>687.6</td>
</tr>
<tr>
<td>O 1s (water)</td>
<td>532.9 ± 0.1</td>
<td>1.4</td>
<td>GL(20)</td>
<td>249.5</td>
</tr>
<tr>
<td>Cr 2p3/2 (metal)</td>
<td>574.4 ± 0.1</td>
<td>1.4</td>
<td>GL(50)T(1.0)</td>
<td>1928.2</td>
</tr>
<tr>
<td>Fe 2p3/2 (metal)</td>
<td>707.0 ± 0.1</td>
<td>1.1</td>
<td>GL(80)T(0.8)</td>
<td>127531.5</td>
</tr>
</tbody>
</table>

3.9.3. Metallic zinc

A sputter-cleaned (3 kV for 60s) metallic zinc sample was analyzed with XPS. The Zn 2p3/2 peak was fitted with a sum of the Gaussian and Lorentzian functions with a tail function SGL(85)T(1.5). This peak was positioned at 1021.8 ± 0.1 eV with a FWHM of 0.7 eV. The peak area correction was applied to compare the peaks Zn 2p3/2, Zn 3s and Zn 3p3/2. This comparison between the first peak at high binding energy with the two others at low binding energy gave a standard deviation of 12 %.

Figure 3.62 a) Survey and b) high resolution spectrum of a sputtered metallic zinc sample.

Table 3.18 Fitting parameters and corrected area for three different peaks of a sputter-cleaned metallic zinc sample.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Position (eV)</th>
<th>FWHM (eV)</th>
<th>Area (CPS eV)</th>
<th>Corr. area (CPS eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn 2p3/2</td>
<td>1021.8</td>
<td>0.7</td>
<td>44287</td>
<td>4459.2</td>
</tr>
<tr>
<td>Zn 3s</td>
<td>139.7</td>
<td>2.3</td>
<td>3393.8</td>
<td>5692.8</td>
</tr>
<tr>
<td>Zn 3p3/2</td>
<td>88.5</td>
<td>2.3</td>
<td>6016.6</td>
<td>5197.2</td>
</tr>
</tbody>
</table>
3.9.4. Zinc oxide

Zinc oxide powder (Riedel-de Haën, Germany) was pressed onto an indium foil and analyzed without sputter-cleaning. The C 1s peak showed contributions from aliphatic carbon at 285.0 eV and of carbonates or carboxylic groups at 289.1 ± 0.1 eV. The O 1s peak had a main contribution of oxide at 530.4 ± 0.1 eV with minor peaks at 531.7 ± 0.1 eV and 532.6 eV corresponding to hydroxide and adsorbed water, respectively. The FWHM was 1.3 eV. The zinc signal Zn 2p$_{3/2}$ at 1022.0 ± 0.1 eV with a FWHM of 1.7 eV was fitted with a line shape of GL(60). After intensity correction, a ratio between zinc and oxygen from oxide of 57% of zinc for 43% oxygen was determined.

Figure 3.63 a) Survey and high resolution spectra of b) carbon, c) oxygen, and d) zinc for a zinc oxide powder.
3.9.5. Zinc carbonate

A zinc carbonate powder (Sigma-Aldrich AG, Switzerland) was pressed onto an indium foil and analyzed following argon sputtering. The main C 1s peak assigned to carbonate was found at 289.6 ± 0.1 eV with a small contribution at 285.0 ± 0.1 eV. A small peak at higher binding energy was found in all carbon C 1s, oxygen O 1s and zinc Zn 2p\(_{3/2}\). This may be due to a charging effect at the beginning of the measurement. When the analysis was repeated with different samples and different sizes of mask, with both positive and negative neutralization, these small contributions were always present. Nevertheless, the position C 1s main peak could be used as reference for carbonate. The main O 1s and the Zn 2p\(_{3/2}\) peaks were found at 531.6 ± 0.1 eV and 1022.1 ± 0.1 eV, respectively.

Figure 3.64 a) Survey and high resolution spectra of b) carbon, c) zinc, and d) oxygen for zinc carbonate powder.
3.9.6. Zinc sulfide

A fresh surface obtained by breaking a piece of zinc sulfide (Sigma-Aldrich AG, Switzerland) was analyzed before and after argon sputtering (Fig. 3.65). As well as an organic contamination, the S 2p and Zn 2p$_{3/2}$ peaks of the non-sputtered sample showed other contributions than those from zinc sulfide. Argon sputtering for 60 s at 3kV removed this compound without provoking a reduction of sulfur or zinc. An S 2p$_{3/2}$ peak was detected at 162.4 ± 0.1 eV with a FWHM of 1.7 eV and a GL(30) line shape. The S 2p$_{1/2}$ peak was set 1.2 eV higher with an area of 50% of the S 2p$_{3/2}$ peak. The Zn 2p$_{3/2}$ peak was at 1022.6 ± 0.1 eV with a FWHM of 2.0 eV and a GL(60) line shape. These gave concentrations of 46% zinc and 54 % sulfur.

![Graphs](attachment:image.png)

Figure 3.65 a) Survey and high resolution spectra of b) carbon, c) zinc, and d) sulfur for zinc sulfide (1) before sputtering and (2) after sputtering.
3.9.7. Zinc sulfate

Powder of zinc sulfate monohydrate (Riedel-de Haën, Germany) was pressed onto an indium foil and analyzed without sputtering. The Zn 2p<sub>3/2</sub> peak was detected at 1023.4 ± 0.1 eV with a FWHM of 2.1 eV and a GL(60) line shape. Sulfur S 2p<sub>3/2</sub> showed only one contribution at 169.2 ± 0.1 eV with a FWHM of 1.8 eV and a line shape of GL(30). Oxygen gave a main peak at 532.5 ± 0.1 eV assigned to sulfate and a minor peak at 534.1 ± 0.1 eV assigned to water. Both sulfur signals were fitted with a GL(20) line shape. The area ratio between oxygen from sulfate and from hydration water corresponded to the ratio 4:1 with an experimental value of 3.95:1.

![Survey and high resolution spectra of zinc, sulfur and oxygen for zinc sulfate without argon sputtering.](image)

Figure 3.66 a) Survey and high resolution spectra of b) zinc, c) sulfur and d) oxygen for zinc sulfate without argon sputtering.
3.9.8. Sodium sulfite

An anhydrous sodium sulfite powder (Riedel-de Haën, Germany) was pressed onto an indium foil. Argon presputtering was necessary to obtain clear signals from the powder. The oxygen O1s peak was positioned in the middle of Auger signals from sodium. The S 2p signal showed three pairs for 2p$_{3/2}$ and 2p$_{1/2}$ that were separated by 1.2 eV and had an area ratio of 2:1. All peaks were fitted with a GL(30) line shape and all FWHM were 1.9 eV. The smallest S 2p$_{3/2}$ peak at 159.9 ± 0.1 eV was assigned to sulfide. The origin of this peak was the argon presputtering. The two other S 2p$_{3/2}$ peaks were detected at 167.2 ± 0.1 eV and 169.4 eV and were assigned to the oxidation states +4 and +6, respectively [13, 21, 43, 44]. Further sputtering did not change the intensity ratio between these three states of sulfur.

![Figure 3.67 a) Survey and b) high resolution spectrum of a sputtered anhydrous sodium sulfite powder.](image)

3.9.9. Adsorbed octanethiol and propanesulfonic acid

Octanethiol and propanesulfonic acid were used as XPS references after deposition onto both AISI 52100 steel and gold substrates. The compounds were dissolved in cyclohexane to a concentration of 5 wt%. A few droplets were deposited on the steel and gold substrate and the solvent was evaporated under low vacuum at room temperature. This resulted in the formation of both an adsorbed layer and excess, unbound material. The S 2p spectra acquired on the four samples are shown in figure 3.68. The S2 p signal consisted of the 2p$_{3/2}$ and 2p$_{1/2}$ peaks due to spin-orbit splitting. The area ratio between the two contributions was set to 2:1 with an energy difference of 1.2 eV [13, 27, 45].
The S 2p signal on gold showed contributions of two doublets (Fig 3.68 b) with the S 2p<sub>3/2</sub> peaks at 162.0 ± 0.2 eV and 163.4 eV. These values are in agreement with literature values for thiolate bound to gold and to unbound thiolate [27, 30, 35]. On steel, only one S 2p doublet was observed at 168.4 ± 0.2 eV and corresponded to oxidized sulfur [21, 46, 47].

Only one contribution for S 2p<sub>3/2</sub> was found at 168.1 ± 0.2 eV, following deposition of propanesulfonic acid on steel, corresponding to oxidized sulfur. On gold, two doublets were found with the 2p<sub>3/2</sub> peaks at 162.4 ± 0.2 eV and at 168.6 ± 0.2 eV. The first peak corresponded to reduced sulfur (-2) bound to gold, and the second peak corresponded to S(+6) [21, 47].

Figure 3.68 High resolution spectra of S 2p signals for octanethiol on a) a steel substrate and b) gold and for propanesulfonic acid on c) a steel substrate and d) gold.
3.10 ToF-SIMS analysis

Adsorption experiments of octanethiol were performed at 23 °C and 80°C onto a DLC-coated plate. The adsorbed products were analyzed with ToF-SIMS in negative mode. Table 3.19 shows the intensities of alkylthiols and SO\textsubscript{x} species, relative to the intensity of the peak assigned to C\textsubscript{3}H\textsubscript{7}S. At 23°C, oxidized sulfur is detected with a large presence of SO\textsubscript{3}\textsuperscript{-}. At 80°C, the relative intensity of the SO\textsubscript{2}\textsuperscript{-} and SO\textsubscript{3}\textsuperscript{-} species increased by a factor 4 and 5.4, respectively.

Table 3.19 Negative secondary ions in the ToF-SIMS spectra after the adsorption of octanethiol at 23°C and at 80°C onto a DLC coating.

<table>
<thead>
<tr>
<th>Ion (charge 1-)</th>
<th>Mass (Da)</th>
<th>23°C</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>31.971</td>
<td>71.3</td>
<td>233.2</td>
</tr>
<tr>
<td>HS</td>
<td>32.980</td>
<td>102.4</td>
<td>322.1</td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{5}S</td>
<td>61.009</td>
<td>341.2</td>
<td>362.1</td>
</tr>
<tr>
<td>SO\textsubscript{2}</td>
<td>63.964</td>
<td>332.7</td>
<td>1297.5</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{7}S</td>
<td>75.025</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>SO\textsubscript{3}</td>
<td>79.961</td>
<td>1625.5</td>
<td>8780.6</td>
</tr>
</tbody>
</table>

Sodium tetraphosphate (Sigma-Aldrich AG, Switzerland) was analyzed with ToF-SIMS in negative mode. Table 3.20 shows the main species detected. Only phosphate species containing 1 or 2 phosphorus atoms were detected. As severe charging occurred, only analyses of small areas were possible, reducing the collected intensities.

Table 3.20 The most prominent inorganic, negative, secondary ions from sodium tetraphosphate. The intensities were normalized with the C\textsubscript{2} peak.

<table>
<thead>
<tr>
<th>Ion (charge 1-)</th>
<th>Mass (Da)</th>
<th>Norm. Int.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>12.000</td>
<td>0.834</td>
</tr>
<tr>
<td>O</td>
<td>15.995</td>
<td>3.970</td>
</tr>
<tr>
<td>OH</td>
<td>17.003</td>
<td>3.275</td>
</tr>
<tr>
<td>C\textsubscript{2}</td>
<td>23.999</td>
<td>1.000</td>
</tr>
<tr>
<td>PO</td>
<td>46.968</td>
<td>0.153</td>
</tr>
<tr>
<td>PO\textsubscript{2}</td>
<td>62.963</td>
<td>16.668</td>
</tr>
<tr>
<td>PO\textsubscript{3}</td>
<td>78.962</td>
<td>26.951</td>
</tr>
<tr>
<td>NaP\textsubscript{2}O\textsubscript{5}</td>
<td>164.908</td>
<td>1.939</td>
</tr>
<tr>
<td>NaP\textsubscript{2}O\textsubscript{6}</td>
<td>180.903</td>
<td>3.209</td>
</tr>
<tr>
<td>C\textsubscript{7}H\textsubscript{16}PO\textsubscript{4}</td>
<td>195.089</td>
<td>0.708</td>
</tr>
</tbody>
</table>
Literature


Results


Results


4. Discussion

4.1. Effect of lubricant on the friction behavior of DLC/DLC

The influence of PAO on the lubrication of a-C:H coatings was investigated by comparison of experiments in air, with 30 % and 70% relative humidity, to those in pure PAO. Pin-on-disc and HFRR experiments were carried out. The DLC coatings on the ball segments were never worn through as showed XPS depth profiling and Raman microscopy. Additionally, Raman spectra did not indicate a degradation of DLC. For pin-on-disc experiments at high sliding speed, the friction coefficient for DLC sliding against DLC was higher at 70 % RH than at 30 % RH (Fig 3.11). This negative effect of humidity has been observed for DLC self-mated contact by Eryilmaz et al. [1]. After 20 km, the friction coefficient did not show a steady-state behavior at 70 % RH, varying between 0.17 and 0.07. At low humidity, the friction coefficient was more stable, but still increased slightly with time up to 0.065 ± 0.002, although the track on the disc showed more scratches (Fig. 3.11 b). At low sliding speed, both pin-on-disc tests showed a continuous increase of the friction coefficient (Fig. 3.10), but the difference was not significant as the running-in behavior was not completed. The introduction of lubricant led to a decrease in the coefficient of friction immediately after the beginning of the test and reached a low friction of 0.01. After 3 km, the coefficient increased sharply, indicating that the contact had changed and that the DLC from the ball segment was worn through.

The wear rate of the ball segments of pin-on-disc experiments (Fig. 3.12 a) was simply calculated by measuring the size of the scar as observed under a microscope, assuming that these areas were flat. From these measurements, the worn height of the calotte always exceeded the thickness of 2 µm of the coating. Nevertheless, in all cases, DLC was present on the contact area of the ball segment. This shows that the simple assumption of a worn flat, calotte is not correct. The elastic deformation gave a contact area diameter of 186 µm, using the equation 2.4. This value is far smaller than the measured values of at least 400 µm. This indicates that plastic deformation occurred in addition to wear. On the coated discs, the worn depth was always smaller than 1 µm, consistent with the observation that the coating was not worn through.
During reciprocating sliding tests, the negative effect of humidity was not observed. With both applied loads, HFRR experiments with 70 % RH showed coefficients of friction near 0.4 (Fig. 3.14). This stable behavior could be attributed to the formation of a transfer layer onto the DLC-coated plate (Fig. 3.17 b). At lower relative humidity, following a short period with a smooth friction coefficient, instabilities appeared and the friction coefficient increased drastically. In this case, no transfer layer was observed on the DLC coating. The introduction of PAO to lubricate the contact caused a decrease the friction coefficient to 0.014 ± 0.007 (Fig. 3.19 b). AFM images did not show a transfer layer onto the DLC plate (Fig. 3.21). As the rounded structure of the as-deposited DLC coating was still observed in the track, the tribological conditions of the HFRR, oil-lubricated experiments can be considered to be in a very low-wear regime that allowed the interaction of oil additives with DLC under mild conditions to be investigated.

4.2. Friction behavior of oil-lubricated steel/steel and DLC/DLC

In HFRR measurements, under the conditions used here, the lubricating regime changes from boundary to mixed during each stroke. The upper specimens were segments of balls with a diameter of 50mm giving an initial Hertzian pressure of 275 MPa for steel/steel contacts. These mild rubbing conditions allowed the formation of tribofilms to be investigated without the effect of large amounts of wear. The temperature of 80°C used for all oil-lubricated tribological experiments as it is a standard operating temperature in engines. A too high temperature was avoided as ZnDTP oil solutions heated above 100°C show a thermal decomposition [2, 3].

Figure 4.1 shows a comparison between the friction coefficients for steel and DLC self-mated contacts in pure PAO or in PAO containing a single additive. HFRR experiments in pure PAO with steel showed a friction coefficient of 0.129 ± 0.016. During the sliding, spikes were observed (Fig. 3.19 a) that were most probably caused by the production of wear particles that were observed with ESEM (Fig. 3.20). This effect of these wear particles was removed by adding ZnDTP or AP, but was still observed with the b-TPPT solution. On steel, the addition of additives always decreased the friction coefficients. The largest effect was a decrease from 0.129 ± 0.016 to 0.074 ± 0.022 on adding AP to PAO. With DLC self-mated contacts, the effect of the additives was inversed and the lowest friction coefficient was obtained in pure PAO. This was probably due to the low shear strength at the surface of the DLC, as demonstrated by the observation of a DLC transfer film onto steel counterparts under oil-
The increase of the friction coefficients with the addition of additives suggests that the additives either adsorbed onto the DLC surface and/or that a tribochemical reaction occurred. AP resulted in a higher friction coefficient with DLC than with steel. The lower standard deviation of the friction coefficient occurred with experiments on DLC with pure PAO and with the AP solution. This is correlated with the absence of tribofilm or third bodies detected with AFM (Fig. 3.21 and 3.45).

Figure 4.1 Average friction coefficient of the last 10 min of sliding for steel/steel and DLC/DLC contacts in pure PAO and PAO containing 1 wt% ZnDTP, 1 wt% b-TPPT and 1 wt% AP.

Sulfur-containing compounds were also added to AP to determine their influence on the tribological behavior. The sliding experiments shown in figure 3.51 were performed on one plate to observe changes caused by varying the adsorption time. The addition of propanesulfonic acid to AP did not significantly influence the tribological performance. The
friction behavior was constant with time, contrary to that of AP and octanethiol. Addition of octanethiol caused the friction coefficient to decrease significantly with higher adsorption times. This suggests that octanethiol acted as a friction modifier. With both sulfur-containing compounds, scratches were observed on the tracks, although these were not observed with PAO containing AP alone.

The role of the amine in AP on the friction between DLC/DLC contacts was also investigated with experiments in a didodecylamine solution. The friction coefficient reached low values between 0.02 and 0.04, but some instabilities of the friction behavior occurred. This could be related with scratches and polishing wear observed with AFM (Fig. 3.57).

4.3. Tribofilm and thermal film formation

On steel, a tribofilm formed with ZnDTP that had a pad-like structure as already observed for example by Bec et al. [5], Aktary et al. [6] or Pereira et al. [7]. AFM topographical observations detected height differences up to 140 nm between the top of tribofilm islands and the deepest valley in between (Fig. 3.26 a). Martin et al. found a maximum film thickness of approximately 100 nm for a ZnDTP tribofilm generated with a Cameron-Plint friction machine during 1 hour at 80°C [8]. Fuller et al. found a maximum average film thickness, measured with XANES, after 6 hours rubbing with a value of approximately 120 nm that decreased to 40 nm after 24 hours [9]. The ZnDTP also reacted on DLC. Patches in the HFRR track were observed with ESEM (Fig. 3.25 d) and AFM (3.26 b). The tribofilm showed a significantly lower adhesion on DLC than on steel. While the tribofilm formed on steel was resistant to ex-situ scratch tests, that on DLC was removed (Fig. 3.27). Therefore, it is possible that the tribofilm is removed by vigorous cleaning.

The tribofilm built up on steel was mostly composed of short chain poly(thio)phosphates, as ToF-SIMS detected polyphosphate fragments containing up to three phosphorus atoms (Table 3.5). Some polyphosphate fragments contained zinc, but it was not possible to detect species from iron phosphates. Peaks assigned to these fragments were present for both the thermal films and the contact regions, but with a higher intensity in the tribofilm. The observation of a thermal film from ZnDTP at 80°C is consistent with the experiments carried out by Dacre and Bovington [10]. They adsorbed 14C-labelled ZnDTP onto steel plates at different temperatures and carried out desorption experiments. The additive desorbed completely at 40°C, but at 62°C, the adsorption was already, at least partially, irreversible. With XPS, the shift of the P
2p$_{3/2}$ peak from 133.4 ± 0.2 eV to 134.0 ± 0.2 eV between the thermal film and the tribofilm is consistent with the formation of a polyphosphate. Piras et al. reported a binding energy of 133.6 ± 0.1 eV for the P 2p$_{3/2}$ peak of frozen ZnDTP [11] and Schuetzle et al. detected the P 2p$_{3/2}$ peak of ferric phosphate at 133.6 eV [12]. These two values are similar to the binding energy measured for the thermal film and assigned to orthophosphates (PO$_4^{3-}$). The binding energy measured on the tribofilm, at 0.6 eV higher, was closer to the value for polyphosphates [11, 13-15]. This was also supported by the oxygen O1s signal measured on the tribofilm that was fitted with two peaks at 531.9 ± 0.2 eV and 533.4 ± 0.2 eV. They were assigned to non-bridging oxygen (NBO), involved in P-O$^-$ or in P=O, and to bridging oxygen (BO) in polyphosphates, respectively [16, 17]. The peak with NBO as main component may also contain a minor contribution from carbon bound to oxygen [18, 19]. As the BO peak was detected at a relatively low energy for polyphosphates, it may also include the bridging oxygen P-O-C [11, 12] or the alkoxy oxygen of ester [12, 19]. Adsorbed water may also be included in this peak [20, 21]. Metallic oxides were absent in the spectrum of the tribofilm, as the O 1s peak at 530.2 ± 0.2 eV was only detected for the thermal film. Furthermore, the presence of the Fe 2p$_{3/2}$ signal, detected at high binding energy (713.9 eV in the tribofilm), also indicated the presence of iron phosphate [16, 22] and was accompanied by another peak assigned to Fe (+3) in the tribofilm. The sulfur S 2p$_{3/2}$ peak detected in the tribofilm at 162.6 ± 0.2 eV was typical of reduced sulfur (-2) species (Table 4.1). Zinc or iron sulfides and P-S were possible compounds. Additionally, both zinc sulfide and zinc phosphate are thermodynamically more stable than the related iron components and were detected with XANES [23]. Nevertheless, iron sulfide was also detected with XANES in the early stages of ZnDTP film formation [24]. Minfray et al. detected iron sulfide on a pin, when sliding a ZnDTP tribofilm against an iron oxide or metallic iron pin in high vacuum [25]. The position of the Zn 2p$_{3/2}$ was important as allowed a comparison to be made with measurements performed with other instruments. As the position is at high binding energy, it is sensitive to differences in the linearity of the binding energy scale and the calibration procedure [26]. The smaller FWHM of the Zn 2p$_{3/2}$ signal, compared to that of Zn 3s, facilitated the separation of two contributions. Reference compounds were analyzed to provide a comparison (Table 4.2). In the thermal film, the Zn 2p$_{3/2}$ peak was detected at 1022.3 ± 0.2 eV. This may correspond to either zinc oxide, zinc carbonate or zinc sulfide, but excluded zinc sulfate. This may also, tentatively, be assigned to the free additive, as Piras et al. measured the peak at 1022.5 ± 0.1 eV in frozen additive [11]. In the tribofilm, the peak was detected at 1022.7 ± 0.2 eV, similar to the binding energy of zinc sulfide.
As ToF-SIMS is a more surface sensitive technique than XPS, it can be concluded that the tribofilm on steel was made of a mixture of short chain polyphosphates with a higher presence of zinc phosphates on top and iron phosphates further down. Sulfur was present in the tribofilm mainly as zinc sulfide. Unreacted ZnDTP molecules were adsorbed at the surface of the tribofilm.

Another source of sulfur was (poly)thiophosphates. With ToF-SIMS, zinc polyphosphates containing 2 or 3 phosphorus atoms were detected in the thermal film, but the intensity was small relatively to the intensity of the PO₃⁻ fragment.

This composition of the tribofilm with orthophosphates and short chain polyphosphates is in agreement with Minfray et al. [27] and Yin et al. [28]. In a tribofilm built up at 80°C, Martin et al. found with XANES a zinc poly(thio)phosphate containing up to 10 phosphorus atoms in the 10 nm-thick top layer of the tribofilm [8].

Table 4.1 Comparison of the binding energies of the S 2p₃/₂ peak of different reference compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Oxidation state</th>
<th>S 2p₃/₂ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-S-R</td>
<td>-2</td>
<td>162.2 ± 0.2</td>
</tr>
<tr>
<td>ZnS</td>
<td>-2</td>
<td>162.4 ± 0.1</td>
</tr>
<tr>
<td>R-S-H</td>
<td>-2</td>
<td>163.4 ± 0.2</td>
</tr>
<tr>
<td>Na₂SO₃</td>
<td>+4</td>
<td>167.2 ± 0.1</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>+6</td>
<td>169.4 ± 0.1</td>
</tr>
<tr>
<td>ZnSO₄</td>
<td>+6</td>
<td>169.2 ± 0.1</td>
</tr>
</tbody>
</table>

Table 4.2 Comparison of the binding energies of the Zn 2p₃/₂ peak of the reference compounds. The uncertainty in the position and of the FWHM is 0.1 eV.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Zn 2p₃/₂ (eV)</th>
<th>FWHM (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn (metal)</td>
<td>1021.8</td>
<td>0.7</td>
</tr>
<tr>
<td>ZnO</td>
<td>1022.0</td>
<td>1.7</td>
</tr>
<tr>
<td>ZnCO₃</td>
<td>1022.1</td>
<td>2.3</td>
</tr>
<tr>
<td>ZnS</td>
<td>1022.6</td>
<td>2.8</td>
</tr>
<tr>
<td>ZnSO₄·H₂O</td>
<td>1023.4</td>
<td>2.4</td>
</tr>
</tbody>
</table>
On DLC, short chain zinc polyphosphates were also detected with ToF-SIMS. The intensity of the corresponding peaks was higher for the HFRR track than for the thermal film. No polyphosphates with more than three phosphorus atoms were detected. PSO$_2$ and PS$_2$O fragments may have originated from unreacted additive, but no fragments with a m/z higher than 200 were identified on DLC, as with steel. With XPS, the P2p peak only shifted from 133.4 to 133.7 or 133.8 ± 0.2 eV between the thermal films and the contact regions. This excluded the presence of long chain polyphosphates, but the formation of short chains as detected with ToF-SIMS was possible during tribological experiments. In the thermal and tribofilms, reduced sulfur (-2) was detected at 162.1 ± 0.2 eV and could be attributed to zinc sulfide by comparison with the reference sample (Table 4.1) or with Eglin et al. [14]. Alternatively, it may be assigned to P-S [11]. An additional S 2p$_{3/2}$ peak was detected at 163.7 ± 0.2 eV for the tribofilm that could be assigned to unbound thiol (Table 4.1) or to C-S-C [19]. This species was absent from the thermal film. Oxidized sulfur was also detected in the HFRR track and, more intensely, in the thermal film at binding energies between 168.8 ± 0.2 eV and 169.2 ± 0.2 eV. This is in the lower range of binding energy for sulfates [29], but is higher than sulfur (+4) species that are found at approximately 167 eV [29, 30]. A mixture of oxidized sulfur (+4) and (+6), as observed for the sodium sulfite reference compound (Table 4.1), cannot be excluded. In the tribofilm, the oxygen O 1s signal was fitted with two contributions at 532.1 ± 0.2 eV and 533.6 eV, corresponding mostly to NBO and BO. In addition to the minor contribution of C-O groups in the NBO peak, sulfates are also included in this peak ([31] and §3.9.7). The Zn 2p$_{3/2}$ peak was detected at 1022.5 ± 0.2 eV in the thermal film, similar to that measured for the zinc sulfide. Whereas, this peak was between 1023.0 ± 0.2 eV and 1023.1 ± 0.2 eV in the tribofilm. This may correspond to sulfate or, perhaps, to zinc sulfide but the presence of zinc oxide or zinc carbonate could be excluded.

Dacre and Bovington found that ZnDTP chemisorbed irreversibly on steel at temperatures higher than 60°C [10]. Furthermore, in a ZnDTP solution containing iron powder, depletion in zinc of the solution occurred when heating above 60°C. At high temperature, ZnDTP undergoes thermal degradation between 130 and 230°C, leading, on steel surfaces, to polymerization of the additive to form polythiophosphates [3]. Spikes explained the further loss of sulfur by either hydrolysis of the thionyl group, or the initial formation of an ultraphosphate network glass followed by the formation of linear polyphosphates.
The oxidation of sulfur (-2) species on DLC was shown with adsorption of octanethiol onto DLC at 23 and 80°C (§ 3.10). With ToF-SIMS, $\text{SO}_2^-$ and $\text{SO}_3^-$ species were already clearly present at 23°C, however, these may be formed in the ToF-SIMS chamber. The increase in oxidized sulfur at 80°C indicates that a reaction has taken place between the thiol and the oxidized species on the DLC surface. Octanethiol was also adsorbed at room temperature onto steel and analyzed with XPS (§ 3.9.9). Nearly all of the sulfur detected was oxidized and the S 2p$_{3/2}$ peak was found at 168.4 ± 0.2 eV. This may be assigned to sulfur (+6) or to a mixture of sulfurs with oxidation states (+4) and (+6), if the oxidation reaction of thiol on iron oxide, shown in figure 4.2, was not completed.

In the ZnDTP thermal film built up at 80°C, the sulfur from ZnDTP was partially oxidized at the surface as indicated by the S 2p$_{3/2}$ peaks detected at 168.6 ± 0.2 eV and 169.0 ± 0.2 eV on steel and on DLC, respectively. The polymerization reaction of the additive may have already begun at 80°C on steel as polyphosphates were detected with ToF-SIMS while on DLC, they were only present with very low intensity. Nevertheless, on DLC coating, thionyl did form at the surface and was detected as oxidized sulfur.

![Figure 4.2 Scheme of the oxidation of thiol on iron oxide [32].](image)

It is well known that thiols are oxidized by iron oxide (Fig. 4.2) but perhaps more surprising that the thiols were also oxidized on DLC. XPS analyses of the DLC surface following sliding against DLC in pure PAO showed the presence of oxidized carbon at the surface. Li et al. detailed the oxidative process of a hydrogenated DLC coating based on XPS analyses after
steel sliding against DLC experiments performed under different atmospheres [36]. This oxidative process can be extended to experiments performed in pure PAO (Fig. 4.3). Shear caused by DLC sliding against DLC may mechanically produce radicals (R’ and R’ ''). In the presence of water and/or oxygen, they react to form peroxide radicals. Then the reaction is propagated with the formation of a new radical due to the capture of a hydrogen atom from an alkyl chain or from DLC to form hydroperoxides. A thermolysis process may decompose the hydroperoxide and produce new radicals. The oxidative reaction may stop if the R-O’ radical captured a free electron produced by rubbing, forming an aldehyde or reacted with another free radical to form ether. A similar oxidative process may be involved in the tribochemical reaction of oil additives with DLC coating. Thus, the thiols may have been oxidized by peroxides attached to the surface.

![Diagram](image)

**Figure 4.3** Diagram of the oxidation process at the hydrogenated DLC coating surface during tribological experiments, adapted from Li et al. [36].

The main difference between the tribofilm built up on DLC and that on steel was the poor adhesion of the tribofilm to the DLC coating, as shown by ex-situ scratch tests (§ 3.4.3). Martin et al. found the tribofilm built up on steel to be composed of a two-layer structure with a 10 nm thick overlayer composed of zinc poly(thio)phosphate and, in the bulk, a mixed iron and zinc short-chain polyphosphate 100 nm thick layer [8]. A gradient concentration of
decreasing zinc and increasing iron concentration with depth was observed. An increasing concentration of iron within the tribofilm was also measured by Yin et al. [28] and Zhang et al. [33]. Bec et al. [5] found a sulfide/oxide interlayer between the steel and the tribofilm while Martin et al. did not observe this interlayer [8]. The diffusion of iron into the tribofilm ensured a good adhesion of the tribofilm with the steel substrate by forming a concentration gradient. The corrosion layer containing oxidized sulfur, detected in the thermal films, may be the responsible for the release of iron allowing an adhesive gradient between the surface and the tribofilm to be formed. Although oxidized sulfur was detected on DLC, it can be expected that the additive only interacts with the upper, oxidized layer of DLC. Therefore, a concentration gradient analogous to that on steel was absent on DLC, thus, the poor adhesion of the tribofilm on the DLC coating.

The tribofilm built up from b-TPPT on steel was composed mainly of iron poly(thio)phosphates as shown by ToF-SIMS. The spectra contained polyphosphate with up to five units while polyphosphates gave weaker peaks for the thermal film (Table 3.7). This was confirmed by XPS, as the P 2p_{3/2} peak shifted from 133.5 ± 0.2 eV to 134.2 ± 0.2 eV for the thermal film and tribofilm, respectively. This was in agreement with the iron Fe 2p_{3/2} signal that showed two important contributions at 712.4 ± 0.2 eV and between 714.0 ± 0.2 eV and 714.1 ± 0.2 eV, attributed to iron phosphates. In comparison, Brow et al. measured the iron phosphates and found Fe (+2) and Fe (+3) at 712.2 eV and 713.7 eV, respectively. Metallic iron at 707.1 ± 0.2 eV was still detectable, consistent with the observation of surface scratches in the AFM images (Fig. 3.37). Iron oxide Fe (+3) was also present between 710.4 ± 0.2 eV and 710.5 ± 0.2 eV in the tribofilm. In the thermal film, peaks were present at 707.0 ± 0.2 eV, 709.3 ± 0.2 eV, 710.4 ± 0.2 eV, 711.7 ± 0.2 eV, 714.2 ± 0.2 eV and 714.8 ± 0.2 eV and were attributed to metallic iron, to iron oxides (+2) and (+3), to iron oxy-hydroxide, to iron phosphate (+3) and finally the satellite peak of Fe (+2). The differences between the thermal film and the tribofilm were, firstly, the presence of Fe (+2) and secondly, the forth peak was preferentially assigned to iron oxy-hydroxide than to iron phosphate as its position was 0.5 eV below the value measured in the tribofilm.

On DLC, no polyphosphates containing more than two units were detected. A possible explanation is the absence of positive, metallic counter-ions that are required to compensate the negative charges of polyphosphates. This is supported by XPS measurements as the P 2p_{3/2} peak shifted by only of 0.3 eV between the thermal film and the tribofilm.
Oxidized sulfur compounds were only detected in non-contact regions on both steel and DLC, at 169.1 ± 0.2 eV and 168.5 ± 0.2 eV, respectively. On steel, the peak may be assigned to sulfates consistent with the XANES measurements of Najman et al. [34]. On DLC, a mixture of oxidized sulfurs with oxidations state (+4) and (+6) were detected as the oxidizing process had probably not been completed, perhaps due to lack of oxygen. In the tribofilms built up on steel and DLC, one single sulfur species with oxidation state (-2) was detected. This is in agreement with results of Heuberger et al. at 80°C [35]. However, the measurements presented in [35] at 150°C showed that sulfates were formed, indicating an oxidation of sulfur between these two temperatures.

Amines were detected on both steel and DLC samples. These consisted of free amines in non-contact regions and protonated amines, with a higher concentration, in the contact regions. As extensive chemical analyses did not detect amines in the additive it could be concluded that the concentration in b-TPPT was lower than 10 ppm. That such a low solution concentration could allow the detection of amine on the surface may be explained by the need for positive counter-ions for the phosphates. On steel, this may be an indication that the formation of iron phosphates is less favorable than zinc phosphates. One very important consequence of the detection of amine is that there is no simple, direct relationship between the chemical composition of the solution and the chemistry at the surface.

On tribofilms formed from AP, polyphosphates containing up to four units were detected on steel and up to two units on DLC. Their intensities were weak in the non-contact regions for both steel and DLC. This was consistent with XPS measurements where the P 2p3/2 peak shifted slightly from 133.7 ± 0.2 eV to 133.9 ± 0.2 eV between the thermal film and the tribofilm on steel. This peak shift 0.4 eV to lower binding energy for the tribofilm on DLC case, indicating that mainly orthophosphates were present. Although the tribofilm formed on DLC could not be detected with AFM (Fig. 3.45), the higher intensity from phosphorus containing species in XPS and ToF-SIMS spectra indicated the formation of a phosphate containing reacted layer under tribological conditions. This was consistent with the higher concentration of protonated amines observed in the track with XPS. In positive mode, ToF-SIMS detected alkylamines containing up to 26 carbon atoms on steel and up to 14 carbon atoms on DLC coating. On average, the intensity of the amine signals was higher in the HFRR track. Further tribological experiments, with DLC/DLC contacts, were performed in PAO containing didodecylamine. In this case, no inversion of the intensity ratio between free
and protonated amines occurred. This ratio even slightly increased from 1.9 ± 0.2 to 2.3 ± 0.2. Remarkably, alkyl amines containing up to 32 carbon atoms were detected with ToF-SIMS mainly in the track although the didodecylamine used contained only 24 carbons. This indicates that a tribomechanical reaction occurred in the track, producing either tertiary amines or alkyl addition to the alkyl chains of the dialkylamine. This may have been a consequence of the oxidative process involving peroxides shown in figure 4.3.

Furthermore, in the high sliding speed region following sliding in the presence of dialkylamine, an additional small peak was necessary at 283.1 ± 0.2 eV to fit the carbon C 1s signal that corresponds to graphitic carbon. A low-binding energy peak (284.0 ± 0.2 eV) was also necessary in the case of experiments performed on DLC in the AP solution. During sliding experiments on DLC in pure PAO, a peak from graphitic carbon was detected at 283.6 ± 0.2 eV in the low sliding speed region. Contribution from graphitic carbon were not detected after sliding experiments in ZnDTP or b-TPPT solutions. This may be due to the presence of sulfur in the additive that is oxidized by oxygen present on DLC surface. In the absence of sulfur oxidation, reactions with peroxides may continue, leading to reactions with the DLC surface.

4.4. Influence of additive chemistry on tribofilm formation

The morphology of the tribofilms built up on steel and on DLC indicated a different behavior of ZnDTP, b-TPPT and AP under sliding. Pad-like structures were observed on steel with ZnDTP with a slightly preferential orientation with the sliding direction. The tribofilm from b-TPPT also showed pads but, additionally, lines were visible. The AP tribofilm had a line structure totally oriented in the sliding direction. The zinc-free additive mixture also showed oriented pads on steel, but the top of the tribofilm islands were flattened. On DLC, ZnDTP and b-TPPT built up tribofilms that were thick enough to detect with AFM. It can, therefore, be concluded that neither Zn nor Fe are required to form a tribofilm. With ZnDTP, the gaps between the rounded structures of the DLC coating were filled by the reacted products from ZnDTP that consisted of a mixture of short chain zinc polyphosphates. Low sliding speed region showed patches of tribofilm while areas were totally covered by a film in high sliding speed regions. These two tribofilms were thinner on DLC than on steel. They showed a low adhesion with the DLC coating and particles of tribofilm were removed. This may explain the higher friction coefficient compared to DLC sliding against DLC in pure PAO. When b-TPPT
was added to the oil, a protective layer was present, however, scratches and impinged particles were observed. This did not occur with ZnDTP on DLC.

The AP showed another behavior on DLC consistent with the absence of polyphosphates in the track. This additive gave a very thin tribofilm on DLC and the highest friction coefficient for DLC/DLC. The AFM profiles show that the structures in the tribofilms on steel are thicker than the tribofilm on DLC as the uncoated DLC surface could be detected between patches of tribofilm. Since the friction coefficient for DLC/DLC was higher in the presence of AP than for steel, differences in heat generation between the two types of contact cannot explain the differences in tribofilm thickness. Another possibility is that iron released from the steel surface during sliding catalyses the reaction of the additive.

**Literature**


5. Conclusion and outlook

5.1 Conclusion

The ability of ashless, anti-wear additives to form protective tribofilms on DLC and steel surfaces was investigated and compared to the reactions of ZnDTP. Oil-lubricated tribological experiments were performed using a reciprocating sliding system under mild rubbing conditions to avoid wearing through the DLC coating. These experiments were performed at 80°C as this is a standard operating temperature in engines and is below the point of thermal decomposition of the additives. In addition to the widely used ZnDTP, b-TPPT was selected as a metal-free, sulfur-phosphorus additive and AP, as a metal and sulfur-free additive. Tribological investigations were performed on steel/steel and DLC/DLC contacts. DLC self-mated contacts allowed the b-TPPT and AP to be studied in a metal-free environment, making the charge compensation of phosphates difficult, in the absence of positive metallic counter-ions.

The morphologies of the tribofilms built up on steel and on DLC were characterized with AFM and ESEM, while chemical surface analyses of both tribofilms and thermal films were performed by XPS and ToF-SIMS. The formation of a tribofilm by ZnDTP in PAO was demonstrated on both steel and DLC surfaces. The well-known, pad-like structure was observed on steel even under the mild tribological conditions used, while smaller patches from ZnDTP were observed in the HFRR track on DLC. Nevertheless the tribofilm built up on DLC only showed a poor adhesion with the coating, as shown with ex-situ scratch tests. A mixture of short chain poly(thio)phosphates was detected on steel with a higher presence of zinc on top and iron phosphates further down. Short chain zinc poly(thio)phosphates were also built up on DLC in the absence of iron. In the ZnDTP thermal film, sulfur was oxidized, presumably on the iron oxide surface. More surprising was the partial oxidation of sulfur on DLC. This was confirmed by adsorption of thiol on DLC showing that oxidation occurred already at 23°C.

The longest polyphosphates species detected with ToF-SIMS were found on the tribofilm built up from b-TPPT on steel and contained up to five units. This additive showed the lowest friction coefficient for steel/steel contacts. A tribofilm from b-TPPT was also detected on DLC. This was particularly interesting as it happened in the absence of positive counter-ions.
for the phosphates. However, the detection of positively charged amine at the DLC surface showed that minor, undetectable, species in the solution can be trapped in the reacted film.

A tribofilm built up from AP on steel that showed a line structure with the steel surface still visible between the lines of tribofilm. This additive showed the lowest friction coefficient for DLC sliding against DLC. Even though positive counter-ions were available from solutions, in the form of dialkylamines, no evidence of a tribofilm was detected with AFM on DLC. Nevertheless, XPS detected a higher presence of orthophosphates and of protonated dialkylamines in the HFRR track than in non-contact regions, indicating that tribochemical reactions had occurred during the rubbing experiments. A further experiment carried out in PAO containing didodecylamine with a DLC/DLC contact led to the detection of alkylamines, in the sliding tract, containing hydrocarbons with more than the 24 carbon atoms from the starting compounds. This indicated that alkylamines not only react to give the protonation of the amine group, but that either tertiary amines are formed or alklylation at the hydrocarbon chains occurred.

A partial degradation of the DLC coating in the HFRR tracks was observed for experiments performed in pure PAO, in PAO containing AP, and PAO containing didodecylamine. With both AP and didodecylamine, polishing wear of the DLC coating was visible. In contrast, no graphitic carbon was detected with XPS after experiments in PAO containing ZnDTP or b-TPPT. This may be attributed to the formation of a thick tribofilm that, even without good adhesion to the substrate, helped to protect the coating. The combination of both protective coating and oil anti-wear additive was of interest as the coating can act as protection during starting or short-term system overload, while additives may protect the coating during steady-state mild operating conditions.

ZnDTP and AP showed a smooth frictional behavior with DLC/DLC contacts while spikes caused by wear particles occurred with b-TPPT despite the presence of a tribofilm in the sliding track.
5.2 Outlook

As oil additives are usually used in packages in oil, the investigation of interactions between additives, as well as with the surface, is of the greatest interest. Tribological experiments performed in PAO containing a mixture of b-TPPT, AP and friction modifiers already gave an insight their behavior. On steel, the friction behavior showed a delayed increase of the friction coefficient followed by a slight continuous decrease until the end of the 1 hour-experiment. On DLC, the friction coefficient decreased continuously during the HFRR tests. Addition of propanesulfonic acid to AP allowed observing a decrease of the friction coefficient during the experiment. Polishing wear was not observed in the track, but scratches were visible. Octanethiol seemed to act as a friction modifier that decreased the friction coefficient with time. Further tribological experiments and detailed chemical analyses would increase the understanding of additive interactions in the oil solution and at the DLC surface as combinations of additives often show synergetic or antagonistic effect.

The use of modified DLC, such as metal-doped DLC coatings or nanostructured DLC coatings, may also improve the interactions between DLC coatings and additives. In addition to varying the coating mechanical properties, changes of coating surface tension or possible chemical interactions may lead to increasing lifetime of mechanical systems and the use of less harmful compounds.
6. Annexes

In annexes, the fitting parameters used to fit the XPS spectra are given. These were measured in the non-contact and in the contact regions for the different tribological experiments presented in this work. This includes the peak shapes, position, FWHM and uncorrected areas.

6.1 Pure polyalpha-olefin

6.1.1 Steel/steel contact

<table>
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<tr>
<th>Peak</th>
<th>Shape</th>
<th>Pos.</th>
<th>FWHM</th>
<th>Area</th>
<th>Pos.</th>
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6.1.2. DLC/DLC contact

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6.2. Zinc dialkyl dithiophosphate

6.2.1. Steel/steel contact

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* This measurement was the only performed of 29.35 eV and a step size of 0.125 eV. All the other analyses were performed with a pass energy of 58.7 eV and a step size of 0.125 eV.

6.2.2. DLC/DLC contact

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6.3. Butylated- triphenyl phosphorothionate

6.3.1. Steel/steel contact

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6.3.2. DLC/DLC contact

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### 6.4. Amine phosphate

#### 6.4.1. Steel/steel contact

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#### 6.4.2. DLC/DLC contact

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</tr>
<tr>
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Education

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2004 Diploma in Materials Science at the Powder Technology Laboratory (LTP) Department of Materials, Swiss Federal Institute of Technology of Lausanne (EPFL), Switzerland.

Subject: Dispersion and sintering of nanometric gamma-aluminas

1998-2004 Studies in Materials Science at EPFL

1994-1998 Maturity, scientific orientation (University entrance), Bulle (Fribourg, Switzerland)

Working experience

2004 Industrial training at the Fonderie de Moudon Gisling SA (Moudon, CH)

Quality control on self-hardening moulding sands

2003 Industrial training at Saint-Gobain Isover SA (Lucens, CH) Development of mechanical tests of quality control on insulating glass wool products according to European standards'.

2001 Summer work at EPFL at the LTP

Improvement of the production of ceramic pieces by electrodeposition
**Publications**

*Tribofilm formation from ZnDTP on diamond-like carbon*
S. Equey, S. Roos, U. Mueller, R. Hauert, N. D. Spencer and R. Crockett
Wear, 2008. 264 (3-4) 316-321.

*Reactions of zinc-free anti-wear additives in DLC/DLC and steel/steel contacts*
S. Equey, S. Roos, U. Mueller, R. Hauert, N. D. Spencer and R. Crockett
Tribology International, 2008. 41 (11) 1090-6

**Presentations**

*Investigation of the interaction between modified diamond-like carbon coatings and lubricant additives* (oral presentation)
SPS Annual Meeting, Lausanne, Switzerland (2006)

*Interactions between diamond-like carbon coatings and zinc dialkyl dithiophosphate* (poster)

*Investigation of the interaction between modified diamond-like carbon coatings and lubricant additives* (oral presentation)
Third Asia International Conference on Tribology, Kanazawa, Japan (2006)

*Interaction entre des couches minces de carbone amorphe et le dithiophosphate de zinc* (présentation oral)
SGO-SST meeting, Solothurn, Switzerland (2007)

*Interaction between diamond-like carbon coating and zinc dialkyl dithiophosphate* (poster)

*Interaction between diamond-like carbon coatings and zinc dialkyl dithiophosphate* (oral presentation)
Leeds-Lyon Symposium on Tribology, Lyon, France (2007)