Doctoral Thesis

Development of a combinatorial approach to lubricant additive characterization

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DEVELOPMENT OF A COMBINATORIAL APPROACH TO LUBRICANT ADDITIVE CHARACTERIZATION

A dissertation submitted to the

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for the degree of

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presented by

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ABSTRACT

During the interaction of a lubricant additive with the rubbing surfaces in a tribological system a large number of parameters are involved (e.g. contact pressure, temperature, relative velocity). To date, it has been very time consuming to analyze the performance of a lubricant additive as a function of the parameters defining the tribological contact. The present work focuses on the application of a combinatorial approach to tribotesting that speeds up and rationalizes tribological testing. In these experiments a set of spatially separated areas are produced on one sample (called a parameter library) under various tribological test conditions (contact pressure, test duration, and temperature). The parameter libraries are analyzed post-mortem by spatially resolved surface analytical and topographical methods and the results are related to the frictional results and the tribological conditions used to produce the library. A ball-on-disc tribometer that allows load, radius, and rotational velocity to be programmed was used to produce the samples. Two different types of combinatorial experiments are presented: the first set focuses on the surface analytical investigation of parameter libraries and the second one on the tribological results (friction, wear).

In the first example, a parameter library was built by varying the applied load between 0.05 N and 5 N. Two sets of tribotests were run, one in presence of a 1 wt-% solution of zinc diisopropyl dithiophosphate in decane at room temperature and a second one at 150°C in presence of a 1 wt-% solution of a commercial secondary zinc dialkyl dithiophosphate in PAO. The parameter library was analyzed by imaging and small-area X-ray photoelectron spectroscopy. The interpretation of the spectroscopic results shows that at room temperature the species originating from the additive adsorb in the non-contact area, inducing a change in the chemical state of the iron oxide compared to the oxide layer prior to the analysis. An inhomogeneous (iron/zinc) phosphate film is formed in the tribostressed area, the amount of phosphate increasing with increasing load. The increasing amount of phosphate in the surface film can explain the decrease in the coefficient of friction measured at higher loads. A different mechanism is involved in the film formation at higher temperature. The experiments at 150°C showed a thermally formed (iron free) poly(thio)phosphate layer on top of the iron surface prior to the tribostress. While tribologically stressing this layer, it has been partially removed and partially modified to form a shorter-chain-length poly(thio)phosphate film. Also in this case a decrease in the coefficient of friction with increasing load was found.
In the second type of experiments a parameter library was produced by oscillating the applied load in a synchronized manner with the angular position on the disc, while on different wear tracks the duration of the test was varied. The test was performed in pure PAO and in a 1 wt-% solution of a commercial purified zinc dialkyl dithiophosphate in PAO. The coefficient of friction, measured during the experiment, showed a strong stick-slip behavior in pure PAO that led to the formation of “pockets” in the wear scar. An increase of the coefficient of friction with increasing load was found. Less stick-slip was observed in the experiments with additive and no “pockets” could be detected in the wear-scars. The coefficient of friction decreased with increasing load, which is in excellent agreement with tribological results from the first type of experiments described above. The worn area, analyzed by laser profilometry, showed an increase with increasing load and duration. The wear results have a lower reproducibility compared to the other tribological results, and thus they could only be interpreted qualitatively on the same sample.

Very good agreement was found by comparing the tribological and surface analytical results of these new experiments with results of standard ball-on-disc tests produced under the same conditions. It can be assessed that the approach developed in the presented thesis and based on the combinatorial experiments appears to be a very promising method for the screening of lubricant additives in a more rapid and consistent way.

In der ersten Art von Experimenten wurde eine Parameter Bibliothek hergestellt, in dem auf unterschiedlichen Radien die Probe mit Normalkräften von 0.05 N bis 5 N tribologisch beansprucht wurden. Zwei Reihen von Experimenten wurden durchgeführt, eine in Gegenwart einer Lösung aus Zink diisopropyl dithiophosphat in Dekan bei 25°C und eine zweite bei 150°C in einer Lösung aus einem kommerziell erhältlichen, gereinigten Zink dithiophosphat in PAO. Die Parameter Bibliothek wurde mit ortsaufgelöster Röntgen-Photoelektronen-Spektroskopie (XPS) untersucht. Die spektroskopischen Resultate zeigen, dass bei den bei 25°C durchgeführten Experimenten in den nicht beanspruchten Gebieten eine dünne Schicht detektiert werden kann, welche aus Molekülfragmenten besteht die vom Additiv stammen. In den tribologisch beanspruchten Gebieten wurde ein inhomogener (Eisen/Zink) Phosphat Film gebildet, wobei der Gehalt an Phosphat mit zunehmender Belastung steigt. Der steigende Phosphatgehalt kann die mit zunehmender Belastung beobachtete Reduktion des Reibungskoeffizienten erklä-


This chapter starts with a short introduction to tribology and lubrication and the motivation for this thesis is given. In section 1.2, the composition of a typical lubricant is summarized and the role of the various additives described. The function of zinc dithiophosphates as an anti-wear additive and the current understanding of the structure of tribofilms produced in their presence are discussed in section 1.3-1.5. Section 1.6 deals with X-ray photoelectron spectroscopy as a surface analytical method used in lubricant-additive research and in section 1.7 imaging surface analytical methods used for characterizing the spatial structure of tribofilms are discussed. An overview of tribological test methods is presented in section 1.8, while in section 1.9 the new concept of combinatorial tribotests is explained.
1.1 Introduction and Motivation

1.1.1 Tribology and Lubrication

History

Tribology as a separate scientific discipline was defined by a UK committee in 1967 as “the science and technology of interacting surfaces in relative motion”. The term “Tribology” is derived from the Greek word “tribos” meaning “rubbing”. However, the scientific study or at least use of tribological principles has a long history. It reaches back to the neolithic period. The use of bearings in door sockets in Assyrian villages before 4000 BC is reported [1]. Since Leonardo da Vinci (late 15th century) and Amontons (1699) four basic empirical laws of friction have been known [2]:

- there is a proportionality between the maximum tangential force before sliding and the normal force when a static body is subjected to increasing tangential load,
- the tangential friction force is proportional to the normal force in sliding,
- the friction force is independent of the apparent contact area,
- the friction force is independent of the sliding speed.

Coefficient of Friction

A number of early works are known that report values for the proportionality between normal force and the tangential force \( F \). However, it was Euler (1750), who first used the Greek symbol \( \mu \) as the proportionality between normal load \( P \) and tangential force \( F \) [1]. This proportionality

\[
F = \mu \cdot P
\]

can also be written as

\[
\mu = F / P
\]

and was later assigned the term “coefficient of friction”, which is still in use today.

Fluid-film Lubrication

With the industrial revolution 1750-1850 the value of lubricants in reducing friction and wear was recognized, but until the publication of the Osbourn Reynolds’ work about hydrodynamic lubrication in 1886 [3] the fluid-film lubrication was not fully understood.
His work had immediate practical application in railway axle bearings [2,4].

Fluid-film lubrication, as described by the Reynolds equation, is based on the complete separation of the two rubbing surfaces and is associated with the physical rather than the chemical properties of lubricants. Modern bearings and other machine components rely substantially on this mechanism. However, since all bearings and machines start and stop, the surfaces of the sliding solids come into contact with each other at every interruption of movement. Furthermore, the major improvements in the 20th century in the efficiency of machinery were caused by the use of higher mean bearing pressures and lower viscosity fluids, i.e. by reducing the effective minimum film thickness in a lubricated contact [4].

**Stribeck Curve**

The graph of the relationship between friction coefficient and fluid-film thickness is commonly known as the “Stribeck curve” [5] (Figure 1.1). Nowadays, this name is also used for any plot of the friction coefficient versus the operating parameters controlling the fluid film thickness (e.g. velocity, viscosity, load) [6].

**Mixed and Boundary Lubrication**

It can be seen in Figure 1.1 that with decreasing fluid film thickness, the friction force is reduced as long as the contact is still operated in the hydrodynamic lubrication regime. If the distance between the two surfaces becomes too small, asperities from the two surfaces eventually come in contact with each other. Contact between asperities causes wear and elevated friction. This condition, where the hydrodynamic film still supports most of the load but cannot prevent some contact between the opposing surfaces, is known as the “mixed lubrication” regime.
A further reduction of the film thickness leads to a complete breakdown of the hydrodynamic lubrication and solid-solid contact occurs. This region is called “boundary lubrication” regime.

It is in the mixed and in the boundary lubrication regime where the chemical properties of the lubricant become more and more important. Additives in the lubricant may reduce friction and wear in these regimes using a variety of mechanisms. Today, almost all lubricants contain one or more additives to enhance the properties of the lubricant. A short overview of the role of lubricant additives in modern lubricant formulation will be given in section 1.2.

1.1.2 Objectives of this Thesis

Some of the most effective and therefore most widely used lubricant additives contain heavy metals or chlorinated compounds. Due to environmental and health considerations there is increasing legislative pressure to reduce or eliminate harmful lubricant additives. The development of new lubricant additives, which could replace the existing ones, has led to an increasing need for testing of candidates. Such tests need to probe the anti-wear performance of
the candidate under a wide range of tribological conditions (contact pressure, velocity, temperature) to evaluate the usability of the additive for different applications.

A promising route to replace current additives is to study the mechanisms by which they function and to try to mimic these mechanisms with new additives. For example, zinc dialkyl dithiophosphates (ZnDTPs), have been investigated thoroughly; they are a family of widely used lubricant additives that prevent wear under boundary-lubrication conditions (see section 1.3). They react via adaptive mechanisms to form protective films depending on the tribological stress to which they are subjected. The systematic investigation of the tribofilm structures, as a function of parameters that define the tribological stress, will increase the understanding of the mechanism of tribofilm formation.

The goal of this thesis is to develop a new class of tribotests, which allow the rapid characterization of the performance of a lubricant additive and to study the tribofilms formed as a function of a range of tribological stresses. These tests will be named “combinatorial tribotests” because they have some resemblance to the combinatorial approach, which is commonly used in pharmaceutical chemistry and materials science (see section 1.5).
1.2 Lubricant Composition

Lubricants for internal combustion engines, gear boxes, gas turbines and other industrial applications are usually based on mineral oils. The composition and properties of a mineral oil are dependant on the crude oil and the refining processes used to manufacture the base stock. It is the role of appropriate lubricant additives to impart new and useful properties to the lubricant or to enhance the properties already present in order to achieve a balance in performance characteristics of the finished lubricant [8].

Additives for lubricating oils were first used during the 1920s, and their use has increased tremendously since then. Today, practically all types of lubricating oil contain at least one additive, and some oils contain additives of several different types. The typical types and content of additives in an engine crankcase lubricant are shown in Table 1.1.

Table 1.1: Typical ranges and composition of engine crankcase lubricants. (Taken from [9])

<table>
<thead>
<tr>
<th>Function</th>
<th>Component</th>
<th>Concentration, wt-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base oil</td>
<td></td>
<td>75-95</td>
</tr>
<tr>
<td>Friction and wear</td>
<td>Viscosity index improver</td>
<td>0-6</td>
</tr>
<tr>
<td></td>
<td>Anti-wear additive</td>
<td>0.5-2</td>
</tr>
<tr>
<td></td>
<td>Friction reducer</td>
<td>0-2</td>
</tr>
<tr>
<td></td>
<td>Rust/corrosion inhibitors</td>
<td>0-1</td>
</tr>
<tr>
<td>Contamination and cleanliness</td>
<td>Antioxidant</td>
<td>0-1</td>
</tr>
<tr>
<td></td>
<td>Dispersant</td>
<td>1-10</td>
</tr>
<tr>
<td></td>
<td>Detergent</td>
<td>2-8</td>
</tr>
<tr>
<td>Maintain fluid properties</td>
<td>Pour-point depressant</td>
<td>0-0.5</td>
</tr>
<tr>
<td></td>
<td>Anti-foam additive</td>
<td>0-0.001</td>
</tr>
</tbody>
</table>

In the following, the role of the most important additives used in mineral oils are briefly summarized [2,4,8]:
Pour-Point Depressant

Certain high-molecular-weight polymers function by inhibiting the formation of a wax crystal structure that would prevent oil flow at low temperatures. They can achieve the lowering of the pour point by 11-28˚C, which may be important for operation (start up) of engines at low temperatures [8].

Viscosity-Index Improvers

The viscosity index (VI) is an entirely empirical parameter, which describes the temperature dependence of the kinematic viscosity of an oil [2]. VI improvers are long-chain, high-molecular-weight polymers that function by increasing the relative viscosity of an oil more at high temperatures than at low temperatures (see Figure 1.2). It is postulated that in cold oil the molecules of the polymer adopt a coiled form, so that their effect on viscosity is minimized. This leads to a more uniform viscosity-temperature curve of the lubricant which is important to keep the performance of a lubricant constant at different temperatures (e.g. start up and running engine) [8].

![Figure 1.2: VI improvers function by increasing the kinematic viscosity preferentially at high temperatures. This decreases the rate by which the viscosity changes with temperature.](image)

Defoamants

The ability of oils to resist foaming varies considerably depending on the type of crude oil, types and degree of refining, and viscosity. In some applications even small amount of foam can be extremely troublesome. Silicone or organic polymers are used at a few parts per million and are thought to attach themselves to the air bubbles...
and either spread or form unstable bridges between bubbles, which then coalesce into larger bubbles [8].

**Oxidation Inhibitors**

When oil is heated in the presence of air, oxidation occurs. As a result of this oxidation, both the oil viscosity and the concentration of organic acids in the oil increase and lacquer deposits may be further oxidized to form hard, carbonaceous materials [8]. In internal combustion engines lacquer or deposit formation between piston-rings and their adjacent grooves prevent free movement of the piston-rings. Scuffing then results because of the high contact forces between the ring and the cylinder wall. Anti-oxidants can be classified into three basic categories: metal deactivators, radical inhibitors (or propagation inhibitors) and peroxide decomposers [2].

**Rust and Corrosion Inhibitors**

A number of kinds of corrosion can occur in oil-lubricated systems. Probably, the two most important types are corrosion by organic acids that develop in the oil itself and corrosion by contaminants that are picked up and carried by the oil. Corrosion inhibitors form a protective film on the surfaces that prevents the corrosive materials from reaching or attacking the metal. The film may be either physically adsorbed or chemically bonded to the metal. Typical materials used for this purpose are amine succinates and alkaline earth sulfonates [8].

**Detergents and Dispersants**

In internal-combustion-engine service, a variety of effects tends to cause oil deterioration and the subsequent formation of harmful deposits. These deposits can interfere with the oil circulation, build up behind piston rings to cause ring sticking and rapid ring wear, and affect clearances and proper functioning of critical components, such as hydraulic valve lifters. The role of detergents and dispersants is to neutralize any acids formed during the burning of fuel and to solubilize wear and dirt particles to prevent the build up of harmful deposits [8].
A detergent or dispersant polar substrate is made up of two functional parts as illustrated in Figure 1.3 (a). The hydrocarbon tail is the part that acts as the solubilizer to enable the additive to be fully compatible and soluble in the base oil. The polar head may attach to wear particles, dirt or sludge. These particles are then solubilized by the hydrocarbon tail, exposed to the oil [4] (Figure 1.3 (b)). In addition, overbased detergents have an alkali-ion-containing core which may react as neutralizer of deposition precursors with high sulfur content or other materials that form acidic combustion by-products. These detergents are present as colloids in the oil [2] (see Figure 1.3 (c)). Typical detergents are calcium and magnesium sulfonates or calcium phenates, typical dispersants are polymeric succinimides, olefin/P$_2$S$_5$ reaction products, polyesters and benzylamides.

An essential factor with this approach is regular draining and replacement of the oil so that the contaminants in it are removed from the engine before the oil’s capacity to hold them is exceeded [8].

**Friction Modifiers** Friction modifiers reduce friction remarkably in the mixed and in the boundary lubrication regimes (low relative velocity, high load). They are soluble surfactant additives, such as carboxylic ac-
ids and their salts. At room temperature, they adsorb in a monolayer on the surface, while with increasing temperatures they may react with the surface to form quite thick (tens of nm), deposited, soap-like films on the rubbing tracks. This film develops during rubbing and is highly viscous, which is probably responsible for its low friction [6].

**Anti-wear Additives**

Anti-wear additives react with the surface through thermal decomposition, chemisorption, and chemical reactions with the oxide [10]. The most important anti-wear additives are organophosphate additives from which ZnDTP is the most prominent one. The reaction mechanism of anti-wear additives is very complex and adaptive. In the case of ZnDTP, combined tribological and thermal reactions form a thick protective (polyphosphate) film which effectively reduces wear. The reaction mechanism and the tribofilm structure of anti-wear films formed from ZnDTPs will be discussed in detail in section 1.3.

**Extreme-Pressure Additives**

Extreme-pressure (EP) additives react with metal surfaces under high load and low velocity as, for example, in heavily loaded gears, metal machining or screw cutting. They react with exposed metallic surfaces creating protective, low-shear-strength surface films, which reduce friction and wear. The differentiation between anti-wear and extreme pressure additives is not very distinct, some additives (e.g. ZnDTPs) may act as anti-wear and as extreme pressure additive. Examples of EP additives are dibenzyldisulfide, chlorinated paraffin, mineral oils or waxes, sulfurized fatty acids and molybdenum disulfide [2].

**Environmental Compatibility of Lubricant Additives**

Some of the most effective additives known today (e.g. ZnDTP or chlorinated compounds) are increasingly subjected to legislation due to their unfavorable influence on health and the environment. Therefore, it is important to develop more environmentally friendly alternatives to these substances. One promising route to replace these additives it to investigate how they function and to try to adapt these mechanisms with new additives. This is one of the reasons why the tribological reaction of ZnDTPs have been studied so intensively.
1.3 Anti-wear Films from ZnDTPs

ZnDTPs constitute the most widely used family of anti-wear lubricant additives. They have first been used as anti-oxidants but soon their capability to act as anti-wear and extreme pressure additives was recognized [11].

Three basic types of ZnDTPs are commonly used as lubricant additives (Table 1.2). Their hydrolytic and thermal stability and their performance as anti-wear additives and oxidation inhibitors depends strongly on the type of the alkyl group bound to the oxygen.

Table 1.2: Three types of ZnDTPs commonly used as lubricant additives.

<table>
<thead>
<tr>
<th>Type</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary alkyl ZnDTP</td>
<td><img src="structure1.png" alt="Primary alkyl ZnDTP Structure" /></td>
</tr>
<tr>
<td>Secondary alkyl ZnDTP</td>
<td><img src="structure2.png" alt="Secondary alkyl ZnDTP Structure" /></td>
</tr>
<tr>
<td>Aryl ZnDTP</td>
<td><img src="structure3.png" alt="Aryl ZnDTP Structure" /></td>
</tr>
</tbody>
</table>

Thermally activated reactions are assumed to be an important step in the formation of ZnDTP anti-wear film [12-14]. Therefore, the thermal reactions of ZnDTPs in solution will be discussed first, followed by the mechanism of formation of a thermal film on a
steel substrate. This will lead to the discussion of the film formation mechanism under tribological stress and a proposed model for the structure of anti-wear films derived from ZnDTP.

1.3.1 Thermal Reactions of ZnDTP

The thermal degradation of ZnDTP in oil was studied by several authors. Dickert et al. investigated solid and volatile thermal decomposition products of isopropyl ZnDTP and proposed a reaction-mechanism scheme in which the degradation was induced by an isomerization of the original molecule (movement of the alkyl group from the oxygen to the sulfur) and the subsequent intramolecular (cis) elimination of an olefin from the isomer [15]. The insoluble residual material was a glass-like solid that was difficult to characterize.

The basic steps of this reaction mechanism were later explained by work based on $^1$H and $^{31}$P nuclear magnetic resonance (NMR) spectroscopy and literature data [16,17]. The proposed mechanism uses the hard and soft acids and bases (HSAB) concept introduced by Pearson [18]. According to this theory, hard acids preferentially react with hard bases and soft acids with soft bases. The initial step, the isomerization of the ZnDTP is reported to be a two-stage process, involving alkyl transfer-retransfer:

\[
\begin{align*}
S=\text{P} & \quad \text{S} + \quad S=\text{P} & \quad \text{S} \\
\text{OR} & \quad \text{OR} & \quad \text{OR} & \quad \text{OR} \\
\text{OR} & \quad \text{OR} & \quad \text{OR} & \quad \text{OR}
\end{align*}
\]

(1)

\[
\begin{align*}
\text{S=P} & \quad \text{SR}^+ & \quad \text{S=PS} & \quad \text{S} \\
\text{OR} & \quad \text{OR} & \quad \text{OR} & \quad \text{OR} \\
\text{OR} & \quad \text{OR} & \quad \text{OR} & \quad \text{OR}
\end{align*}
\]

(2)

The negative charge on the oxygen may also move to the sulfur atom,

\[
\begin{align*}
S=\text{P} & \quad \text{SR} \\
\text{OR} & \quad \text{OR}
\end{align*}
\]

(3)

from which the second stage of the isomerization can start. There
follows an exactly analogous sequence, resulting in the migration of the second alkyl group from oxygen to sulfur (reaction (4)-(5)).

Subsequent reactions will lead to the formation of insoluble compounds with P-O-P structure plus soluble dialkyl sulfide, olefins and trialkyltetra thiophosphate. For n-butyl ZnDTP the following thermal decomposition product has been proposed:

The proposed mechanism also explains the degradation rate and the distribution of the soluble and gaseous products depending on the alkyl structure of the ZnDTP [17].

1.3.2 Thermal Film Formation

At room temperature, ZnDTP interacts only weakly with the steel surface, although it begins to decompose at around 50˚C on an iron substrate [19]. The iron surface is assumed to have a catalytic effect because for di-isopropyl-ZnDTP it was found that at 125˚C it forms a thermal film on an iron substrate, while the thermal decomposition of the molecule did not start until 150˚C [20]. The isomerization process described above is assumed to be an important step in the formation of thermal films [13,14]. The product of reaction (5) (so called linkage isomer, LI-ZnDTP) is assumed to be a precursor to the formation of a long-chain polyphosphate film on the surface [13].

X-ray adsorption near-edge spectroscopy (XANES) of thermal films formed on steel in a solution of primary and secondary ZnDTP in base oil showed that the composition of the thermal films is determined by the total decomposition time of the solution
(at which the sample is removed from the solution) and not by the immersion time of the sample in the solution [13]. This indicates that the decomposition of the molecule determines the structure of the thermal film. In addition, the adsorption of LI-ZnDTP on degradation products extracted from the solution after 12-18 h are reported. In an earlier work by the same group, thermal films were found to consist of a mixture of short- and long-chain polyphosphates, the proportions of short chain to long chain changing with the temperature [20].

In-situ attenuated total reflection (ATR) experiments on an iron-coated germanium crystal show a concentration dependence in the thermal film formation mechanism [21]. Thermal film formation at 150°C is delayed from 38 h (in pure ZnDTP) to 126 h (in a 20 wt-% solution of ZnDTP in PAO). The ATR spectra and the ex-situ XPS analysis confirm the formation of P-O-P bonds. All the functional groups present in a poly(thio)phosphate could be detected by either ATR or XPS.

The thermal stability and structure of the films formed is dependant on the type of ZnDTP used. The thermal stability of ZnDTPs increases in the order secondary alkyl < primary alkyl < aryl ZnDTP [16]. The connection between thermal stability, the antiwear performance and the film structure of different ZnDTPs will be discussed in more detail in section 1.5.

To summarize the literature, it is generally agreed that the iron surface catalyzes the thermal film formation. Thermal films on steel from ZnDTP consist of long- and/or short-chain poly(thio)phosphates depending on the temperature, concentration and the decomposition time of the solution, and the type of ZnDTP used.

1.3.3 Tribofilm Composition and Structure

The formation of tribofilms is suggested to be closely related to the formation of thermal films. Analogous to the thermal film, the isomerization to LI-ZnDTP is the first step, which is followed by the adsorption of LI-ZnDTP and ZnDTP onto the steel surface, which was reported to take place at 150°C in a solution of mixed primary and secondary ZnDTP after 6-12 h of immersion [13]. Tribological and thermo-oxidative reactions lead to the formation
of long-chain polyphosphates. Also the deposition of colloidal zinc phosphates on the surface has been proposed [13]. Most of the organic sulfur species remain soluble in the lubricant phase, leading to the depletion of sulfur in the (tribo) film [14]. Polyphosphate films are observed on tribostressed samples below the temperature for thermal-film formation. This demonstrates that the tribological stress initiates film formation [20].

**Vertical Film Structure**

On samples which are tribostressed in the presence of ZnDTP, a multi-layer structure has been proposed. A soft, weakly bound alkyl phosphate film was found to cover a polyphosphate film. Surface forces apparatus measurements showed that this soft film has a thickness of several hundreds of nanometers and is removed by solvent washing or mechanical movement of a diamond tip [22]. Since solvent washing is necessary for most surface-analytical measurements, this soft film is usually removed prior to the analysis of the film. To avoid this problem, the film can be frozen without solvent washing and be analyzed in the frozen state [23]. Results of Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) on frozen films produced from deuterated ZnDTP show that this outer layer consists of organic material which contains alkyl groups from the ZnDTP [24]. The polyphosphate film below this soft layer was found to consist of short-chain iron/zinc polyphosphates, which cover long-chain zinc polyphosphates [25,26]. This was demonstrated by the use of XANES in the total electron yield (TEY) and the fluorescence yield (FY) mode, which probe the top 5 nm (TEY) and 50 nm (FY) of the surface. Dynamic SIMS measurements indicate that a sulfide-rich interlayer between the polyphosphate layer and the underlying substrate may be present [27].

**Lateral Film Structure**

The lateral structure of ZnDTP tribofilms has also been investigated extensively [28-30]. On an anti-wear film, pads of the size of a few tens of micrometers were observed by SEM [28,31]. In agreement with this work, Graham et al. found smooth pads (ca. 10-20 µm in diameter) elongated in the sliding direction in between smaller pads (ca. 2-4 µm in diameter) on films formed with alkyl ZnDTP [29]. The mechanical properties of these films were investigated with interfacial force microscopy (IFM). The center of the larger pads showed a remarkably high elastic modulus of 209 GPa with a low plasticity, while the smaller pads are softer and show a
Introduction

higher plasticity. On films formed from aryl-ZnDTP with poor anti-wear performance compared to the alkyl-ZnDTP, no large pads could be detected. Only smaller streaks (patches) of film elongated in the sliding direction with low elastic modulus and medium plasticity were found. The authors assume that the large pads are responsible for supporting the load during the wear test and represent the nanoscale locations of the origin of the difference in wear protection between the two films.

Similar lateral structures were observed on films derived from alkyl and aryl-ZnDTP and analyzed with XANES [30]. The large pads on the alkyl-ZnDTP films consisted of long-chain-length polyphosphates, while on the smaller pads in the alkyl and all features in the aryl-ZnDTP film shorter chain-length species were found. Unreacted ZnDTP was located in the valleys between the pads.

1.3.4 Model of Film Structure and Film Formation Mechanisms

On the basis of the above results, the following model for tribofilms derived from ZnDTPs has been proposed [12]: The steel surface is covered by multiple layers. The first layer above the metallic substrate is thought to consist of an iron oxide (original oxide) or sulfide film (formed if the nascent iron is exposed to the solution). This film is covered by two poly(thio)phosphate layers, of which the lower one consists of short-chain iron/zinc poly(thio) phosphates and the upper one mainly of long-chain zinc poly(thio) phosphates. In these two layers iron/zinc oxides/sulfides are present as inclusions. The chemical composition and the mechanical properties of the two layers change gradually and they are also inhomogeneous in the lateral direction. On the top, a layer of alkyl phosphates is present, which may serve as a reservoir for the formation of the polyphosphate films. This layer is soft and is removed if the sample is solvent washed.
Anti-wear Films from ZnDTPs

Models for Film Formation

The formation of the two-layer structure of the polyphosphate film is not yet fully understood. Martin et al. [25] explain this structure by the shortening of the initially long-chain polyphosphate through an acid-base reaction between zinc phosphates and iron oxides. According to the HSAB principle, the Fe$^{3+}$ ion, a hard Lewis acid, reacts with phosphates (hard bases). Starting from the polymer-like zinc metaphosphate a possible route for the reaction of Fe$_2$O$_3$ could be given as

$$5\text{Zn}(\text{PO}_3)_2 + \text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_2\text{Zn}_3\text{P}_{10}\text{O}_{31} + 2\text{ZnO}.$$ (7)

Also, other intermediate reactions starting from a zinc (thio)phosphate are possible, leading to the formation of a mixed iron/zinc polyphosphate, zinc oxide and zinc sulfide. The ion exchange from the oxide to the phosphate needs more negative charges in the phosphate to balance the reaction and this results in a shortening of the chain length. According to Martin, the reaction of the iron oxide has the advantage that hard oxide particles (wear debris) are digested and softer zinc oxides and sulfides are formed, which is a benefit in wear protection. There seems to be a need for tribological action to initiate this digestion process because the chemi-
sorbed film outside the wear scar did not attack the iron oxide layer significantly.

A second proposal for the shortening of the chain length in the bulk of tribofilms is that the long-chain polyphosphate films come into contact with water dissolved in the oil and are hydrolyzed [13] according to the following or similar reaction:

\[ 2\text{Zn(PO}_3\text{)}_2 + 3\text{H}_2\text{O} \rightarrow \text{Zn}_2\text{P}_2\text{O}_7 + 2\text{H}_3\text{PO}_4 \]  

(8)

This model is supported by the fact that no iron polyphosphates could be detected in the tribofilms, therefore excluding any chain-shortening according to reaction (7). In addition, the model assumes that the film formation mechanism is strongly dependant on the extent of ZnDTP degradation in the solution.

There are two main points, which made the development of the understanding of the structure of tribofilms derived from ZnDTP difficult. Firstly, as seen above, the film structure is strongly inhomogeneous in both the lateral and the vertical directions. In addition, the different methods used to investigate ZnDTP tribofilms analyze a different portion of the tribofilm, the lateral resolution and the information depth may vary by an order of a magnitude, and it is therefore not surprising that sometimes contradictory results are reported.

Secondly, the film structure and anti-wear performance is strongly dependant on the physical (thermal, mechanical) conditions employed, as well as on the chemical structure of the ZnDTP used to generate the film. The dependence of the ZnDTP tribofilm on load and temperature and on the ZnDTP structure will be discussed in the next two sections.

1.4 Load and Temperature Dependence of Tribofilms from ZnDTPs

**Temperature Dependence of Tribofilms**

Due to the thermally activated formation of the LI-ZnDTP and the thermo-oxidative processes involved in the film formation, the composition of the protective films formed change with temperature [26,32]. At higher temperatures (e.g. 200°C), ZnDTP decom-
poses faster, which increases the film-formation rate, while at lower temperatures (100°C) longer polyphosphate chains are found [26]. At temperatures below 50°C the reactivity of the additive seems to be so low that only a very thin film is formed in the contact region [33]. At temperatures around 100°C sulfur was found to be present as ZnS, while higher temperatures (200°C) seem to favour FeSO₄ [26].

A problem in comparing results from different work on tribological films is that different geometrical setups are used to produce the tribostressed samples (refer to section 1.8). The different geometrical setups lead to different tribological stresses and to differences in the structure of the tribofilm. One important parameter which influences the tribofilm is the contact pressure. Its influence on film structure has been investigated by several authors (see below).

Contact Pressure Dependence of the Thickness and Stability of Tribofilms

In general, an increase of the contact pressure (applied load) leads to an increase of the wear scar width on tribostressed samples [34,35]. Interestingly, in experiments performed at 100°C, it was found that at low loads the wear rate decreases if ZnDTP is added to a base oil, while it increases at higher loads [36]. Based on in situ ellipsometer measurements, Choa et al. proposed that the applied load affects the film formation rate but also the film removal rate [33]. It is assumed that the increase in film formation rate is due to an increase in the reactivity of the additive (caused by higher contact temperatures). The increase in film removal rate is probably due to the stronger mechanical interaction at higher load. The balance between film formation rate and film removal rate determines, if the film is stable (anti-wear) or not (pro-wear).

Effect of Contact Pressure onto the Composition of Tribofilms

Differences in the chemical composition of tribofilms were found to depend on the contact pressure. Unreacted ZnDTP was found to be present on a surface that was tribostressed with lower load, while it is absent at higher loads [26]. This was explained by the faster decomposition of ZnDTP at high load, probably due to increased contact temperatures. Also a shortening of the polyphosphate chain length was observed at higher load [26].

Some authors reported that the sulfur concentration in the wear track increases with increasing load [35,37], while others did not
observe any change [26]. Energy-filtered transmission electron microscopy (EF-TEM) of wear particles showed an increase of iron and sulfur under severe conditions [14]. The increase of sulfur in the wear scar and wear particles under heavy loading could be explained by the reaction of organic sulfides (a thermal degradation product) with exposed nascent iron and the formation of iron sulfide [14]. This would be an explanation for the EP capabilities of ZnDTPs.

1.5 Anti-wear Performance and Thermal Stability of ZnDTPs

The activity and the anti-wear performance of a ZnDTP additive can be related to its thermal stability. High thermal stability may lead to a slow anti-wear film formation and to a poor anti-wear performance, while low thermal stability means faster film formation and better anti-wear performance. This is supported by the fact that alkyl ZnDTPs show superior wear performance than aryl ZnDTPs [29,30], while the thermal stability of aryl ZnDTPs is higher than that of alkyl ZnDTPs [20]. In general, the thermal stability is in the order secondary alkyl > primary alkyl > aryl ZnDTP [16] and can be explained by the ease with which nucleophilic substitution (reaction (1)) can take place at the α-carbon atom of the alkyl group [17].

It would be short-sighted to choose the additive only by its anti-wear behavior. A ZnDTP also acts as anti-oxidant and the thermal and hydrolytic stability may play an important role in the long-term behavior of a lubricant additive package (see
X-ray Photoelectron Spectroscopy in Lubricant-Additive Research

section 1.2). The properties of the three groups of lubricant additives are summarized in Table 1.3.

**Table 1.3**: Structure-activity dependence of ZnDTPs. (Taken from [38])

<table>
<thead>
<tr>
<th>Structure</th>
<th>Oxidative inhibition</th>
<th>Wear protection</th>
<th>Thermal stability</th>
<th>Hydrolytic stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>primary ZnDTP</td>
<td>satisfactory</td>
<td>satisfactory</td>
<td>good</td>
<td>satisfactory</td>
</tr>
<tr>
<td>secondary ZnDTP</td>
<td>good</td>
<td>good</td>
<td>moderate</td>
<td>good</td>
</tr>
<tr>
<td>aryl ZnDTP</td>
<td>moderate</td>
<td>bad</td>
<td>very good</td>
<td>bad</td>
</tr>
</tbody>
</table>

It can be seen in Table 1.3 that none of the additives fulfill the requirement of long-term stability at high temperature, good oxidative inhibition, and wear protection. Therefore, most of the commercial lubricant additive packages contain a mixture of two or more different types of ZnDTPs. In addition, one has always to keep in mind that additional components of the lubricant additive package also strongly influence the performance of additives and the anti-wear film structure.

### 1.6 X-ray Photoelectron Spectroscopy in Lubricant-Additive Research

X-ray photoelectron spectroscopy (XPS) has been widely used to investigate thermal and tribological films formed in the presence of ZnDTPs. Details on the method can be found in section 2.4. In pioneering work carried out by Bird and Galvin in 1976 [31], the surface of thermal and tribostressed samples produced in the presence of elemental sulfur, dibenzyl disulphide, a commercial ZnDTP and a pure ZnDTP (zinc di-n-butylidithiophosphate) as well as a series of reference substances were thoroughly investigated. For the ZnDTP samples they found that the binding energies of the elements present on the surface do not show large differences between the samples, but the elemental composition varies considerably. Since this work, numerous articles have been published about the chemical composition of films derived from lubricant additives using XPS as the sole analytical method or together with other analytical tools.
Introduction

1.6.1 Chemical States of the Elements

Oxygen (1s) Oxygen is always present in films formed from lubricant additives. The O1s signal can be used to separate contributions arising from oxygen bound in an oxide or in a phosphate group. The O1s signal of an oxide can be found at approximately 530 eV, while oxygen bound in a phosphate is reported at 531.6-533 eV [27,33,39,40]. It was shown that the signal from a phosphate group can further be separated into non-bridging oxygen (P-O-, POH, P=O) at 531.7-532.0 and bridging oxygen (P-O-P) at 532.9-534.0 eV [39,40]. These assignments are also in agreement with studies on polyphosphate reference compounds [41]. The relative intensities of the bridging-oxygen and the non-bridging oxygen allows the chain length of a polyphosphate chain to be estimated [25,40]. It has to be noted that other oxygen species may interfere with the above mentioned signal positions. For instance iron hydroxide shows a peak at 531.6 eV [42], which can be confused with the non-bridging oxygen at the same position.

Carbon (1s) Carbon is hardly ever considered in XPS analysis of tribostressed surfaces. The most important reason may be that there are many different carbon sources from which a signal may arise. These contributions cannot easily be distinguished from each other. Almost all tribostressed samples are produced in oil, which consists of hydrocarbon chains. These may be embedded into the tribofilm during the tribological stress or adsorb onto the tribostressed film. Organic sulfides, a thermal degradation product of ZnDTP, may also be embedded in the film or adsorbed on the surface.

Phosphorus (2p) Phosphorus is usually found to be in an oxidized state [27]. The reported binding-energy value of the 2p$_{3/2}$ peak varies between 133.0 eV and 134.5 eV [39,40]. It was shown that this variation can be used to distinguish orthophosphates and metaphosphates from each other [40]. The difficulty of this assignment is that the P2p peak is rather wide (approximately 2 eV with unmonochromatized X-ray sources). This width is due to the spin-orbit splitting of the 2p$_{3/2}$ and the 2p$_{1/2}$ electron level, which are separated by approximately 0.9 eV and lead to a broadening of the signal. The spin-orbit splitting has to be considered in peak fitting and makes the peak modeling complex, if more than one contribution is present.
Sulfur (2p)  
Also the S2p signal is rather broad due to the spin-orbit splitting. Signals from tribostressed surfaces are generally found in the sulfide position at approximately 162 eV or it is found at 169 eV and can then be assigned to sulfate [25,27,31,33,39]. It has been pointed out that from the S2p position alone it is not possible to determine if the sulfide signal is due to zinc sulfides, iron sulfides or organic sulfide species [43].

Zinc (2p, 3s, LMM)  
The most intense signal from zinc is the 2p$_{3/2}$ signal. Only a small difference in the chemical shift of the Zn(2p) peak can be observed between the chemical structures which are found in the tribofilm (ZnO, ZnS, Zn (poly)phosphates) [33] and also the peak position of the Zn 3s signal varies only little [31]. However, the Zn$_{LMM}$ signal shows a stronger dependence and can be used to investigate the chemical environment of Zn [31,39,44]. The Auger parameter $\alpha'$ ($=E_k(Zn_{LMM})+E_b(Zn2p_{3/2})$) has the advantage of being independent of sample charging. In addition, a two-dimensional chemical-state plot of zinc can effectively distinguish between zinc sulfide and oxide [45]. This method can also be extended to differentiate between zinc phosphate or polyphosphate in the contact and non-contact areas of tribostressed surfaces [46].

Iron (2p)  
In some work it has been reported that no iron can be detected on tribofilms from ZnDTP [25], while others describe the presence of it on the surface [33]. This difference is probably due to differences in the applied tribological stress. However, the Fe2p signal has a rather complex peak shape. Difficulties in background subtraction and the contribution of satellites of the Fe2p$_{1/2}$ signal arising from the non-monochromatic X-ray sources used in most of the studies onto the Fe2p$_{3/2}$ signal require a precise procedure for X-ray satellite subtraction, background subtraction and curve fitting based on reference compounds. In addition, shake-up satellites of the Fe$^{2+}$ and Fe$^{3+}$ species have also to be considered. Despite these difficulties, the Fe2p spectra have been used to estimate the film thickness using Ar$^+$ ion sputtering [33]. Also, the approximate ratios between metallic Fe, Fe$^{2+}$ and Fe$^{3+}$ have been used to study the oxidation of the iron surface under thermal treatment in the presence of additives [43,47]. Recently, it has been shown that it is possible to identify iron phosphates in the Fe2p signal [48].
1.6.2 Film Composition

XPS is a quantitative surface-analytical method. The measurement of peak areas and the use of appropriate sensitivity factors allow the determination of the surface-film composition. However, in surface quantification it has to be considered that the surface layer is inhomogeneous in the z-direction. In some work, the relative intensity of all elements detected are used to calculate the “composition” of the surface film. Such an analysis is incorrect and may lead to wrong conclusions because the elements on the outside of the layer (e.g. adsorbed carbon species) will be overestimated in comparison to the tribofilm buried underneath. Only relative intensities of elements which are assumed to have the same depth distribution (e.g. arising from the tribofilm) should be compared with each other.

1.6.3 Film Thickness

Depth profiling with Ar\(^{+}\) ion etching is a widely used technique for gaining information about the depth structure of tribofilms. The Ar\(^{+}\) ion-etching technique has to be used with care because it may produce misleading results. Selective sputtering of light elements [49], the roughness of the surface of tribostressed samples [27,31] and reduction of the surface due to the Ar\(^{+}\) ion bombardment [33,50] may produce artifacts. Despite these problems, Ar\(^{+}\) ion sputtering was used in many studies to obtain information about the depth structure of tribofilms [27,31,33,47,51].

Another method for estimating the film thickness and distribution of the elements in the film is angle-resolved XPS. In this method the escaping electrons are measured at different angles with respect to the surface normal (refer to Figure 2.20) and the different sampling depth is used to acquire information about the depth distribution of the elements. No work has been found using this method in the study of tribological films, most probably because high surface roughness, usually present on tribostressed samples, may falsify the results.
1.7 Imaging Methods

Nearly all of the surface analytical studies analyzed several mm$^2$ or larger areas of the tribostressed samples, and thus an average chemical composition is obtained despite the well-known fact that the films at the micron level are inhomogeneous and “patchy”, as revealed by SEM [28] and AFM [29]. The first application of imaging XPS to tribology showing the spatial distribution of the elements and of their respective chemical states was a tribochemical study on a commercial additive (Irgalube 349) using pin-on-disc test on steel [52]. The high concentration of phosphates formed in the wear track could easily be recognized. Commercial ZnDTP diluted in PAO base oil on iron surfaces has been studied more recently with imaging and small-area XPS [53], both after thermal and tribochemical testing. Photoemission microscopy has been used to examine the chemistry and morphology of ZnDTP anti-wear films on the micrometer level [30] showing that the microchemistry of the films formed from alkyl or aryl ZnDTP are different. The alkyl-ZnDTP formed large pads (ca. 25 µm$^2$) composed of long-chain polyphosphate and smaller pads composed of short-chain polyphosphate, while the aryl-ZnDTP formed a thin uniform films containing ortho- or pyrophosphates. Different P species (unreacted ZnDTP and phosphate) could also be mapped: phosphate was found on the asperities and adsorbed ZnDTP in the valleys.

Scanning Auger Microscopy (SAM) could be very useful for obtaining elemental images of these films because sub-micron resolution is easily obtained and the information depth of 5 - 10 nm is well suited. Up to now mostly backscattered or secondary electron images of wear tracks have been published [12] and in some cases also AES elemental maps are shown [54]. The group of Ecole Centrale de Lyon published results obtained in a special UHV tribotester on MoDTP [55] and on mixed MoDTC / ZnDTP [56]. In our own group, elemental Auger images of wear films obtained in a pin-on-disc arrangement studying commercial additive (Irgalube 349) have been presented [57]. Elemental AES maps may give complementary information to the i-XPS maps.
1.8 Tribological Testing

In this section the first part gives a general overview of tribological tests used in the industry and academia. In the second part, tests which are used for lubricant and additive performance characterization are described.

1.8.1 Overview

Friction and wear are ubiquitous phenomena that determine the performance and the lifetime of a machine. Therefore, there is a huge interest in the tribological properties of material pairs. The tribological performance of a pair of materials depends on the material properties (e.g. elastic modulus, hardness and tensile strength) of both materials and on the tribological situation (e.g. lubricant, surface roughness, relative velocity, contact pressure, and temperature). Tribological tests have been developed for many tribological contacts, which leads to a large number of tribotests. More than 400 wear-testing standards are in use around the world. Many of these are slight variations of each other but still more than 100 basic types of tests can be discriminated [58].

In general, tests for characterizing tribological properties can be divided into four groups: physical and chemical tests, bench tests, applied tests and field tests. The cost, duration and relevance for a practical application increase in the given order, while the control of the stress in the contact decreases (Table 1.4). In the following, the general characteristics of these types of tests will be described [59]. Examples of the four types used in engine testing can be found in Table 1.5.
Physical and Chemical Tests

These are well-controlled, cheap and repeatable tests to assess the quality or nature of a product (e.g. elemental composition, viscosity, tensile strength). Their relation to the real application is remote but they may give valuable information for screening candidates or as an aid to quality control. The large number of physical and chemical tests are regulated by the American Society of Testing and Materials (ASTM), the Institute of Petroleum (IP) or other regulation authorities.

Bench Tests

Bench tests range from general tests (e.g. pin-on-disc, reciprocating pin-on-plate) to the use of a particular section of an engine, with its actual components run on a rig. The latter may provide valuable results for the selection of materials in the particular application but this information may not easily be transferred to other applications. On the other hand, simple experiments lack relevance to the actual running conditions of a machine but may produce general reference data for a range of similar applications. They may also be used for more fundamental studies on tribology. Also, a large portion of these tests are regulated but there exists also a lot of tests which are designed to meet the need of a particular company.

Applied Tests

Applied tests involve the running of a real machine under controlled conditions. As an example, in the development of vehicle

<table>
<thead>
<tr>
<th>Test</th>
<th>Duration</th>
<th>Cost per test ($)</th>
<th>Relevance for application</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical and chemical</td>
<td>Hours</td>
<td>50-500</td>
<td>low</td>
<td>Well controlled, repeatable but relates to specific properties, not performance</td>
</tr>
<tr>
<td>Bench</td>
<td>Days</td>
<td>500-5000</td>
<td>medium</td>
<td>Well controlled, repeatable and can be related to practical performance</td>
</tr>
<tr>
<td>Applied</td>
<td>Weeks</td>
<td>15’000 -40’000</td>
<td>high</td>
<td>Poor control and repeatability but close to practical performance</td>
</tr>
<tr>
<td>Field</td>
<td>Months</td>
<td>400’000 plus</td>
<td>very high</td>
<td>Very little control but is the real application</td>
</tr>
</tbody>
</table>

Table 1.4: Tribological test methods with the costs and benefits. Adapted from [59].
motors, engine tests are routinely used to assess either lubricant and material properties in so called “fired tests” or aim at the testing of specific components such as valve trains (“motored tests”). The mechanical setup of applied tests are very close to the real application, which is not necessarily true for the environmental conditions, since these tests are usually run in test laboratories. Most of these tests are used only in one company to simulate their practical conditions, thus, there exists no (public) regulation for these tests.

**Field Tests** Field tests are done with the finished product, which is run for a long time under real conditions. Field tests do not give specific feedback on the performance of a particular part of the machine but on the overall performance of the product. The running conditions are not well controlled but meet the real working conditions. Because of the involvement of the finished product and the long time required for these tests, field tests are very expensive.

**Table 1.5:** Examples of tribological tests used in engine testing, divided into the four categories of tribological tests. Taken from [59].

<table>
<thead>
<tr>
<th>Category</th>
<th>Physical</th>
<th>Mechanical</th>
<th>Chemical</th>
<th>Bench</th>
<th>General</th>
<th>Applied</th>
<th>Engine (Applied)</th>
<th>Fired</th>
<th>Motored</th>
<th>Field</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tensile strength, hardness, ductility, fatigue strength, shear stability, viscosity</td>
<td>Elemental composition, total base number, volatility, flash point, pour point, foaming, seal compatibility, water separation</td>
<td></td>
<td>Abrasion test, pin-on-disc, block-on-ring, reciprocating pin-on-plate</td>
<td></td>
<td>Standard four-ball EP, four-ball, Falex, Timken, FZG gear scuffing</td>
<td>Peugeot TU3, Mercedes M103E, Sequence, III, IV and V tests</td>
<td></td>
<td>Examples include Toyota 3AU, P-VW 5106 cam/tappet wear, PSA XN-1 cam tappet pitting, instrumented single cylinder engines</td>
<td>Real production vehicles</td>
</tr>
</tbody>
</table>

For the solution of a tribological problem in industry it may be necessary to combine some of the different types of tests. Physical and bench tests may be used to select or exclude materials for the particular application. This selection saves time and cost for applied
or field tests, where the candidates are tested under the real operating conditions.

For academic research, the performance in the application is often only of secondary interest. The research focuses on the fundamental tribological mechanisms, which may lead to the understanding of more applied situations. Therefore also in academic research bench tests play an important role. However, the choice of the appropriate bench test is in both cases very important.

**Basic Types of Wear**

For the selection of the wear test, it is important to identify first the dominant wear mechanism present in the situation under study. In a survey done by the British National Physical Laboratory (NPL) in the UK industry in 1997, seven basic types of wear were identified to be economically significant for industry (see Table 1.6).

**Table 1.6:** Seven types of wear of industrial relevance and where they occur, determined from a survey in the UK industry (1997) [58].

<table>
<thead>
<tr>
<th>Type of Wear</th>
<th>Examples of industrial application where this wear is likely to occur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abrasive wear from moving contact with hard granular material</td>
<td>Earth-moving machines, rotors of powder mixers, extrusion dies</td>
</tr>
<tr>
<td>Abrasive wear from hard particles trapped between moving surfaces</td>
<td>Pivot pins in construction machinery, scraper blades in plaster-mixing machines</td>
</tr>
<tr>
<td>Adhesive wear from the rubbing together of relatively smooth surfaces</td>
<td>Rubbing bearings, clutches, press tools, breaks, piston rings, cylinder liners</td>
</tr>
<tr>
<td>Fretting from small movements between relatively smooth surfaces</td>
<td>Connecting rod joints in internal combustion machines, gear couplings with misalignment</td>
</tr>
<tr>
<td>Cavitation erosion from the collapse of low-pressure vapor bubbles</td>
<td>Marine propellers, Pump rotors, Hydraulic control valves</td>
</tr>
<tr>
<td>Particle erosion from hard particles in a stream of fluid or air</td>
<td>Valves controlling the flow of sandy crude oil, pipelines carrying abrasive materials, helicopter rotors in desert operation</td>
</tr>
<tr>
<td>The release of particles from a surface as a result of fatigue</td>
<td>Rolling bearings, clutches subjected to excessive slip, surfaces in intermittent contact with molten materials</td>
</tr>
</tbody>
</table>
In the same survey, a large number of wear tests were conducted on a number of machines, with variation of the operating conditions and the machine design details, to check for sensitivities and likely errors in results. It was found that a small number of tests would meet the industrial needs for wear testing. This led to the proposal of 13 standardized (bench) tests and the associated operating conditions which would be sufficient to fulfill the needs of the industry. The reduction to a small number of tests should increase the reproducibility of results the reliability of published results of the wear performance of various types of materials [58].

1.8.2 Bench Tests for Lubricant Additive Performance Characterization

The focus of this thesis is on the interaction of lubricant additives with the steel surface under tribological stress and the development of new methods to investigate this interaction. To develop such methods, first, the underlying wear mechanism has to be determined in which the lubricant additives under study are used to prevent wear. It can be seen in Table 1.6 that the applications where such lubricant additives are used (bearings, cylinder liners, piston rings) are associated with adhesive wear. Therefore, test methods for adhesive wear have to be used to study the performance of lubricant additives.

Three test methods for adhesive wear have been proposed by the NPL report mentioned above. These are unidirectional pin-on-disc, reciprocating pin-on-plate and the thrust washer test [58]. The pin-on-disc and the reciprocating pin-on-plate test will be described shortly, the thrust washer test will not be covered because it is mainly used for the evaluation of thrust washers and break disc materials, where no lubrication is employed and is therefore not relevant for the situation under study in this work.

Unidirectional Pin-on-disc Test

The pin-on-disc test (ASTM G99) has been widely used. A stationary pin or ball is pressed against a rotating disc. Friction is measured by the force needed to restrain the pin or ball in the tangential direction. Wear can be measured by use of a linear displacement transducer in the vertical direction, by gravimetric means or by profilometry of the worn sample.
Test load can be up to 10’000 N, the test speed is 0.001-10 m/s. The contact geometry is flat-ended pin, rounded pin or ball against flat.

**Reciprocating Pin-on-flat Test**

The reciprocating test system (ASTM G133) has also been widely used. A stationary pin or ball is pressed against a flat sample that is moved backwards and forwards in a reciprocating motion. Friction can be measured by measuring the force needed to restrain the pin or ball against the direction of travel. Wear can be measured by the use of a linear displacement transducer in the vertical direction, by gravimetric means or by profilometry of the worn sample.

**Figure 1.5:** Schematic diagram of a pin-on-disc test. Taken from [58].
The test load can be up to 10’000 N, the frequency 0.1-50 Hz and the stroke length (travelling distance) 0.25-50 mm. The contact geometry is flat-ended pin, rounded pin or ball against flat.

The pin-on-disc and the reciprocating pin-on-flat test are in fact the most widely used tests for lubricant-additive research. Their drawback is usually that only one set of tribological parameters (load, velocity, temperature) can be tested at once or, if more than one set is applied, they are run after each other on the same wear track (e.g. a complete stribeck-curve). As it was shown in section 1.4, the morphology and chemical composition of anti-wear films is dependent on the applied conditions (e.g. load). If one wants to study the dependence of the film structure on a parameter, one has to produce multiple samples, which are analyzed in sequence. A new approach, which could circumvent this problem would be a “combinatorial tribotest” where multiple tribological conditions are applied on the same sample, spatially separated from each other.

Figure 1.6: Schematic diagram of a reciprocating pin-on-flat test. Taken from [58].
1.9 Combinatorial Tribotesting

The combinatorial synthetic approach, together with high-throughput screening of compounds has been applied in pharmaceutical chemistry since the early eighties. A large number of molecules is synthesized in parallel and subsequently probed for chemical, physical and medicinal properties. This approach was first brought into materials science in the field of high-temperature superconductors [60], where a spatially addressable library of potential candidates for high-Tc was fabricated and tested. The combinatorial approach has been adapted to different fields in materials science, such as semiconductors [61] or metallurgy [62].

The advantage of the combinatorial synthetic approach in both chemistry and materials science is the rapid production of many substances of varying compositions which are subsequently analyzed in a massively parallel way. This method speeds up the search for new substances with the desired properties.

A modification of this combinatorial synthetic approach could be used in the investigation of lubricant additive reactions under a variety of tribological stresses. In this type of experiment a parameter library is built, applying various tribological conditions (as a function of the lateral position on the disc) on a single sample, which is subsequently analyzed by (imaging) surface analytical techniques. The tribological information (coefficient of friction, wear) and the spectroscopic results can afterwards be mapped onto the parameter library (Figure 1.7). This would allow the parallel analysis of a range of tribological conditions, which can give information about the structure of the tribofilm depending on the applied conditions or speed up the screening of new lubricant additive candidates.
Only very little work has been done applying a combinatorial approach to tribological problems. Green and Lee used an AFM with chemically patterned cantilevers and tip arrays to probe adhesive forces between carboxylic acid, alcohol and methyl groups [64]. This approach reveals frictional information on the molecular scale, depending on the chemical modification of the cantilever.

A different approach was used by Hogmark et al. [65,66]. A tribological load scanner was used in a crossed-cylinder configuration to evaluate hard coatings. In this setup, two elongated cylinders repeatedly slide across each other with varying load in a manner that each point along the sliding track of both cylinders experiences a unique load.
No work was found applying a similar approach to lubricant additive characterization or analysis of tribofilms. As there is an increasing pressure to reduce the use of chlorinated and heavy metal containing additives due to environmental and health considerations, there will be an increasing demand for testing the performance of new lubricant additives. Compared to the traditional tribotests, combinatorial tribotests may offer the advantage of a fast investigation of the performance of such candidates for a wide range of tribological parameters. In addition, dependence of the tribofilm structure on the applied conditions may be investigated.

1.9.1 Combinatorial Approach to Lubricant Additive Characterization

In this work, the use of the combinatorial approach to lubricant additive characterization is investigated. A programmable pin-on-disc tribometer is used to create tribological “libraries”. Two types of libraries are created, a first one to characterize the tribological performance of a lubricant additive and a second one to analyze the tribofilm formed by lubricant additives.

Figure 1.8: Tribological load scanner. Two cylinders repeatedly slide across each other with varying load in a manner that each point along the sliding track of both cylinders experiences a unique load. (Taken from [66]).
Introduction

The first type of library is created with oscillating load tests, in which the normal load is repeatedly ramped from a minimum to a maximum load in synchronization with the angular position on the disc. On different radii, the number of rotations is varied. On this load-duration parameter library, the coefficient of friction and the wear results (obtained with optical laser profilometry of the wear tracks) are mapped.

A second type of combinatorial tribotest is used to produce a parameter library (at room temperature and at 150°C) with a series of load on different radii. The surface composition of the tribofilms is characterized by X-ray photoelectron spectroscopy.
References

Introduction


Introduction


This chapter is concerned with the materials used and the experimental methods applied in this study. First, the substrates, lubricants and additives are listed with their chemical and physical properties, followed by the sample preparation methods. The tribometer used in this study is described together with the experimental setup of the tribotests. An introduction into the theory of X-ray photoelectron spectroscopy is given, completed with the experimental settings applied in this study. The chapter ends with a short description of further experimental methods employed.
2.1 Materials

2.1.1 Tribopairs

Steel discs made of 100Cr6 (AISI 52100, DIN 1.3505) were used for the tribotests unless otherwise noted. This steel, a ferritic Cr alloy, is known as one of the most widely used materials for bearings (for composition see Table 2.1). The steel discs used were hardened, a hardness of 64 HRC was measured.

As countersurface in the tribotests, 4 mm ball-bearing balls, made of the same steel, were used.

2.1.2 Lubricants

Decane (analytical grade) and a commercial poly-\(\alpha\)-olefine (PAO166) were used as base oils. The physical properties of the two lubricants are shown in Table 2.2.

| Table 2.1: Elemental composition of 100Cr6 steel. |
|-------------------|-------------------|-----------------|-----------------|-----------------|-----------------|
| C                 | Cr                | Mn              | S               | P               | Si              |
| 0.95-1.10         | 1.35-1.85         | 0.25-0.45       | <0.025          | <0.025          | 0.15-0.35       |

| Table 2.2: Physical properties of decane and PAO 166. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
|                                | Decane [1,2]    | PAO 166 [3]     |
| Melting Point (℃)              | -29.7           | <-40*           |
| Boiling Point (℃)              | 174.1           | >270*           |
| Density (20℃) (kg/m\(^3\))    | 730             | 830             |
| Viscosity (25℃) (mN·s/m\(^2\))| 0.752           | 43              |
| Viscosity (100℃) (mN·s/m\(^2\))| 0.338           | 4.8             |
| Viscosity (150℃) (mN·s/m\(^2\))| 0.252           | 2.3             |

*General values for poly-alpha-olefines [4].
2.1.3 Additives

i-ZnDTP

Zinc diisopropyl dithiophosphate (i-ZnDTP) was used in this work as a model compound, in order to study its anti-wear behavior. Its chemical structure is shown in Figure 2.1. The substance (a white powder) was provided by Prof. J.M. Martin (EC Lyon, France). It was synthesized according to [5]. Bulk chemical analysis (Leco CHNS) are in good agreement with the calculated values (Table 2.3).

![Chemical structure of ZnDTP](image)

**Table 2.3**: Bulk chemical analysis (wt.-%) of i-ZnDTP with the calculated values.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>O</th>
<th>H</th>
<th>S</th>
<th>P</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical</td>
<td>29.3</td>
<td>13.0</td>
<td>5.7</td>
<td>26.0</td>
<td>12.6</td>
<td>13.3</td>
</tr>
<tr>
<td>Chemical analysis</td>
<td>29.4</td>
<td>13.0</td>
<td>5.7</td>
<td>26.2</td>
<td>12.5</td>
<td>rest</td>
</tr>
</tbody>
</table>

Commercial ZnDTP

A commercial secondary ZnDTP (C3+C6) (Hitec 7169, Ethyl Petroleum Additives International, England), purified by liquid chromatography, was also used as lubricant additive. More details about the additive and the purification can be found elsewhere [7].
2.1.4 **List of Materials and Suppliers**

**Table 2.4:** Suppliers of materials used in this thesis and remarks.

<table>
<thead>
<tr>
<th>Name</th>
<th>Supplier</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>100Cr6 balls</td>
<td>Hydrel AG, Romanshorn, Switzerland</td>
<td>4 mm diameter</td>
</tr>
<tr>
<td>100Cr6 discs</td>
<td>CSEM SA, Neuchatel, Switzerland</td>
<td>Former Project (PPM 3.4B)</td>
</tr>
<tr>
<td><strong>Additives</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>i-ZnDTP</td>
<td>Prof. J.M. Martin, Ecole Centrale de Lyon</td>
<td></td>
</tr>
<tr>
<td>commercial ZnDTP</td>
<td>Ethyl Petroleum Additives International, England</td>
<td>purified by HPLC</td>
</tr>
<tr>
<td>(Hitec 7169)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Lubricants</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Decane, purum</td>
<td>Fluka, Buchs, Switzerland</td>
<td></td>
</tr>
<tr>
<td>PAO166</td>
<td>ICC Inchem GmbH, Wolfratshausen, Germany</td>
<td></td>
</tr>
<tr>
<td><strong>Solvents</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol, puriss p.a.</td>
<td>Fluka, Buchs, Switzerland</td>
<td></td>
</tr>
<tr>
<td>Acetone, puriss p.a.</td>
<td>Fluka, Buchs, Switzerland</td>
<td></td>
</tr>
<tr>
<td>Cyclohexane, (&gt;99.5%)</td>
<td>Fluka, Buchs, Switzerland</td>
<td></td>
</tr>
<tr>
<td><strong>Reference Compounds</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc oxide, puratronic (99.9995%)</td>
<td>Alfa Aesar, Karlsruhe, Germany</td>
<td></td>
</tr>
<tr>
<td>Zinc sulfide 99.99</td>
<td>Alfa Aesar, Karlsruhe, Germany</td>
<td></td>
</tr>
<tr>
<td>Iron(II) phosphate hydrate</td>
<td>Fluka, Buchs, Switzerland</td>
<td></td>
</tr>
<tr>
<td><strong>Polishing Supplies</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diamond Paste</td>
<td>Struers GMBH, Birmensdorf, Switzerland</td>
<td>1/4 µm, 1 µm, 3 µm</td>
</tr>
<tr>
<td>DP-Paste, P</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polishing cloths</td>
<td>Struers GMBH, Birmensdorf, Switzerland</td>
<td></td>
</tr>
<tr>
<td>DP-Plus, DP-Nap</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.2 Sample Preparation

To avoid contamination from glassware, it was cleaned with soap under hot tap water and subsequently flushed several times with tap water prior to rinsing with distilled water. Finally it was rinsed with acetone and dried under a gas stream (Nitrogen or Argon).

Grinding

All samples were ground with silica paper on a rotating polishing wheel to remove any surface contamination. The samples were subsequently polished. Table 2.5 shows the detailed grinding and polishing procedure.

Polishing

After the final polishing step, the surface was checked with XPS for surface contamination. The samples were stored in a desiccator for typically 3 days in order to allow a natural oxide film to grow. This allows the tribological test to consistently start from a well defined surface. Immediately prior to the tribological experiment, the samples were cleaned again in EtOH and the surface composition was analyzed with XPS.

i-ZnDTP solution was prepared by dissolving the ZnDTP in decane while stirring the solution at 60°C for 30’.

After the tribological experiment, the samples were cleaned in cyclohexane in the ultrasonic bath once or twice for 30”, depending
Experimental

on the amount of debris on the surface. The samples were dried under an argon stream and introduced into the analysis chamber of the XPS.

2.3 Tribological Experiments

2.3.1 CETR Tribometer

For the tribological experiments a CETR UMT-2 (Center for Tribology, Campbell CA, USA) was used (see Figure 2.2). A schematic diagram of the tribometer is also shown in Figure 2.2.

![CETR Tribometer Diagram](image)

**Figure 2.2:** Picture and schematic diagram of the CETR Tribometer.

The tribometer consists of the carriage, on which the upper sample holder is mounted, and the sample table bearing the lower sample holder. The carriage can be moved up and down with motor 1 (M₁) and has a two dimensional load cell mounted on the vertical slider, driven by motor 2 (M₂). The upper sample holder is connected to the load cell by a spring with a spring constant k₁. The lower sample holder is mounted on the sample table, which is driven by the rotational drive (M₃). All three motors are equipped with encoders, which monitor the position of the respective direction of movement (M₁: z-position (Z), M₂: radial position (R), M₃: rotational.
position (ROT)). The motors can be manually operated from the CETR UMT software (V1.43) or are automatically driven during a tribotest.

**Load Cell**

The load cell is capable of measuring the load in two directions (x- and z-axis). The z-axis is perpendicular to the sample plate and the x-axis is tangential to the rotational direction. During a tribotest, the normal load can be programmed and is maintained by a feedback loop. The normal load is measured continuously and is adjusted by moving the carriage up or down with motor M1. Two different load cells with a maximum capacity of 5 N and 20 N have been used (see Table 2.6). The resolution of the load cell is given by the manufacturer as 0.1% of the maximum capacity.

A tribotest has to be programmed with a “test script”. A test script consists of a series of sequences containing a number of sheets. In a sequence the general parameters used to control the tribometer are defined (mainly feedback loop parameters and data-saving properties). In a sheet, the parameters of the actual test (normal load, rotational velocity, radius and duration) can be programmed. For each sequence, normal load (Fz), friction force (Fx), time (t) and the three encoder positions (ROT, Z, R) can be recorded.

The load cell was calibrated using standard weights. After biasing the load cell, the standard weight was applied and the range of the A/D signal set for the correct load to display. The same procedure was repeated for the second load axis.
Depending on the load cell used, an appropriate spring had to be chosen. The spring constants were determined using the semi-automatic mode of the tribometer. The upper sample was brought close to the sample plate and while recording $F_z$ and $F_x$ the carriage was driven down to reach the maximum load. A hysteresis can be seen between the loading and the unloading cycle (Figure 2.3). The spring constant ($k_1$) of the springs used have been calculated using the loading cycle (Table 2.6). The spring constant in the tangential direction ($k_2$) was measured correspondingly by driving the upper specimen holder slowly into an obstacle fixed on the lower specimen table, while recording $F_x$ and $F_z$.

![Figure 2.3: Force curve ($F_z$) while loading and unloading the 5 N load cell. A small hysteresis can be seen. A spring constant of 2.7 N/mm has been calculated for the loading cycle.](image)

<table>
<thead>
<tr>
<th>Load Cell</th>
<th>Spring Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max Load</td>
<td>Resolution</td>
</tr>
<tr>
<td>5 N</td>
<td>5 mN</td>
</tr>
<tr>
<td>20 N</td>
<td>20 mN</td>
</tr>
</tbody>
</table>
In Figure 2.4 the cross coupling between the normal load ($F_z$) and the tangential force ($F_x$) is displayed. It shows that the tangential force is affected by both the applied load and by the history of previous loading, since a hysteresis effect can be seen.

**Figure 2.4:** Coupling between normal load ($F_z$) and tangential force ($F_x$) during pure loading and unloading in z-direction. It is mainly upon unloading that $F_x$ deviates from the theoretical zero force.

**Data Acquisition**

Data acquired during a tribotest were processed first with the Viewer (V2.3) program shipped with the tribometer. The program is capable of displaying the acquired data ($F_z$, $F_x$, R, Z, ROT versus time, ROT or Z). Furthermore the COF is calculated as $F_x/F_z$ and can also be displayed. In addition, average values of COF can be calculated for a single test sheet and displayed versus the linear or rotational velocity. For further data processing, data was exported into an ASCII file and analyzed with IGOR Pro (WaveMetrics Inc., Lake Oswego, OR, USA) software.

The liquid sample holder is mounted on the sample table (Figure 2.5). The sample is placed in a recess and fixed with a ring. The cup can be filled with lubricant.
Sample Planarity

It was found essential that the sample plane is perpendicular to the rotational axis and thus that the sample is aligned parallel to the rotational plane. If the sample is not planar, varying frictional behavior can be observed depending on the angular position on the disc (Figure 2.6). In a non-planar experiment, regions with and without stick-slip are found, while in an experiment with a planar sample alignment a continuous friction behavior is observed (under the otherwise same experimental conditions). Therefore the planarity of the sample was adjusted before each experiment. It was measured by applying a low load (100 mN with the 10 N cell and 50 mN with the 5 N load cell) outside of the region where the tribotest was done and measuring the z-position of the carriage during one full turn. The planarity was adjusted by putting Al-foil between the sample plate and the sample holder.

Figure 2.5: Design of the sample holder. Aluminium foil was put between the sample holder and the sample plate to adjust the planarity of the sample, as necessary.
A heating stage (Figure 2.7) can be mounted on the tribometer. It is manufactured from polytetrafluoroethylene (PTFE), which is protected from the heating plate and the sample holder by a ceramic layer. The temperature is measured with a platinum thermoresistor inside the stage and controlled by a thermo controller (OMEGA CN76000). A maximum temperature of 150°C can be reached. In order to equilibrate the temperature, the sample holder was mounted on the sample plate and the stage heated for at least 30 minutes prior to the tribotest. The temperature in the oil was monitored by means of a thermocouple (Digisense, Cole Parmer, Niles, USA). Once the temperature reached an equilibrium state, it was found to vary by less than ±2°C.

Figure 2.6: The coefficient of friction (high friction = bright color) of a tribotest is displayed versus the angular position on the disc (x-axis) and the number of revolutions (y-axis). On the left-hand side the sample is not perpendicular to the rotational direction - during one full turn the carriage has to move more than 30 µm - while on the right hand side a deviation of less than ±10 µm is found. The first case leads to a varying friction behavior depending on the angular position on the disc. This behavior cannot be observed in the latter case.
A substantial thermal drift was found in the load cell. In order to minimize this influence, the upper sample holder was immersed into the lubricant while heating up the stage. A thermal drift of up to 70 mN in Fx and 10 mN in Fz was observed in the 5 N load cell while increasing the Temperature from 25°C to 150°C. The load cell was biased prior to the experiment. If the experiment consisted of a number of sequences, the load cell was biased prior to each sequence.

2.3.2 Combinatorial Tribotests

The aim of a combinatorial tribotest is the generation of a parameter library on a single sample. This is done by the spatially separated application of various tribological stresses. The parameter library can be spanned in two dimensions: the radial position on the disc and the angular position on the disc. In the radial direction the differently stressed regions are separated in discrete annuli, leading to discrete wear tracks. If the angular direction is used for separation, the applied load is varied synchronized with the angular position on the disc. In addition, the characteristics of a single wear track can be changed. This leads to a set of tribotests that can

Figure 2.7: Heating stage, mounted on the tribometer. On the left hand side the temperature controller (bottom) and the thermocouple (top) can be seen.
be separated according to three attributes: The number of wear tracks on one sample, the rotational characteristic of a wear track and the radial characteristic of a wear track.

**Number of wear tracks** Libraries containing from 1 to 6 wear tracks have been created (Figure 2.8). Each wear track corresponds to a particular mean radius. If multiple wear tracks are carried out on a sample, one or more parameters are varied between the tests. Parameters which can be varied are load (L), velocity (v), temperature (T) and duration of the test (t).

![Figure 2.8: Tribotest with 5 wear tracks. In each wear track a different set of parameters (L, v, T, t) can be applied.](image)

**Rotational characteristics of a wear track** Two types of rotational characteristics were possible using the CETR tribometer and were denoted as constant load test and oscillating load test (Figure 2.9). While in the constant load test the load was kept constant during the test, in the oscillation load test it was synchronized with the rotational position. Typically the load was ramped four times during one revolution of the disc in order to create redundancy.
Radial characteristic of the wear track

Often the wear-scar width of a ball-on-disc contact is smaller than the diameter of the analyzed area of a surface analytical technique. This problem can be solved by increasing the width of the tribostressed region, either by moving the ball continuously (spiral test) or in discrete steps (step test) in the radial direction during the test. In this way uniform concentric tribostressed annuli of a predetermined width can be created.

**Figure 2.9:** In a constant load test the load is kept constant during one turn of the disc, while in an oscillating load test the load is cycled in synchronization with the rotational position.
In principle the attributes mentioned above can be combined to produce combinatorial tribotests. Four basic types of experiments were used in this thesis, each designed to address a particular tribological or analytical problem. The experimental settings of these tribotests will be presented in the following.

**Figure 2.10:** In a step test, the radius of the wear track is changed in small discrete steps (typically 25 μm steps). The step size should be chosen to be small enough to ensure the overlapping of subsequent wear tracks. The schematic picture on the right-hand side shows the apparent contact area of a 1 N ball-on-disc experiment (circle) in relation to the step size.

### 2.3.3 Experimental Settings of Combinatorial Tribotests

In principle the attributes mentioned above can be combined to produce combinatorial tribotests. Four basic types of experiments were used in this thesis, each designed to address a particular tribological or analytical problem. The experimental settings of these tribotests will be presented in the following.
The standard tests correspond to classical ball-on-disc experiments. They consist of one or more wear tracks, where each wear track is run at a particular radius. Load and velocity are kept constant within each wear track but may vary between the tracks. The setup of a two-wear-track standard test is shown in Figure 2.11; the experimental settings are summarized in Table 2.7.

Table 2.7: Experimental settings of the two-wear-track standard test.

<table>
<thead>
<tr>
<th>Load</th>
<th>Radius</th>
<th>Velocity</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N)</td>
<td>(mm)</td>
<td>(mm/min)</td>
<td>(min)</td>
</tr>
<tr>
<td>running in</td>
<td>10 N</td>
<td>6.5</td>
<td>31.4</td>
</tr>
<tr>
<td>1 N test</td>
<td>1 N</td>
<td>5</td>
<td>31.4</td>
</tr>
<tr>
<td>10 N test</td>
<td>10 N</td>
<td>4.5</td>
<td>31.4</td>
</tr>
</tbody>
</table>

A running in of the ball was performed prior to the tribotests at a load of 10 N and at a radius of 6.5 mm. The running in produced a
small flat spot on the bottom of the ball, which defined the later apparent contact area between the ball and the disc. Two tests were run at 1 N and 10 N with radii of 5 mm and 4.5 mm, respectively. The total time of the experiment was 90’ for each test.

Spiral and Step Test

Combined spiral and step tests were used in order to characterize these two methods for enlarging the wear scar width. On one sample a spiral and a step test were done (Figure 2.12). The experimental settings are given in Table 2.8.

Table 2.8: Experimental settings of the combined step test and spiral test.

<table>
<thead>
<tr>
<th>Load</th>
<th>Radius</th>
<th>Velocity</th>
<th>Time</th>
<th>Turns</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N)</td>
<td>(mm)</td>
<td>(mm/min)</td>
<td>(min)</td>
<td>(#)</td>
<td></td>
</tr>
<tr>
<td>running in</td>
<td>5</td>
<td>6.5</td>
<td>31.4</td>
<td>120</td>
<td>92</td>
</tr>
<tr>
<td>step test</td>
<td>1</td>
<td>4.5-5.5</td>
<td>31.4</td>
<td>180</td>
<td>160 20x50 µm steps</td>
</tr>
<tr>
<td>spiral test</td>
<td>1</td>
<td>3.5-4.5</td>
<td>31.4</td>
<td>16</td>
<td>65 radial movement with 1 µm/s</td>
</tr>
</tbody>
</table>

A running in of the ball in solution was performed at a radius of 6.5 mm and a load of 5 N for 120’ and a speed of 31 mm/min prior to the actual tribotests. The step test consisted of 20 steps of 50 µm creating a total width of the tribostressed area of 1 mm. The nor-
Experimental

mal load was 1 N and the speed 31 mm/min. The whole experiment took 3 h to complete. In the spiral test, the slider motor was continuously run at its lowest speed of 1 µm/s. The normal load and the relative speed between the ball and disc was 1 N and 31 mm/min. This produces a spiral, where the passes at a particular angular position on the disc are radially separated by approximately 25 µm, the spiral test took 16’ to create a tribostressed area with a width of 1 mm.

Combinatorial Step Test

![Diagram of experimental setup of a combinatorial step test. The experiment consists of a set of concentric tribostressed annuli, where in each annulus a set of concentric wear tracks (step test) is produced at a particular load and velocity.]

**Figure 2.13:** Experimental setup of a combinatorial step test. The experiment consists of a set of concentric tribostressed annuli, where in each annulus a set of concentric wear tracks (step test) is produced at a particular load and velocity.

A combinatorial step test is the basic type of experiment in this thesis for combination with spectroscopic analysis. A number of step tests are combined on one sample to produce a parameter library which can be analyzed by XPS. The setup of a combinatorial tribotest is shown in Figure 2.13, the experimental settings are shown in Table 2.9.
A running in of the ball was done for 120’ prior to the actual combinatorial experiment. The experiment consisted of the formation of five concentric tribostressed annuli, where each annulus consisted of a step test with 11 overlapping concentric wear tracks with a stepping distance of 25 $\mu$m (see the inset of Figure 2.13). To keep the number of “passes” of the ball constant for each tribostressed area, 5 full revolutions of the disc were done at each step.

Large Area Step Test

For the angular resolved XPS measurements a wear track with a width of 1 mm was produced in order to make sure that the analyzed area was completely within the wear track. In this case a step test with 41 steps of 25 $\mu$m was done. The experimental settings are summarized in Table 2.10.

Table 2.9: Experimental settings of the combinatorial step test.

<table>
<thead>
<tr>
<th>Load</th>
<th>Radius*</th>
<th>Velocity</th>
<th>Time</th>
<th>Turns</th>
<th>Steps</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N)</td>
<td>(mm)</td>
<td>(mm/min)</td>
<td>(min)</td>
<td>(#)</td>
<td></td>
</tr>
<tr>
<td>running in</td>
<td>5</td>
<td>6.5</td>
<td>31.4</td>
<td>120</td>
<td>92</td>
</tr>
<tr>
<td>5 N test</td>
<td>5</td>
<td>5.5</td>
<td>31.4</td>
<td>55</td>
<td>5x11</td>
</tr>
<tr>
<td>1 N test</td>
<td>1</td>
<td>5.0</td>
<td>31.4</td>
<td>50</td>
<td>5x11</td>
</tr>
<tr>
<td>0.5 N test</td>
<td>0.5</td>
<td>4.5</td>
<td>31.4</td>
<td>45</td>
<td>5x11</td>
</tr>
<tr>
<td>0.1 N test</td>
<td>0.1</td>
<td>4.0</td>
<td>31.4</td>
<td>40</td>
<td>5x11</td>
</tr>
<tr>
<td>0.05 N test</td>
<td>0.05</td>
<td>3.5</td>
<td>31.4</td>
<td>35</td>
<td>5x11</td>
</tr>
</tbody>
</table>

*The radius is given as the centre of the 250 $\mu$m tribostressed annuli.

Table 2.10: Experimental settings of the large area step test used for angular resolved XPS measurements.

<table>
<thead>
<tr>
<th>Load</th>
<th>Radius*</th>
<th>Velocity</th>
<th>Time</th>
<th>Turns</th>
<th>Steps</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N)</td>
<td>(mm)</td>
<td>(mm/min)</td>
<td>(min)</td>
<td>(#)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>31.4</td>
<td>200</td>
<td>41x5</td>
<td>41x25 $\mu$m</td>
</tr>
</tbody>
</table>

*The radius is given as the centre of the 1 mm tribostressed annuli.
In an oscillating load test the applied load is varied depending on the angular position of the disc. An experiment may consist of multiple wear tracks. While on each wear track the load is cycled in a particular range, a second parameter (duration, velocity) may be altered between the tracks. For the applied conditions (load, duration velocity) tribological information can be extracted from the experiment.

The experiments were performed using polished pure iron discs. They were carried out in PAO 166 both in the presence and the absence of a purified, commercial ZnDTP (Hitec). As countersurface a ball bearing ball (100Cr6) was used.

An example of an oscillating load test is shown in Figure 2.14. Five concentric wear tracks were produced. In each track the load was cycled four times from 1 N to 10 N during one full turn of the disc. In the radial direction the number of turns per wear track is changed.

![Experimental setup of an oscillating load test. The load is cycled four times from 1 N to 10 N during one full turn of the disc. In the radial direction the number of turns per wear track is changed.](image-url)
2.3.4 Elevated Temperature Experiments

**Tribotests at Elevated Temperature**

For the experiments at elevated temperature the sample was mounted in the sample holder which was then placed into the heating stage (see section 2.3.1 “Heating Stage”). The cup was filled with the lubricant and the stage was heated to 150°C within 30’ while slowly rotating the sample holder to produce an even temperature distribution in the heating stage. The tribological experiments were then run at 150°C (±2°C) according to the combinatorial tribotest described in section 2.3.3.

**Pure Thermal Test**

In pure thermal tests the sample was mounted in the sample holder which was then placed in the heating stage. The stage was heated to 150°C within 30’ and then kept at 150°C for 5.5 h. The sample holder was slowly rotated during the whole experiment to produce an even temperature distribution in the heating stage.

After the tests, the sample was removed from the heating stage and left 5’ in air to cool down. The excess of the lubricating oil was removed from the surface using cyclohexane as solvent prior to the introduction of the sample into the analysis chamber of the XPS.

### Table 2.11: Experimental settings for the oscillating load test.

<table>
<thead>
<tr>
<th>Duration (rev)</th>
<th>Radius (mm)</th>
<th>Load (N)</th>
<th>Velocity (mm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>3.5</td>
<td>1-10</td>
<td>31.4</td>
</tr>
<tr>
<td>30</td>
<td>4</td>
<td>1-10</td>
<td>31.4</td>
</tr>
<tr>
<td>10</td>
<td>4.5</td>
<td>1-10</td>
<td>31.4</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>1-10</td>
<td>31.4</td>
</tr>
<tr>
<td>1</td>
<td>5.5</td>
<td>1-10</td>
<td>31.4</td>
</tr>
</tbody>
</table>

2.3.5 Data Processing Friction Forces

During the execution of a test script, normal load, friction force and the three encoder positions (z-position of the carriage, radial position and rotational position) can be recorded together with the
time. This data can be evaluated using the CETR test viewer program or converted into an ASCII file for further processing. For a combinatorial tribotest it is necessary to evaluate the data depending on the applied conditions, which means in this case the lateral position on the disc. There is also the need for a time-dependant evaluation of the frictional information. Therefore the data was further analyzed with IGOR Pro (V3.16, WaveMetrics Inc., Lake Oswego, OR, USA) software. The basic concepts in data processing will be explained in the following.

Data acquired during a tribological experiment may consist of several 100’000 data points. Combinatorial experiments provide tribological information that depends on the applied conditions but careful data processing needs to be performed to extract this information from the raw data. Three different data processing or data reduction methods will be discussed. The first is a reduction according to time scale, the second is based on the tribological significance of the data and the third on the rotational position and time.

**Time Averaging**

The reduction according to time scale is a simple averaging of the data acquired during a given period. Also the standard deviation of the values acquired during this period can be evaluated. Often this period was chosen to be one full rotation of the disc. This concept is useful when constant conditions are used during one revolution of the disc (not angular dependent experiments) and when time dependent information is required. The averaged data originates from a tribological contact area that experienced the same tribological history.

**Tribological Significance**

The averaging of the data according to the tribological significance was mainly used when stick-slip phenomena were detected. A schematic stick-slip curve is shown in Figure 2.15. It can be assumed that during the “sticking” phase no information regarding the tribological contact is acquired. The use of the term coefficient of friction is is in this phase incorrect because there is actually no “friction force” and thus no “coefficient of friction” which could be calculated [8]. The most valuable information is probably the force at the onset of the “slipping” phase, representing a “static friction force”. Therefore, a possible data reduction method is to use just the peak values for further processing.
The third data-reduction method is also a new way to represent frictional data. For this representation one rotation of the disc is divided into a number of sectors. Each sector corresponds to a particular range of the rotational encoder position. All frictional data from a given sector and a particular rotation is averaged and stored in a two-dimensional matrix. Each value in this matrix represents the frictional information at a given rotational position and following a given number of turns. This matrix can be represented as an image with color-coded frictional information (example see Figure 2.6).

2.3.6 Topographic Measurements and Data Processing

In an oscillating wear test each spatial point in a wear track has experienced a particular load and a specific number of turns. The sample spans a parameter library with the parameters load and duration. This parameter library can be evaluated in respect to the wear at the specific load and duration by analyzing the topography of the tribostressed discs.

The surface topography was measured by laser profilometry (refer to section 2.5.3). The whole worn area was analyzed in one measurement and the z-coordinates saved in a matrix containing 2400x2400 data points for an area of 12x12 mm. This data was imported to IGOR Pro (WaveMetrics Inc., Lake Oswego, OR, USA)
Experimental

for further processing. The left-hand side of Figure 2.16 shows an example of the topography of a surface tribostressed in a cycle load test. The wear tracks can clearly be seen increasing in width and depth while going to smaller radius (longer duration). Along the wear scar the modulation produced by the four load cycle can be seen. In the middle of each quarter turn the wear scars become deeper and wider and reduce the width and depth again at the end of the quarter turn. In the software a grid was produced and laid on the map (Figure 2.16 right-hand side). Each circle represents a particular duration, while along a particular radius the applied load was constant. Thus, each intersection in the grid represents a particular load-duration combination.

![Figure 2.16: Left: Topographic map of an oscillating load test, acquired with laser Profilometry. The wear scars can be seen. Right: A grid was laid on the map, each circle represents a particular duration while along a particular radius the load is constant. Wear was evaluated at each intersection in the grid (for details see text).](image)

At each intersection of the grid the cross-section of the wear track was measured. Figure 2.17 shows a profile extracted from the map along one radius. The different size of the wear scar can be seen. For each wear scar a background (straight line) was applied an the area above and below the background determined (see Figure 2.17). The area below ($A_1$) the background represents the
worn area, while the area above \( (A_2) \) the background is a measure for the material deposited beside the wear scar (see Figure 2.18).

**Figure 2.17:** Left: profile extracted along a radius in Figure 2.17 with the various wear scars.
Right: Wear scar of the profile. A straight line is used as background.

In oscillating load tests, the load is cycled four times from the minimum value to the maximum value during one rotation. During each rotation, a particular load is applied eight times (four times at increasing load and four times at decreasing load). For each parameter set (load, duration) these eight values are averaged to get the wear. Exceptions are the values at the highest and the lowest load, for these only four values are averaged.

**Figure 2.18:** In each cross-section of the grid (Figure 2.16), the worn area \( (A_1) \) and the deposited material \( (A_2) \) were determined.
2.4 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is the most important method used in this thesis for the study of the surface films formed during the tribological contact. Being a surface sensitive method that allows quantitative elemental and chemical state information to be acquired makes it a unique tool for the chemical characterization of surfaces. In the following, a brief introduction into the theory is given. More detail can be found elsewhere [9,10].

2.4.1 Theory

XPS uses mono-energetic 200eV to 2000eV X-rays for sample excitation to induce the photoelectric effect. When the energy of the irradiating X-rays exceeds the binding energy ($E_b$) of an electron bound to the atom, it can leave the atom and travel through the material to the surface. The kinetic energy ($E_{kin}$) of the emitted electrons is analyzed and by knowing the energy of the irradiating X-rays ($h\nu$) and the spectrometer work function ($\Phi$), the binding energy of the electron can be calculated from Equation 2.1.

$$E_b = h\nu - E_{kin} - \Phi \quad \text{Equation 2.1}$$

The binding energy can be regarded as the energy difference between the final and initial state of the photoelectron process. In each atom, there is a variety of possible energy levels, from which the photoelectron can be emitted. Thus, a variety of kinetic energies of the photoelectrons will be collected and discriminated in the analyzer. This results in a unique set of photoelectron peaks with particular binding energies for each element. As a consequence, it is possible to identify the elements present on the surface. Variations in the elemental binding energies of a particular electron transition (the chemical shifts) arise from differences in the chemical potential and polarizability of compounds. These chemical shifts can be used to identify the chemical state of the elements in the analyzed material.

Quantitative Analysis

Each ionization process has a relative probability, allowing the quantification of the elements present at the surface depending on the peak intensity of the collected electrons at the respective ener-
X-Ray Photoelectron Spectroscopy

gy. The relative elemental concentration $X$ of element A in a homogeneous semi-infinite solid can be calculated using the intensity $I_{Aq,m}$ (peak area) of a particular energy level q (excited with the X-ray source m) and the corresponding sensitivity factor $S_{Aq,m}$ (Equation 2.2).

$$X_A = \frac{I_{Aq,m}/S_{Aq,m}}{\sum_{i=A,B,C} I_{iq,m}/S_{iq,m}}$$  \hspace{1cm} \text{Equation 2.2}

**Sensitivity Factor**

Several approaches are known for determining the sensitivity factor $S_{Aq,m}$. In this work a first principle model is used for quantification [9]. $S_{Aq,m}$ is calculated according to

$$S_{Aq,m} = T_{Aq} \cdot \lambda_{Aq} \cdot \cos(\theta) \cdot \sigma_{Aq,m} \cdot L_{Aq,m}(\gamma)$$  \hspace{1cm} \text{Equation 2.3}

where $\sigma_{Aq,m}$ is the photoionization cross section according to Scofield [11], $\lambda_{Aq}$ the inelastic mean-free path or attenuation length of the electrons, $\theta$ the take-off angle of the electrons and $T_{Aq}$ the transmission function of the electron analyzer, which will be discussed below. $L_A(\gamma)$ is the angular asymmetry function, which describes the intensity distribution of the photoelectrons ejected by X-rays and $\gamma$ is the angle between X-ray source and detector. If $\gamma=54^\circ$ (“magic angle configuration”), the angular asymmetry function can be set to 1.

**Inelastic Mean Free Path**

Even though the X-rays penetrate several micrometers into the material, the emitted electrons travel only a short distance without energy loss. According to Seah and Dench [12] the inelastic mean free path $\lambda_{Aq}$ in a solid can be approximated depending on the kinetic energy ($E_{kin}$) of the electrons:

$$\lambda_{Aq} = \frac{A}{E_{kin}} + B \times \sqrt{E_{kin}}$$  \hspace{1cm} \text{Equation 2.4}

$A$ and $B$ are parameters which were determined for different classes of materials (organic solids, inorganic solids or elements) [12].
Attenuation Length

According to ASTM E 673, the attenuation length is the average distance that an electron travels between successive inelastic collisions as derived from a particular model, in which elastic scattering is assumed to be insignificant. In contrast to the inelastic mean free path, which is a measured quantity, the attenuation length is a theoretical value. In this work, the inelastic mean free path according to [12] is used.

Auger Electrons

In addition to photoelectrons emitted in the photoelectric process, Auger electrons may be emitted simultaneously. In the Auger process an electron of an outer shell relaxes into an inner vacancy (from a previous photoelectron emission). The energy released may be transferred to a second electron, which will be emitted from the surface with the energy $E_{\text{kin}}$ (Figure 2.19). The Auger electron possesses kinetic energy equal to the difference between the energy of the initial ion and the doubly charged final ion. Therefore the kinetic energy of the Auger electron is, in contrast to the photoelectric process, not dependent on the energy of the X-ray source.

![Diagram of Photoelectric and Auger Processes](image)

**Figure 2.19:** Left: Photoelectric process. Right: Auger electron process.

Auger Parameter

The Auger parameter concept bases on the idea that there is a fixed energy difference between two line energies (Auger and photo-
electron) [13]. This makes charge corrections and work function corrections unnecessary because they simply cancel out during the estimation of the Auger parameter. The Auger parameter $\alpha'$ is defined as [14]

$$\alpha' = E_K(C'C''C''') - E_b(C).$$  \hspace{1cm} \text{Equation 2.5}$$

$E_K(C'C''C''')$ is the kinetic energy of the Auger transition involving electrons from $C'$, $C''$, $C'''$ core levels, and $E_b(C)$ is the binding energy of the photoelectron from core level $C$.

### 2.4.2 Experimental

A PHI 5700 (Physical Electronics Inc., Eden Prairie, MN, USA) system was used for the XPS measurements. The system is equipped with a twin (Al/Mg K$\alpha$) X-ray source and a monochromated Al K$\alpha$ source. Typically the unmonochromated Al K$\alpha$ source was used.

The emitted electrons are guided through the OMNIFOCUS IV lens system into a concentric hemispherical electron analyzer. An aperture between the lens system and the electron analyzer determines the analyzed spot size together with the area mode setting of the lens system. The lens system was typically run in the minimum area mode with aperture #3 or #2, defining an analyzed spot size diameter of 0.4 and 0.12 mm respectively.

**Sputter Gun**

The system is equipped with an Argon ion gun (Physical Electronics 04-303A) for sample cleaning and depth profiling. The un rastered spot size is 0.25 mm at 3 KeV and at a current of 3.9 $\mu$A. The typical raster size is 3x3 mm.

**Binding Energy Scale Calibration**

The binding-energy scale of the instrument was calibrated according to [15]. Au, Ag and Cu foils were sputtered immediately prior to the analysis for 3’, 3’ and 5’ respectively. The spectral lines of Au(4f$_{7/2}$) and Cu(2p$_{3/2}$) at 83.95 eV and 932.63 eV, respectively were used for the calibration. Ag(3d$_{5/2}$) and Cu(LVV) peak energies at 368.22 eV and 567.93 eV respectively, were used to verify the linearity of the binding-energy scale. The accuracy was $\pm 0.05$ eV.
Experimental

Transmission Function

The transmission function corrects the intensity calibration of the analyzer depending on the experimental settings [16,17]. The function

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

Equation 2.6

was used with \( RR \) being the retard ratio (\( RR = E_{\text{kin}}/E_p \)). \( a \) and \( b \) are parameters that have to be determined by fitting a series of peak intensities measured at different pass energies versus the retard ratio in a log/log plot. The parameters used in this thesis are collected in Table 2.12 for two typical settings of acquisition parameters.

Angle Resolved Measurements

The take-off angle of the electrons determines the depth from which an electron can originate from (see Equation 2.3 and Figure 2.20). The escape depth can be calculated to be approximately \( d = 3 \cdot \lambda \cdot \sin(\theta) \) [9].

![Figure 2.20: The escape depth of the electrons is depending on the emission angle \( \theta \).](image)

By changing the take-off angle, the information depth changes. This relationship can be used to evaluate the variation of the atomic concentration with depth.

Cooling Stage

The sample stage can be cooled with liquid nitrogen via a thermally conductive copper wire. If a substance was proved to outgassing (e.g. reference compounds), it was cooled prior to the introduction of the sample into the analysis chamber and during the analysis in order to maintain a low pressure in the analysis chamber.
2.4.3 Spectroscopy

Two sets of parameters (aperture, pass energy, energy step size) were used for XPS analysis (Table 2.12). The first set with aperture #2 was used when small area analysis was required, the second set with aperture #3 was used if faster acquisition was needed (e.g. due to sample degradation) and when the sample was laterally homogeneous over at least 0.4 mm. The small aperture size of the first set reduces the electron intensity, which was partially compensated using a larger pass energy. To still achieve a reasonable signal-to-noise ratio the acquisition time per energy step had to be increased. To keep the total acquisition time within a reasonable limit, the step size was chosen to be 0.1 eV. This resulted in a slight increase in the full-width-at-half-maximum (FWHM) of the Ag 3d$_{5/2}$ (compared to the second set).

Table 2.12: Typical settings of acquisition parameters. The first set allows the analysis of a smaller spot but the larger pass energy results in an increased FWHM of the Ag 3d$_{5/2}$ peak. The second set gives better energy resolution and higher signal intensity but has the disadvantage of averaging the signal over a larger area. The coefficients a and b were used for the transmission function correction.

<table>
<thead>
<tr>
<th>Aperture</th>
<th>Pass Energy</th>
<th>Step Size</th>
<th>FWHM Ag 3d$_{5/2}$</th>
<th>Transmission Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>Diameter</td>
<td>eV</td>
<td>eV</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>120 µm</td>
<td>46.95 eV</td>
<td>0.1 eV</td>
<td>1.13 eV</td>
</tr>
<tr>
<td>3</td>
<td>400 µm</td>
<td>23.5 eV</td>
<td>0.05 eV</td>
<td>1.08 eV</td>
</tr>
</tbody>
</table>

Data was processed with CASA XPS software (Casasoftware Ltd., UK). An iterated Shirley-Sherwood background subtraction was applied prior to curve fitting with a product of Gaussian-Lorentzian curves. The Gaussian-Lorentzian ratios for each peak were determined from measurements on reference compounds. FWHM, peak position and area ratios could be constrained to reference values or determined according to theoretical considerations, depending on the specific problem. For Fe2p signals the built-in satellite subtraction routine was used to remove the contribution of the Fe2p$_{1/2}$ signal in the Fe2p$_{3/2}$ signal arising due to the non-monochromatic X-ray source.
2.4.4 XPS Imaging

The OMNIFOCUS IV lens system provides imaging capabilities to the PHI 5700 system. To produce an XPS map, the analyzed spot is rastered over the sample. In each spot a full XPS spectrum is acquired.

There are two modes of acquisition for XPS maps: the unscanned mode and the scanned mode. In the unscanned mode the electrons coming from the analyzed spot are projected onto the electron multiplier array of the analyzer. The linear array, consisting of 16 elements, discriminates the electrons into 16 energy channels. Selecting a pass energy determines the full range of the energy discrimination and the distribution into the 16 channels. The parallel analysis of the electrons from different energies allows a fast acquisition of the XPS map, with the disadvantage of a limited energy range and energy resolution.
In the scanned mode the whole energy range of the determined region is scanned in each pixel of the map. This provides more flexibility in the selection of energy range and resolution but increases the acquisition time considerably.

Furthermore, it is important to consider the aperture size. Figure 2.21 shows four XPS maps (2x2.8mm) of a Cu grid with 0.5 mm spacing. The white spot in the lower left corner shows the size of the analyzed area at this aperture is shown. The signal intensity changes by approximately a factor of 10 upon moving from one aperture to the next.

Figure 2.21: Cu 2p maps of a Cu grid with a 0.5 mm spacing, acquired with different apertures. In the lower left corner the size of the analyzed area at this aperture is shown. The signal intensity changes by approximately a factor of 10 upon moving from one aperture to the next.

In the scanned mode the whole energy range of the determined region is scanned in each pixel of the map. This provides more flexibility in the selection of energy range and resolution but increases the acquisition time considerably.

Furthermore, it is important to consider the aperture size. Figure 2.21 shows four XPS maps (2x2.8mm) of a Cu grid with 0.5 mm spacing. The white spot in the lower left corner shows the size of the analyzed area at this aperture. It is clear that with aperture #4 (0.8 mm diameter) the grid can not be resolved, because the aperture size is larger than the analyzed feature. With aperture #3 (0.4 mm), which is similar to the size of the structure of the grid (0.5 mm) it is still hard to detail the map. Only using aperture #2 (0.12 mm) and #1 (0.03 mm), can the spacing of the Cu grid be clearly resolved. Further, one has to consider the signal intensities. Reducing the aperture from #4 to #1 reduces the signal intensity.
Experimental intensity by approximately a factor of 10 for each aperture. Therefore a compromise has to be found between lateral resolution and signal intensity.

**Experimental Conditions**
Maps with 64 by 64 pixels were acquired using aperture #2 (0.12 mm diameter) and a pass energy of 46.95 eV. With these settings it is possible to measure elements with a strong signal intensity within a reasonable time frame and with an acceptable signal-to-noise ratio. The typical analysis time of an O1s map was 4-6 hours, while for elements with lower signal intensity (e.g. P, S, Zn on a tribostressed sample) it would increase by a factor of 10. Therefore only O1s maps were acquired.

**LLS Routine**
XPS maps were processed using Multipak 6 (Physical Electronics Inc., Eden Prairie, USA) software. Spectra can be extracted from the map by selecting an area of interest. ‘Chemical state maps’ are created using the linear-least-squares routine (LLS). A particular spectrum, extracted from the total intensity map, is fitted to the spectrum at each pixel of the map. A higher correlation produces a more intense pixel in the LLS map and if the extracted spectrum is representative for a particular chemical state, the resulting map can be interpreted as a chemical state map. An example of the LLS procedure is shown in Figure 2.22.
2.5 Other Experimental Methods

2.5.1 Auger Electron Spectroscopy

Auger electron spectroscopy (AES) is based on the Auger process (Figure 2.19). In contrast to the X-ray excited Auger signals found in the XP spectra, the core hole in AES is created by irradiating the surface with an electron beam. The advantage of the electron beam is that it can be rastered over the surface and by recording the intensity of a particular Auger signal depending on the lateral position on the sample, elemental microscopy can be carried out. Since the emitted electrons also originate from a few nanometers depth (as in XPS), Scanning Auger microscopy (SAM) is considered to be a surface sensitive method.
Auger mapping was performed on a VG ESCALAB 200 at the University of Cagliari (Italy) using an electron gun, which allows 2000 Å lateral resolution. The electron beam, of energy of 10keV (inducing a specimen current of 20 nA), was rastered to produce 128x128 pixel maps, which were recorded on an IBM 486 computer. Auger maps were corrected for topographical effects using the (peak-background)/background algorithm.

2.5.2 Optical Microscopy

A Reichert Jung Polyvar microscope with objectives from 5x to 100x and a Leica WILD M10 zoom stereo microscope were used for optical microscopy. Both microscopes are equipped with a digital video capture tool.

2.5.3 Laser Profilometry

Laser profilometry uses the auto-focus principle [18] to measure the height profile of a sample quantitatively. A laser beam is focused on the sample surface by minimizing the spot size of the reflected beam by moving a collimator lens. From the position of the collimator lens, the z-position on the surface is determined. Area measurements can be performed by moving the sample with translation stages.

An UBM laser profilometer (UBM Messtechnik, Germany) with a microfocus™ sensor was used. The vertical resolution is determined by the spot size of the laser beam, which was 1 µm. The vertical resolution was 10 nm with a maximum range of 100 µm. Pores, sharp step features, or small tips may distort the measurement of the z-position and result in artifacts in the profile.
Other Experimental Methods

References


CHAPTER 3

RESULTS

In this chapter the experimental results are described. The first three sections contain both tribological and surface-analytical results. First the results of the standard tests (one wear track at constant conditions) are presented. They are compared in the discussion with the results from the combinatorial tests. Secondly the results from spiral and step tests are shown. These types of experiments are necessary to enlarge the width of the wear tracks in a way that the tribostressed area is wide enough to be analyzed with XPS without contributions from the non-contact area. In section 3.3 the results of the combinatorial experiments at room temperature and at elevated temperatures are presented. In section 3.4 the tribological results of an oscillating load test (synchronized cycling load during one full revolution) are given. In section 3.5 the XPS results obtained from reference compounds are reported.
3.1 Standard Tests (Two Wear Tracks)

A standard test is an experiment that is carried out at a particular load on one single radius for a given amount of time. In a two-wear-track standard test a steel disc was tribostressed in the presence of a 1 wt-% solution of i-ZnDTP in decane. After running in, two wear tracks with load of 1 N and 10 N were produced (Figure 3.1). Details of the experimental settings can be found in section 2.3.3. The disc was analyzed after the test with (i-)XPS, whereas the ball and the disc were imaged with optical microscopy.

![Figure 3.1: Sketch of the experimental setup of the two-wear-track test.](image)

**Optical Microscopy**  
The microscopic image of the two wear scars (Figure 3.2) shows that the surface was severely worn during the tribotest. The surface looks scratched and inhomogeneous. The wear scar width of the 1 N and the 10 N experiment are approximately 75 µm and 200 µm. Not all of the apparent contact area of the ball is causing this severe wear scars since the apparent contact area (Figure 3.2) is larger than the wear scar width in the 1 N region.
Coefficient of Friction

In Figure 3.3, the COF is displayed versus time for the running in, the 1 N and the 10 N wear test. It shows irregular behavior. During the running in, the COF increases from 0.2 with a high scatter (large stick-slip could be observed) to 0.4 and then drops again to lower values. The experiment at 1 N shows a steady increase from 0.2 to 0.28 with a small scatter of the data (smooth sliding, no stick-slip). The COF during the 10 N experiment shows first a slight increase, with a sharp drop to 0.17. The COF increases again with an irregular behavior.
Results

Figure 3.3: COF versus time during running in, the 1 N and the 10 N wear test. The error bars show the standard deviation of the COF during one full turn of the disc.

Imaging XPS In the total intensity O1s XPS map (left image in Figure 3.4) the wear scars show a more intense signal than the non-contact area. Spectra extracted from the wear tracks and from the non-contact area show a different shape: the spectrum from the non-contact area has a peak at 530 eV with a shoulder at 531.7 eV. In the spectrum extracted from the tribostressed area the shoulder is more pronounced, thus revealing a double peak. The LLS routine of the Multipak software shows the distribution of the two type of spectra. Non-contact areas and wear tracks can be clearly distinguished from each other. Small-area XPS analyses were performed in the areas marked in the chemical state map in Figure 3.4. Other elements than oxygen were either not acquired because the signal intensity was very weak and due to this the acquisition time would have been very long (P, S, Zn) or the peak shape did not show dis-
distinct differences between the contact and the non-contact area which could be only poorly resolved with the limited energy resolution of the imaging mode. Therefore only O1s maps will be shown.

**Figure 3.4:** On the left-hand side the total-intensity image of the O1s region of the tribostressed area is displayed. Two different type of spectra can be extracted from the map, one with a peak at 530 eV and a shoulder at 531.7 eV and a second with two peaks at 530.2 eV and 531.7 eV. The chemical-state map shows the distribution of the two spectra. The spectrum with the double peak shows a higher intensity in the wear scars, while the other spectrum is present in the non-contact area.

**XPS Spectroscopy**  
The elements C, O, Fe, P, S and Zn were found in all three areas (10 N, 1 N, non-contact). The detailed spectra acquired in these areas were fitted with Gaussian-Lorentzian curves. The peak maxima of the spectra in the three areas were almost identical but the relative intensities of the peak areas were different. The peak position of the main peaks are shown in Table 3.1. The curve-fitting parameters are given in Appendix A. As it can be seen in Figure 3.2, the wear-scar width of the area tribostressed at 1 N is approximately 75 µm, while the spot size of the XPS analysis is 120 µm. For this reason the analysis of the 1 N area will have a contribution of the non-contact area and the data has to be interpreted carefully.
In the C1s region, one main peak with a tail to higher binding energy was found (Figure 3.5). It was fitted with three peaks with a FWHM of 1.9 eV each. The main peak is shifted to lower binding energy compared with the binding energy of aliphatic carbon. The O1s peak shows three contributions (Figure 3.5). A first peak at 530.2 eV is typical for an oxide peak. The second peak at 531.7 eV can either be assigned to a phosphate [1] or to an (iron) oxy-hydroxide peak [2]. Both peaks were found within ±0.1 eV for all areas. A third minor contribution is present at 533.3, attributable to adsorbed water and/or to bridging oxygen if polyphosphates would be present. It was within ±0.2 eV for the three areas.

Table 3.1: Peak positions of the main peaks from the detailed analysis of the 10 N, 1 N and the non-contact area. All values are given in the binding energy scale (eV). The accuracy of the acquisition was ±0.1 eV.

<table>
<thead>
<tr>
<th></th>
<th>C1s</th>
<th>O1s</th>
<th>O1s</th>
<th>S2p</th>
<th>S2p</th>
<th>P2p</th>
<th>Zn2p3/2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>main</td>
<td>oxide</td>
<td>II</td>
<td>sulfide</td>
<td>C-S(H)</td>
<td>P*O4</td>
<td></td>
</tr>
<tr>
<td>10 N</td>
<td>284.7_5</td>
<td>530.1_5</td>
<td>531.7</td>
<td>161.7_5</td>
<td>163.0</td>
<td>133.4_5</td>
<td>1022.3_5</td>
</tr>
<tr>
<td>1 N</td>
<td>284.7_5</td>
<td>530.1_5</td>
<td>531.6_5</td>
<td>161.8_5</td>
<td>163.0</td>
<td>133.4</td>
<td>1022.4_5</td>
</tr>
<tr>
<td>non contact</td>
<td>284.8_5</td>
<td>530.1_5</td>
<td>531.7_5</td>
<td>161.8</td>
<td>163.0</td>
<td>133.3</td>
<td>1022.3</td>
</tr>
</tbody>
</table>

The S2p peak shows a FWHM of 2.5 eV, which is 0.2 eV wider than the corresponding peaks in reference spectra. This leads to the assumption that two doublets have to be used for fitting the S2p peak. Each doublet consists of two peaks with a fixed FWHM of 1.65 eV and separated from each other by 1.25 eV. The peak area ratio between the 2p3/2 and the 2p1/2 peak was fixed to 2:1, in accordance with the spin-orbit coupling. The first doublet was left free to vary, while the second was fixed at 163.0 eV. The first doublet was always found to have a higher intensity than the second one, the peak position of the 2p3/2 peak was at 161.8 eV, within ±0.1 eV for all three areas analyzed.

For the P2p peak one doublet was used for curve fitting. The peak area ratio was fixed at 2:1, the peak separation at 0.95 eV. The peak position of the P2p3/2 peak was found to be at 133.4 eV, with-
Standard Tests (Two Wear Tracks)

in ±0.1 eV for all areas. The peak position of the Zn2p3/2 peak was found to be 1022.4, within ±0.1 eV for all three areas.

The Fe2p3/2 peak acquired in the detailed analysis shows a complex shape (Figure 3.5). Four contributions could be determined: metallic iron from the substrate at 706.9 eV, Fe2+ at 709.3 eV (including a satellite 5.5 eV to the high-binding-energy side with an intensity of 8% of the main peak) and Fe3+ at 711.2 eV. The fourth peak at 712.6 eV was assigned to iron phosphate. The metallic iron and the Fe3+ varied ±0.1 eV between the different areas, the Fe2+ varied ±0.2 eV, while the iron phosphate peak position was fixed.

**Figure 3.5:** C1s, O1s and Fe2p3/2 Spectra acquired in the 10 N and the 1 N contact area, as well as in the non-contact area.

The Fe2p3/2 peak acquired in the detailed analysis shows a complex shape (Figure 3.5). Four contributions could be determined: metallic iron from the substrate at 706.9 eV, Fe2+ at 709.3 eV (including a satellite 5.5 eV to the high-binding-energy side with an intensity of 8% of the main peak) and Fe3+ at 711.2 eV. The fourth peak at 712.6 eV was assigned to iron phosphate. The metallic iron and the Fe3+ varied ±0.1 eV between the different areas, the Fe2+ varied ±0.2 eV, while the iron phosphate peak position was fixed.
for the fit. The Fe$^{2+}$ signal intensity was higher in the 10 N area than in the 1 N and the non-contact area, while the Fe$^{3+}$ signal showed the opposite trend. In the non-contact area the relative intensity of the Fe$^{2+}$ signal is higher than the Fe$^{3+}$ signal which is opposite in the Fe signal acquired on the sample prior to the tribotest (section 3.5.1).

For the quantitative analysis of the spectra, it was assumed that a layered system is present. The metallic iron substrate is covered with a mixed film consisting of iron oxide and the tribofilm, which contains the elements P, S, Zn as well as the contribution of oxygen at 531.7 eV (phosphate oxygen). On top of the intermediate layer a hydrocarbon film is present. Table 3.2 shows that in the tribofilm the P/S and P/Zn ratio is increased in comparison to the pure additive. The O(II)-to-P ratio is close to 4, as it would be expected for a phosphate. The high value in the non-contact area indicates that in this case not all of the O1s signal at 531.7 eV is arising from phosphate but that the signal might be from the iron oxy-hydroxide, which is usually found on an oxidized iron surface.

### Table 3.2: Elemental ratios of P, S, Zn and O measured on the tribofilm produced at 1 N and 10 N and in the non-contact area.

<table>
<thead>
<tr>
<th></th>
<th>P/S(tot)</th>
<th>P/Zn</th>
<th>O(II)/P</th>
</tr>
</thead>
<tbody>
<tr>
<td>10N</td>
<td>1.1</td>
<td>2.3</td>
<td>4.6</td>
</tr>
<tr>
<td>1N</td>
<td>1.6</td>
<td>2.2</td>
<td>4.4</td>
</tr>
<tr>
<td>non-contact</td>
<td>0.8</td>
<td>2.4</td>
<td>8.9</td>
</tr>
<tr>
<td>i-ZnDTP</td>
<td>0.5</td>
<td>2.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

#### 3.2 Spiral Test and Step Test

Spiral tests and step tests enlarge the tribostressed area. This may be needed if XPS is used to characterize a tribostressed sample. The wear scar width of a 1 N wear track was found to be 75 µm (Figure 3.2), which is smaller than the size of the analyzed spot in a typical XPS experiment (120 µm). If such a sample is analyzed by XPS the information of the tribostressed area is averaged with the non-contact area, which makes the interpretation of the results
difficult. If a spiral test or a step test are used to produce the tribostressed area this problem can be avoided because a wide enough wear scar is produced.

A sample which combines the step test and the spiral test has been produced in order to characterize the two types of experiments. After running in of the ball, the step test and the spiral tests were run in two concentric annuli (Figure 3.6). The experiment was done in a 1 wt-% i-ZnDTP solution in decane applying 1 N load. Experimental details can be found in section 2.3.3.

**Optical Microscopy**

Optical investigation of the tribostressed surfaces showed that the step test and the spiral test create different surface scratching. The step test produces grey areas textured in the sliding direction but also in between these areas a scratching of the surface can be observed. The spiral test produces deep wear scars. They are separated by approximately 15 µm, exactly the distance the ball moves in radial direction during one turn of the disc.

**Figure 3.6:** Sketch of the combined step test and spiral test. The tests were done at 1 N load in a 1 wt-% solution of i-ZnDTP in decane.
Results

Coefficient of Friction

The COF during the running in increases from 0.25 to 0.65 and drops afterwards to 0.25 (Figure 3.8). This shows that the running in of the ball is completed. During the step test approximately 9 turns are completed at the same radius. In the beginning of each sequence, an increase of the COF can be observed, then the COF decreases until it levels off at approximately 0.2 after approximately four turns. It is assumed that after this time a tribofilm is formed, protecting the surface. In the beginning of the spiral test a running in effect can also be seen. The COF levels off at approximately 0.22, equal (within experimental error) to the value in the step test.

Figure 3.7: Microscopic image of areas tribostressed at 1 N load in a 1 wt-% i-ZnDTP solution. In the step test (left), the 50 µm spacing of the steps can be seen. Darker areas textured in the sliding direction are visible but also in between these areas surface scratches from the sliding can be observed. The spiral test (right) shows for each turn of the disc a deep scar. In between this scar no scratching of the surface is visible.
In the O1s total intensity map (Figure 3.9), areas with different signal intensities are visible. O1s spectra extracted from the various areas are different. The spectrum extracted from the step test area shows a double peak with one contribution at 530 eV and a second one at 532 eV. In the spectrum extracted from the spiral test area, the contribution of the peak at 532 eV is smaller compared to the spectrum acquired in the step-test area. The area of this peak is further reduced in the spectrum acquired in the non-contact area.

**Figure 3.8:** COF versus time during the running in, the step test and the spiral test. The tests were done in a 1 wt-% i-ZnDTP solution at 1 N load. The error bars show the standard deviation of the COF during one full turn of the disc.

**Imaging XPS** In the O1s total intensity map (Figure 3.9), areas with different signal intensities are visible. O1s spectra extracted from the various areas are different. The spectrum extracted from the step test area shows a double peak with one contribution at 530 eV and a second one at 532 eV. In the spectrum extracted from the spiral test area, the contribution of the peak at 532 eV is smaller compared to the spectrum acquired in the step-test area. The area of this peak is further reduced in the spectrum acquired in the non-contact area.
If the spectrum of the step-test area is used to produce a chemical-state map, the highest intensity can be found in the step-test area. The intensity in the spiral test area is slightly reduced, while in the non-contact area it is very small. In contrast, when the spectrum from the non-contact area is used to create the chemical-state map, the opposite picture can be seen. This type of spectrum is most dominant in the non-contact area, while it is slightly reduced in the spiral test and almost absent in the step test.

**XPS Spectroscopy**

Detailed spectra were acquired in all three areas. Peak positions are summarized in Figure 3.3, the curve-fitting parameters can be found in Appendix A. The peak positions were found to show only
minor differences between the three regions but the relative intensities of the contribution were found to vary.

The C1s region was fitted with two peaks. The main peak was found at 285.0 eV in the tribostressed areas. In the non-contact area a slightly higher value was found. For the O1s region three peaks were used to fit the spectra (Figure 3.10). Two peaks were found to have the same position for all three regions, namely 530.3 eV and 531.8 eV, within ±0.1 eV for all areas. A third, smaller peak was found to vary between 533.0 and 533.2 eV.

The S2p region was fitted with two doublets. The area ratio was fixed according to the spin-orbit coupling, the separation between the 2p$_{3/2}$ and the 2p$_{1/2}$ was set to 1.25 eV and the FWHM was fixed at 1.65 eV. The first S2p$_{3/2}$ peaks was found at 162.0, while the second was always fixed at 163.0 eV. The P2p was fitted with one doublet (fixed area ratio (2:1), delta=0.95, FWHM=1.65). The peak position was found to vary slightly between the different areas, it was found to be 133.7 eV for the step test, 133.65 eV for the spiral test and 133.5 eV for the non-contact area.

The Fe2p$_{3/2}$ peak was modeled with four contributions (Figure 3.10). The metallic iron signal was found at 707.0 eV, varying ±0.1 eV between the areas. The Fe$^{2+}$ peak was found at 709.4 eV (including a satellite 5.5 eV to the high binding-energy side with an intensity of 8% of the main peak) and the Fe$^{3+}$ peak at 711.2 eV (both varying ±0.2 eV between the areas). The Fe$^{2+}$ signal intensity is much higher in the step test than in the spiral test. A fourth contribution was modelled at 712.6 eV with a fixed binding energy value and assigned to iron phosphate. It showed a higher intensity in the step test than in the spiral test. In the non-contact area the relative intensity of the Fe$^{2+}$ signal is stronger than the Fe$^{3+}$ signal, which is opposite to the spectrum acquired on the steel prior to the tribostress (section 3.5.1).
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Figure 3.10: O1s and Fe2p$_{3/2}$ spectra acquired in the step test, the spiral test and the non-contact area. For details see text.
Quantitative analysis was done for the elements assumed to be present in the tribofilm (O, P, S, Zn). The P/S ratio was highest in the step-test region as well as the P/Zn ratio, indicating that phosphorus is enriched in the contact area compared to the other elements present from the additive (Table 3.4). The ratio of the O(II) peak area at 531.8 eV to the P2p peak area was found to be close to 4 in the step-test region, indicating the formation of a phosphate. The increase of this ratio in the spiral test and non-contact region indicates that in these areas hydroxides are also present.

### Table 3.3: Peak positions of the main peaks from the detailed analysis of the spiral test, the step test and the non-contact area. All values are given in the binding energy scale (eV). The accuracy of the acquisition was ±0.1 eV.

<table>
<thead>
<tr>
<th></th>
<th>C1s</th>
<th>O1s</th>
<th>O1s</th>
<th>S2p</th>
<th>S2p</th>
<th>P2p</th>
<th>Zn2p3/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>main oxide</td>
<td>285.0</td>
<td>530.3</td>
<td>531.8</td>
<td>162.0_5</td>
<td>163.0</td>
<td>133.7</td>
<td>1022.4_5</td>
</tr>
<tr>
<td>step test (1 N)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>spiral test (1 N)</td>
<td>285.0</td>
<td>530.3</td>
<td>531.8</td>
<td>161.9_5</td>
<td>163.0</td>
<td>133.6_5</td>
<td>1022.3_5</td>
</tr>
<tr>
<td>non contact</td>
<td>285.4</td>
<td>530.3</td>
<td>531.8_5</td>
<td>162.0</td>
<td>163.0</td>
<td>133.5</td>
<td>1022.3_5</td>
</tr>
</tbody>
</table>

### Table 3.4: Area ratio between various elements present in the tribofilm.

<table>
<thead>
<tr>
<th></th>
<th>P/S(tot)</th>
<th>P/Zn</th>
<th>O(II)/P</th>
</tr>
</thead>
<tbody>
<tr>
<td>step test</td>
<td>1.7</td>
<td>2.6</td>
<td>4.2</td>
</tr>
<tr>
<td>spiral test</td>
<td>1.0</td>
<td>1.8</td>
<td>5.5</td>
</tr>
<tr>
<td>non-contact</td>
<td>0.8</td>
<td>1.8</td>
<td>10.0</td>
</tr>
<tr>
<td>i-ZnDTP</td>
<td>0.5</td>
<td>2.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

### 3.3 Combinatorial Step Test

In the combinatorial step test a parameter library is constructed which can subsequently be analyzed by (i-)XPS. The load was chosen as parameter to be analyzed, and its range was varied between 0.05 N and 5 N. In each tribostressed annulus a different
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load was applied (Figure 3.11). A step test was used to enlarge the tribostressed area in each annulus. Experimental details can be found in section 2.3.3.

![Experimental setup of the combinatorial step test](image)

**Figure 3.11:** Experimental setup of the combinatorial step test.

Combinatorial step tests were performed at both room temperature (section 3.3.1) and at elevated temperature (section 3.3.2). In the room temperature experiments, the time between the final polishing step and the tribotest (ageing) was found to be critical for the load-carrying ability of the oxide film, therefore this will be investigated as well.

### 3.3.1 Ambient Temperature

Combinatorial step tests were carried out immediately after the polishing and after ageing the sample 3 days in dry air. First the results of the aged samples will be presented.

**Optical Microscopy**

The surface of the tribostressed disc was investigated with optical microscopy (Figure 3.12). In the tribostressed areas with 5 N and 1 N applied load, scars were observed on the surface. The surface looks evenly scratched although some deeper scratches are sometimes visible. The scratching is more or less homogeneous, in some areas the 25 µm spacing caused by the step test can be observed. In the 5 N area the scratches are clearly visible, while they are less severe in the 1 N area and no wear tracks could be detected in the areas tribostressed at lower load.
Combinatorial Step Test

In Figure 3.13 the COF of the running in, the 0.1 N, 0.5 N, 1 N and the 5 N step tests are shown. The COF is averaged over one full turn of the disc and the standard deviation during this turn is shown with error bars. In the top graph the running in is shown. The COF increases in the beginning with a high scatter in the data (large error bars) and decreases to a value of about 0.4 at the end of the running in. In the step-tests it can be seen that after each five turns the COF shows a change. In the 1 N and the 0.5 N test a clear increase in the COF can be seen after five turns, followed by a decrease to an almost constant COF value at the end of a 5-turn cycle. In the 0.1 N test the same behavior is seen but with a much smaller peak. In the 5 N experiment the behavior is different. The steps at the end of a 5-turn cycle seem to go into the negative direction, followed by a slight increase of the COF value towards the end of a cycle. The standard deviation during the 5 N test is higher compared to the other tests, indicating stick-slip behavior during the experiment.

**Figure 3.12:** Optical micrographs of the tribostressed annuli at 1 N and at 5 N load. Scratches in direction of the sliding of the ball are visible in both areas. In the areas tribostressed at lower load (not shown), no wear scars are visible.

**Coefficient of Friction**

In Figure 3.13 the COF of the running in, the 0.1 N, 0.5 N, 1 N and the 5 N step tests are shown. The COF is averaged over one full turn of the disc and the standard deviation during this turn is shown with error bars. In the top graph the running in is shown. The COF increases in the beginning with a high scatter in the data (large error bars) and decreases to a value of about 0.4 at the end of the running in. In the step-tests it can be seen that after each five turns the COF shows a change. In the 1 N and the 0.5 N test a clear increase in the COF can be seen after five turns, followed by a decrease to an almost constant COF value at the end of a 5-turn cycle. In the 0.1 N test the same behavior is seen but with a much smaller peak. In the 5 N experiment the behavior is different. The steps at the end of a 5-turn cycle seem to go into the negative direction, followed by a slight increase of the COF value towards the end of a cycle. The standard deviation during the 5 N test is higher compared to the other tests, indicating stick-slip behavior during the experiment.
Results

Figure 3.13: COF versus the number of revolutions on the disc for the running in (top graph) and the tribotests at different loads (bottom graph). The error bars are the standard deviation during one full turn of the disc.

Imaging XPS In the O1s total intensity map, areas of high signal intensity can be seen (Figure 3.14). The high-intensity areas are found in the tribostressed annuli. A spectrum extracted from the high-intensity area shows a peak maximum at 532 eV and a shoulder at 530 eV, while a spectrum extracted from the low-intensity area show the peak maximum at 530 eV, with a shoulder at 532 eV. These signals can be assigned to a oxygen bound in a phosphate or hydroxide
Combinatorial Step Test

(532 eV) or bound in an oxide (530 eV). The LLS routine was used to create a chemical-state map of the extracted signals (maps on the right-hand side of Figure 3.14). These maps clearly show where the surface has been tribostressed. The phosphate type O1s spectrum is dominant in the areas tribostressed at all loads. Detailed spectra were acquired from the areas indicated in the chemical-state map of the “phosphate” type spectrum (Figure 3.15).

Figure 3.14: Total O1s intensity map (left) of a combinatorial step test. The tribostressed annuli are visible with higher O1s signal intensities. The Spectrum extracted in the brighter area (middle) shows a peak at 532 eV with a shoulder at 530 eV (“phosphate spectra”) whereas the spectrum extracted in the darker area shows the peak maximum at 530 eV with a shoulder at 532 eV (“oxide spectra”). Using the LLS routine to extract the chemical-state map for these two spectra shows the non-contact area (oxide map) and the wear annuli (phosphate map).

XPS Spectroscopy

Detailed spectra of the elements present on the surface have been acquired in the tribostressed areas (Figure 3.15). The C1s, O1s and Fe2p spectra are shown in Figure 3.16. The C1s signal was fitted with two contribution, the main peak was found at 284.85 eV, varying ±0.1 eV between the various spectra. A second peak was used to fit the tail to the low-energy side. The tail was found to be
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rather broad (e.g. Figure 3.16, 0.5 N area) therefore the second peak showed a large variation in peak position (287.6-289.0 eV)

Three signals were used to fit the O1s spectra (Figure 3.16). The first one was always found at 530.2 eV, a second one at 531.7 and a third at 533.2, varying ±0.2 eV between the analyzed areas. An increase of the oxygen signal at 531.7 eV (“phosphate signal”) can be seen with increasing load [1]. The signal at 530.2 eV (“oxide signal”) is also present at all loads. The third component may be assigned to adsorbed water or oxygen bound in a P-O-C configuration (see section 3.5.2 and [3]). This component increases with increasing load.

The Fe2p3/2 peak acquired in the various areas are shown in Figure 3.16. The signal was corrected for the X-ray satellites of the Al Kα source and background subtracted with the Shirley-Sherwood algorithm. Four contributions had to be used to fit the envelope: one for the metallic iron from the substrate at 706.9, a second at 709.4 eV (including a satellite 5.5 eV to the high binding-energy side with an intensity of 8% of the main peak) attributed to Fe2+, a third (Fe3+) at 711.0 eV and a fourth peak fixed at 712.6 eV. The peak positions vary ±0.1 eV between the analyzed areas for the metallic iron and the Fe3+ region and ±0.2 eV for the Fe2+ region. The relative intensity of the metallic contribution at 706.9 eV in-

Figure 3.15: O1s chemical state map of the tribos-tressed region produced using the “phosphate sig-nal” (see Figure 3.14). In the areas marked, high-resolution detail spectra have been acquired.
creases with decreasing load. Observing the relative intensity of the Fe$^{2+}$ and the Fe$^{3+}$ peak it can be seen that the Fe$^{2+}$ increases with increasing load. The fourth peak, which has been modeled at 712.6 eV, was assigned to iron phosphate, according to the reference measurement on pure iron phosphate (section 3.5.5). This peak shows an increase with increasing load.

The relative intensity of the Fe$^{2+}$ compared to the Fe$^{3+}$ signal is higher in the non-contact area spectrum compared to the steel sample prior to the tribotest. In contrast to this the steel surface of a disc after immersing into a 1 wt-% solution of i-ZnDTP in decane without tribotest does not show this change in the relative intensities of the different oxidation states of the iron signal (results not shown).

Table 3.5: Peak positions of the main peaks from the detailed analysis of the tribos-tressed areas and the non-contact area. All values are given in the binding energy scale (eV), except for Zn$_{LMM}$, which is given in the kinetic energy scale (eV).

<table>
<thead>
<tr>
<th></th>
<th>C1s</th>
<th>O1s</th>
<th>O1s</th>
<th>O1s</th>
<th>S2p</th>
<th>S2p</th>
<th>P2p</th>
<th>Zn2p$_{3/2}$</th>
<th>Zn$_{LMM}$</th>
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<tr>
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<td>530.2</td>
<td>531.7</td>
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<td>133.5</td>
<td>1022.3</td>
<td>988.1</td>
</tr>
<tr>
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<td>530.2</td>
<td>531.7</td>
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<td>163.0</td>
<td>133.5</td>
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</tr>
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<td>531.7</td>
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<td>161.8</td>
<td>163.0</td>
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<td>163.0</td>
<td>133.5</td>
<td>1022.4</td>
<td>988.5</td>
</tr>
<tr>
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<td>530.2</td>
<td>531.7</td>
<td>533.0</td>
<td>161.8</td>
<td>163.0</td>
<td>133.4</td>
<td>1022.4</td>
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<tr>
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<td>163.0</td>
<td>133.4</td>
<td>1022.4</td>
<td>989.5</td>
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</table>
Figure 3.16: C1s, O1s and Fe2p3/2 spectra acquired in the tribostressed areas (Figure 3.15). For details see text.
Figure 3.17: P2p, Zn3s, S2p and Zn2p spectra acquired in the tribostressed areas (Figure 3.15). For details see text.
Results

The P2p and S2p peaks were fitted using a doublet (Figure 3.17), taking into account the theoretical ratio of the spin-orbit coupling (2:1). The separations of the two peaks were kept constant at 1.25 eV for sulfur and 0.95 eV for phosphorus. The P2p$_{3/2}$ peak position is found at 133.5, varying ±0.1 eV between the analyzed areas. The total intensity of the phosphorus signal decreases with decreasing load.

The FWHM values of the S2p peak in the contact areas were found to be 2.5 eV. This suggested that more than one chemical state is present, therefore two doublets were used for the fit. The signal at lower binding energies was found at 161.85 (varying ±0.1 eV between the areas) and the second has a peak maximum at 163.0 eV, which was fixed for the fit. Due to the low sulfur content in the non-contact area, the S2p spectra has a low S/N ratio, which makes it difficult to produce a proper peak fit. The Zn2p signal was always found at 1022.4, varying ±0.1 eV between the analyzed areas. The total intensity of the sulfur signal decreases with decreasing load (Figure 3.17).

In Figure 3.18 the ratio of the total phosphorus intensity to the total sulfur intensity is shown for two independent samples. At low loads the ratio is close to 0.5, which is the P-to-S ratio in the pure additive. With increasing load the ratio increases. The ratio between the O1s contribution at 531.7 eV (“phosphate” peak) and the phosphorus intensity (Figure 3.19) is decreasing with increasing load. At high load the ratio is close to 4:1, the value which would be expected for a phosphate.
Figure 3.18: Total phosphorus to the total sulfur intensity (corrected for the respective sensitivity factors) in the areas tribostressed at various loads. The values are for two independent samples.

Figure 3.19: The intensity of the O1s peak at 531.7 eV versus the total phosphorus intensity (corrected for the respective sensitivity factors) for the areas tribostressed at various loads. The values are for two independent samples.

Figure 3.20: The ratio of the Zn3s signal intensity versus the P2p signal intensity (corrected for the respective sensitivity factors) for the area tribostressed at the various loads. The values are for two independent samples.
Results

In Figure 3.20, the zinc-to-phosphorus ratio is shown. For this ratio the Zn3s signal was used, because it has approximately the same inelastic mean free path as phosphorus. The phosphorus content of the film increases with increasing load in both samples but in the absolute ratio differences can be seen between the two samples. While in sample 1 the relative phosphorus content is lower than in the pure ZnDTP, the content is increased in sample 2.

Scanning Auger Microscopy

Scanning Auger microscopy was carried out on a combinatorial step-test sample. Figure 3.21 shows an O KLL map of a 1 N tribotested area. Stripes of higher and darker intensities can be seen running from the top to the bottom of the picture. The bright intensities are separated by approximately 25 μm. This spacing leads to the assumption that the stepping during the tribotest (25 μm intervals) leads to the non-uniform distribution of the oxygen species.

Figure 3.21: O KLL Scanning Auger Microscopy picture of the 1 N wear scar area. Different Oxygen signal intensity can be seen as stripes running in the scratching direction. They show a spacing of approximately 25 μm.

Sample Ageing

The results reported above for combinatorial step tests were all from samples aged 3 days in dry air prior to the tribotest. For experiments done with freshly polished samples, no differences in the qualitative results (peak positions) were detected but interesting observations were made in the quantitative results and in the tribotests. In Figure 3.22 the average COF during a tribotest is shown for a series of aged and non-aged samples. At low loads (0.1 and 0.05 N) a large scatter of the data can be seen, which can be
explained by the limitation of the load cell. At medium load (0.5 and 1 N) all COF values are at 0.2±0.025, while at a load of 5 N the experiments with non-aged samples show a higher value than the aged samples.

Figure 3.22: Comparison of the COF vs. load for samples tribostressed immediately after polishing (non-aged) and samples tribostressed after 3 days of ageing in dry air. The high scatter at low loads can be explained by the limitation of the load cell. At high load (5N) the non-aged samples show a higher COF than the aged samples.

On the other hand, the comparison of O1s spectra acquired in the 5 N and the 1 N tribostressed areas shows that the relative signal intensity between the phosphate and the oxide O1s signal is different in the aged and the non-aged samples (Figure 3.23). In the aged samples the phosphate signal is much stronger than the oxide signal and the phosphate signal increases with increasing load, as already seen in Figure 3.16. In the non aged samples on the other hand the phosphate signal intensity is less pronounced. In addition, in two of three experiments the relative intensity of the phosphate signal compared to the oxide signal is even smaller at 5 N than at 1 N.
Figure 3.23: Comparison of the O1s spectra acquired in the areas tribostressed with 5 N (left) and 1 N (right). The upper graphs show spectra from samples tribostressed immediately after polishing (non-aged samples); the lower graphs show spectra from samples aged 3 days in dry air prior to tribostress.
3.3.2 Elevated Temperature

Combinatorial step tests were done on one sample after ageing for 3 days in dry air. The sample was mounted on the sample holder and the cup filled with the lubricant containing 1 wt-% ZnDTP (Hitec). The sample was heated to 150°C within 30’. The temperature was kept at 150±2°C for the rest of the experiment. For details on the tribological test see section 2.3.3, details on the elevated temperature test can be found in section 2.3.4.

Optical Microscopy

The surfaces of the tribostressed samples were investigated with optical microscopy. No scratching of the surface could be found. The non-contact area was slightly brownish, while the tribostressed area showed no discoloration. On the surface of the ball used to perform the tribostress, no change of the surface can be seen (Figure 3.24).

Coefficient of Friction

During running in (Figure 3.25), the COF showed the same trend as observed at ambient temperatures (Figure 3.3). The COF first increased to 0.4, followed by a sharp drop to a constant value of 0.23. In the 5 N test the COF showed a fast increase to 0.19 in the beginning and remained almost constant for the rest of the test. In the tribotest at 1 N and 0.5 N the COF showed a plateau at 0.19. This plateau is intercepted by sharp drops in the COF and a following slow increase to the plateau value. These drops coincide with
the 25 µm steps done every five turns. At 0.1 N no such pattern can be observed. An increase from 0.19 to almost 0.3 can be seen with some scatter. At the end of the 0.1 N test the $F_x$ value was found to be 10 mN without any load applied.

The excess of the lubricating oil was removed from the surface using cyclohexane as solvent prior to the introduction of the sample into the analysis chamber of the XPS.

**Figure 3.25**: COF of the tribotests at 150°C at various loads and during running in. The error bars are the standard deviation during one full turn of the disc.
**Imaging XPS** In the O1s total intensity map (Figure 3.26), high-intensity stripes can be seen arising from the tribostressed areas. Spectra extracted from the contact and the non-contact area reveal a different shape. Both spectra show a peak maximum at 531.8 eV. A small contribution can be observed on both sides of the main peak in both spectra. In the non-contact area spectrum the shoulder on the high-energy side is more prominent, while the contact area spectrum shows a stronger shoulder on the low-energy side. Chemical-state maps produced with the LLS routine of the Multipak software show the distribution of these types of spectra. The wear tracks can clearly be seen.

**Figure 3.26:** In the total O1s intensity map (left-hand side) areas with different signal intensities can be seen. Spectra extracted from these area (middle) show different shape, they can be assigned to the contact area and the non-contact area. The LLS analysis using the contact area and the non-contact area signal reveal chemical state maps with the distribution of the corresponding signal intensities.

**XPS Spectroscopy** Detailed spectra were acquired in the areas tribostressed at the various loads and in the non-contact area (Figure 3.27). The main peak positions are shown in Figure 3.6. The detailed peak-fit parameters can be found in Appendix A.
The C1s peak was fitted with two contributions. The main peak was found at 285.0 eV for the 5 N area but decreased as loads was reduced and in the non-contact area. This change of the C1s peak might also be caused by X-ray degradation of the tribofilm (see Appendix B).

Figure 3.27: O1s peak fit from spectra extracted in the areas shown in the LLS map. The sample was tribostressed at 150°C in the presence of a 1 wt-% ZnDTP (Hitec) solution in PAO.
The O1s spectra was fitted with 3 model-curves (Figure 3.27). The main peak was always found at 531.9 eV, decreasing to 531.5 eV in the non-contact area. It can be assigned to oxygen in a phosphate [1] or non-bridging oxygen in a polyphosphate [4,5]. A peak to the high-energy side was found at 533.2 eV, and one at the low energy side at 530.1 eV. The peak positions were varying ±0.2 eV between the analyzed areas on the high-binding-energy side and ±0.1 eV for the low-binding-energy side. The signal at 533.2 eV can be assigned to a bridging oxygen (BO) [4,5]. It shows the highest intensity in the 5 N and the non-contact area and is slightly reduced in the experiments at lower loads. The peak at 530.1 eV can be assigned to an oxide. Its intensity increases with increasing load, but the 5 N area shows a lower intensity than the 1 N area.

Table 3.6: Peak positions of the main peaks from the detailed analysis of the tribos-tressed areas and the non-contact area. The sample was produced at 150°C in presence of a 1 wt-% ZnDTP solution in PAO. All values are given in the binding energy scale (eV), except for Zn\(_{LMM}\), which is given in the kinetic energy scale (eV). The results are presented without any charge correction.

<table>
<thead>
<tr>
<th></th>
<th>C1s</th>
<th>O1s</th>
<th>O1s</th>
<th>O1s</th>
<th>S2p</th>
<th>S2p</th>
<th>P2p(_{3/2})</th>
<th>Zn2p(_{3/2})</th>
<th>Zn(_{LMM})</th>
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<tr>
<td><strong>5 N test</strong></td>
<td>285.0</td>
<td>530.2</td>
<td>531.9(_5)</td>
<td>533.3(_5)</td>
<td>162.1</td>
<td>169.0</td>
<td>133.5(_5)</td>
<td>1022.6</td>
<td>987.8</td>
</tr>
<tr>
<td><strong>1 N test</strong></td>
<td>284.6</td>
<td>530.2</td>
<td>531.8</td>
<td>533.4(_5)</td>
<td>162.1</td>
<td>168.9</td>
<td>133.5</td>
<td>1022.3(_5)</td>
<td>987.8</td>
</tr>
<tr>
<td><strong>0.5 N test</strong></td>
<td>284.6</td>
<td>530.0(_5)</td>
<td>531.6(_5)</td>
<td>533.2</td>
<td>161.9(_5)</td>
<td>169.0</td>
<td>133.5</td>
<td>1022.3</td>
<td>988.0</td>
</tr>
<tr>
<td><strong>0.1 N test</strong></td>
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<td>529.9(_5)</td>
<td>531.6</td>
<td>533.3(_5)</td>
<td>161.9(_5)</td>
<td>168.7</td>
<td>133.4(_5)</td>
<td>1022.2(_5)</td>
<td>988.2</td>
</tr>
<tr>
<td><strong>non-contact</strong></td>
<td>284.5</td>
<td>530.0</td>
<td>531.5</td>
<td>533.1</td>
<td>161.9(_5)</td>
<td>168.9(_5)</td>
<td>133.5</td>
<td>1022.2(_5)</td>
<td>988.4</td>
</tr>
</tbody>
</table>

In the S2p spectra, two main contributions can be seen (Figure 3.28). The most intense peak is found at 162 eV, while a second contribution is found at 169 eV. The peak at 162 eV was fitted with one doublet, while for the peak at 169 eV two doublets had to be used. Each doublet had a fixed area ratio and the difference between the peak maxima was also fixed at 1.25 eV. The peak maxima of the first S2p\(_{3/2}\) peak was found at 162.0 eV (varying ±0.1 eV between the areas), and was assigned to a sulfide con-
Results

distribution. From the peak position it can not be determined if it is a metal sulfide or an organic sulfide. The intensity of this signal is highest in the non-contact area and decreases with increasing load. Again an exception can be found at 5 N, where the intensity is higher than in the 1 N area. The intensity of the peak at 169 eV is highest in the tribostressed areas and almost absent in the non-contact area. The peak position of the 2p\textsubscript{3/2} peak was found at 168.9 eV, with a variation of ±0.2 between the areas. It can be assigned to a sulfate. In the 0.1 N and the 0.5 N area an additional peak was found at 167.1 eV and 167.3 eV, respectively, and may probably be attributed to a sulfone [6]. This doublet is almost absent in the peak fit of the other loads and in the non-contact area.

![Figure 3.28: Zn3s, P2p, S2p and Fe2p\textsubscript{3/2} spectra acquired in the areas tribostressed at various load. The test was run at a temperature of 150°C in the presence of a 1 wt-% ZnDTP (Hitec) solution in PAO.](image-url)
The Fe$_{2p}$ signals acquired in the tribostressed areas (Figure 3.28) have a low intensity and a low signal-to-noise ratio. Due to this no peak fit was done on this signal. Anyway, in Figure 3.28 it can be seen that the signal is completely absent in the non-contact area and its intensity increases with increasing load, except for the 5 N area, where it decreases again. It can also be seen that no contribution of the metallic signal at 706.9 eV can be detected, thus all of the analyzed iron is in the oxidized state.

The P$_{2p}$ peak was found to have only one contribution (refer to Figure 3.28). It was fitted with one doublet with a fixed area ratio and peak separation (0.95 eV). The peak maximum was found at 133.5, almost independent of the applied load.

The Zn$_{2p}$ peak position was found to shift to lower binding energy with decreasing applied load. At 5 N load it was 1022.6 while in the non-contact area 1022.25 eV was found.

<table>
<thead>
<tr>
<th></th>
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<th>P/Zn</th>
<th>$(O^{NBO}+O^{BO})/P$</th>
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<td>0.9</td>
<td>3.5</td>
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<td>0.8</td>
<td>1.0</td>
<td>4.2</td>
</tr>
<tr>
<td>0.5N</td>
<td>0.8</td>
<td>0.9</td>
<td>4.8</td>
</tr>
<tr>
<td>0.1N</td>
<td>0.8</td>
<td>0.7</td>
<td>4.1</td>
</tr>
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<td>non contact</td>
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<td>0.7</td>
<td>2.8</td>
</tr>
<tr>
<td>ZnDTP</td>
<td>0.5</td>
<td>2.0</td>
<td>2.0</td>
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</table>

The elemental ratio between the P$_{2p}$ signal and the total S$_{2p}$ signal (including the contribution at 162 eV and 169 eV) reveals a value of approximately 0.8 for all loads and the non-contact area. This ratio is higher than in the ZnDTP (0.5) but lower than the values found in the experiments at room temperatures (0.8 (non-contact) to 1.5 (5 N)).
The P-to-Zn ratio increases with increasing load, with the exception of the 5 N area. Comparing this results to the room temperature experiments (Figure 3.20), one can see that at lower temperatures, the phosphorus-to-zinc ratio is higher than in the experiments at elevated temperatures.

The ratio of the sum of the bridging oxygen and the non-bridging oxygen to phosphorus shows values between 4 and 5, except for the 5 N area and the non-contact area, where smaller values are found.

**Angle-Resolved XPS**

Angle resolved XPS measurements can give an insight into the depth distribution of the species present in the tribofilm. Therefore a step test with 41x25 µm steps was performed in order to produce a tribostressed area of a total width of 1 mm (see section 2.3.3). This is necessary to be able to focus the analyzed area completely inside the tribostressed area. The tribotest was done at 5 N. The XPS analysis of the tribostressed area showed the same qualitative results as reported in the 5 N and 1 N area of the combinatorial step test (Table 3.6). The quantitative results were angular dependent.

As discussed above, the O1s signal can be divided into three components, the oxide signal at 530.2 eV, the phosphate signal at 531.7 eV and a third component at 533.3 eV. The relative intensity between the components changes depending on the emission angle (Figure 3.29). The higher the emission angle, the higher the intensity of the oxide signal. This can be interpreted as showing that the oxide species are located below the other oxygen species.

Also in this case the Fe2p signal shows no metallic iron contribution. The relative intensity of the Fe2p signal to the other signals is higher at high angles than at low angles, which indicates that the iron is covered by a layer. Despite the small signal-to-noise ratio in the Fe2p spectra differences in the relative intensities of the Fe$^{2+}$ signal and the Fe$^{3+}$ signal can be observed. Fe$^{2+}$ is stronger in the spectrum acquired at 75° compared to the spectra at lower angle. This suggests that the Fe$^{2+}$ signal arises from the inner part of the oxide layer, while the Fe$^{3+}$ signal is located on the outer side of the layer.
XPS analysis of Thermal Film

As can be seen in Figure 3.28, no iron can be detected by XPS in the non-contact area. Since the iron signal is not visible, a thermal film, which is formed independently from the tribological stress on the disc, must be covering the steel surface. In order to have a reference measurement of this film, a steel sample was analyzed by XPS after 5.5 hours (the usual total time of a combinatorial step test experiment) of immersion in a 1 wt-% solution of ZnDTP (Hitec) in PAO166 at 150°C.
The spectra of the elements present in the film are shown in Figure 3.30, the peak positions are presented Table 3.8. Detailed peak-fit parameters can be found in Appendix A.

Two peaks were used to fit the C1s spectra, the main peak being found at 285.96 eV. This high value probably arises from sample charging due to the insulating character of the thermal film. The sample charging was compensated by referencing the C1s peak at 285 eV (aliphatic carbon).
285.96 eV to 285 eV (aliphatic carbon), thus shifting all peak values by -0.96 eV. All peak positions are corrected for sample charging.

In the O1s peak three contributions were found. They were all fitted with a fixed FWHM of 1.75 eV. An initial very small peak was detected at 530.25 eV, probably due to the presence of (zinc) oxide. The two main contributions were found at 532.0 eV and at 533.25 eV. They can be assigned to phosphorus bound in an orthophosphate (non-bridging oxygen, NBO) [1] and a P-O-C or P-O-P bonding environment (bridging oxygen (BO)) [3,4].

Table 3.8: Peak positions and elemental composition of the main peaks of the pure thermal test at 150˚C in a 1 wt-% solution of ZnDTP (Hitec) in PAO166. All values are given in the binding energy scale (eV) and corrected for sample charging of 0.96 eV by referencing the main carbon contribution to 285 eV (aliphatic carbon). The elemental composition is calculated assuming that a homogeneous layer is present.

<table>
<thead>
<tr>
<th></th>
<th>C1s</th>
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<th>O1s</th>
<th>O1s</th>
<th>S2p</th>
<th>S2p</th>
<th>P2p3/2</th>
<th>Zn2p3/2</th>
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<td><strong>main oxide</strong></td>
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<td>532.0</td>
<td>533.25</td>
<td>162.45</td>
<td>169.3</td>
<td>133.8</td>
<td>1022.65</td>
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<td>Elemental Comp. (%)</td>
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<td>10</td>
<td>8</td>
<td>2</td>
<td>9</td>
<td>14</td>
</tr>
</tbody>
</table>

Table 3.9: Elemental ratio between the P2p3/2, S2p3/2, Zn3s, and the O1s signals of a pure thermal film produced at 150˚C in a 1 wt-% ZnDTP (Hitec) solution in PAO. For the oxygen, only the bridging oxygen and the non-bridging oxygen were used.

<table>
<thead>
<tr>
<th></th>
<th>P/S(tot)</th>
<th>P/Zn</th>
<th>(O(II)+O(III))/P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal film</td>
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<td>0.7</td>
<td>3.6</td>
</tr>
</tbody>
</table>

The S2p spectra revealed two main contributions. Each was fitted with a doublet with a fixed area ratio and a delta between the 2P3/2 and the 2P1/2 of 1.25 eV. The 2P3/2 peak of the first doublet was found at 162.45 eV. This peak might be assigned to a C-S bond [7]. The 2P3/2 peak of the second doublet was found at 169.3 eV. This peak can be assigned to a sulfate [6].
Results

The P2p peak was fitted with a doublet with fixed area ratio and a delta of 0.95 eV. The peak position was found at 133.8 eV. This value is typical for a phosphate [1]. The peak maximum of the Zn2p3/2 signal was found at 1022.65 eV.

As it will be shown in Appendix B, the peak positions of the XP signals from thermal films may change with ongoing X-ray irradiation due to sample degradation. Therefore these peak positions have to be treated carefully.

The elemental composition, assuming a homogeneous layer is given in Table 3.8. Elemental ratios are shown in Table 3.9.

Angular Resolved Measurements

Angular resolved XPS experiments (not shown) revealed a slight increase of the C1s signal at small take off angles but no significant differences in the peak position or elemental ratio of the other elements could be detected.
3.4 Oscillating Load Tests

In an oscillating load test a load interval is cycled from the minimum value to the maximum value synchronized with the angular position on the disc. Figure 3.31 shows the experimental setup of such a test, where the load is cycled four times from 1 N to 10 N during one full rotation of the disc. The experiment was done in pure PAO 166 and in a 1 wt-% solution of commercial ZnDTP (Hitec) in PAO. Five concentric wear tracks with 1 to 100 turns were done on one disc. The experimental details can be found in section 2.3.3.

![Figure 3.31: Sketch of the oscillating load test. The load is ramped four times from 1 N to 10 N to 1 N during one full turn of the disc. On each wear track an experiment with different duration (1-100 turns) is performed.](image)

Both experiments (with and without ZnDTP) were repeated once. The tribological results were very reproducible qualitatively and quantitatively. Therefore, only one pair of results will be presented. The wear results were less reproducible, especially quantitatively. Therefore, in the wear results all four experiments will be presented.
3.4.1 Tribological Data

Tribological data ($F_x$, $F_z$) were recorded together over time ($t$) and the encoder values of the rotational encoder (ROT). The frictional data plotted versus the rotational encoder position are shown in Figure 3.32 for one (particular) full turn of the disc. The normal load ($F_z$) was cycled four times from 1 N to 10 N to 1 N. The forces in between the minimum and maximum value are almost linear, which shows that the tribometer was able to maintain the programmed load. Only at the lowest and highest values a small deviation from the ideal behavior can be observed. Besides the increase and decrease due to the oscillating load a scattering in the friction force ($F_x$) can be observed. This is due to the stick-slip occurring at higher loads. The coefficient of friction was calculated by dividing the friction force ($F_x$) by the normal load ($F_z$) at each measured value. The scattering due to the stick-slip can still be seen, but the overall shape of the curve is flattened. The COF shows high values in the areas where low load is applied. The tribological behavior is very reproducible within the four cycles.
The data shown in Figure 3.32 were processed using IGOR Pro (see section 2.3.5) to produce a graph where the coefficient of friction is plotted color coded in dependence of the angular position on the disc (x-axis) and the duration of the test (y-axis). Graphs of 100 turn experiments are shown in Figure 3.33 and Figure 3.34 for experiments with pure PAO and a 1 wt-% ZnDTP/PAO solution. In the bottom of the graphs the applied normal load is shown as a function of the angular position of the disc.

**Figure 3.32:** Normal load (top), friction force (middle) and calculated coefficient of friction (bottom) of one full turn of the disc during an oscillating load test in a solution of 1 wt-% ZnDTP (Hitec) in decane.
Results

Figure 3.33: The coefficient of friction (COF) is shown color coded depending on the rotational position on the disc (x-axis) and on the duration for the oscillating load test in pure PAO166.

Figure 3.34: The coefficient of friction (COF) is shown color coded depending on the rotational position on the disc (x-axis) and on the duration for the oscillating load test in a 1 wt-% solution of ZnDTP (Hitec) in PAO166.
The experiment with pure PAO shows differences in its behavior depending on the load and on the duration (Figure 3.33). Clearly four sections can be seen, representing the four load cycles during one revolution. At low load, the COF shows an almost constant value, while in the high-load areas a patterned signal picture is observed. This patterned signal arises from stick-slip motion. Moving from left to right on one line the COF steadily increases from a low value (black) to a high value (red) and drops quickly back to a low value. Each of these increases and drops represents one single stick-slip event. After a particular running in time the stick-slip event always seems to happen at the same angular position on the disc, probably induced by a surface modification from the previous stick-slip events. These stick-slip locations may move slowly in the direction of the movement, or stay at the same position. The stick-slip behavior is much less obvious in the low-load regions.

The experiment with additive shows a different trend (Figure 3.34). Also in this experiment the COF shows four sections, representing the four load cycles. In contrast to the experiment without additive, the low load region shows higher COF than the high load region. In addition much more but much smaller stick-slip events are observed in the high-load region. The maximum load at each stick-slip event is reduced.

**Polar Plots**

In Figure 3.35 and Figure 3.36 polar plots of the tribological data from the experiments presented above are shown. The position on the disc is used as the angular axis ($\Theta$), while the duration is represented in the radial direction. While on the left side the raw data is used to produce the polar plot, on the right side the data processed according to the “tribological significance” is shown (section 2.3.5). Only the maximum values of the stick-slip events are used to produce the polar plot. In this representation it can be seen where (spatially) a stick-slip event is occurring and the value of the COF at the moment of the “slip” event. It is assumed that this value is representative of the tribological condition in this slip-event, which depends on the applied load and the duration.
Results

**Figure 3.35:** Polar plot of the coefficient of friction (color coded) depending on the rotational position of the disc (Θ) and the duration (radius) for the oscillating load test in PAO166. The left-hand image shows the raw data, while the right-hand image shows the data processed according to the “tribological significance” (section 2.3.5) representing the maximum load values in a stick-slip event.

**Figure 3.36:** Polar plot of the coefficient of friction (color coded) depending on the rotational position of the disc (Θ) and the duration (radius) for the oscillating load test in a 1 wt-% solution of ZnDTP (Hitec) in PAO166. The left-hand image shows the raw data, while the right-hand image shows the data processed according to the “tribological significance” (section 2.3.5) representing the maximum load values in a stick-slip event.
Clear differences can be seen between the experiment in pure PAO (Figure 3.35) and in the experiment with additive (Figure 3.36). The stick-slip events are much less frequent in the pure oil and reach much higher maximum COF values than with the additive. After “running in” the slip-events are always located close to the slip-event from the previous turn and tend to move in the direction of rotation.

The experiment with additive shows a lot of small stick-slip events. The slip-events of subsequent rotations also seem to be connected with each other but not as strictly as in the pure additive experiment. It can again be seen that in the low-load areas the COF is higher than in the high-load areas.

![Graph showing Coefficient of friction plotted versus the normal load (Fz) for the cycle load experiments with and without additive. The duration of the experiments is color coded.](image)

**Figure 3.37**: The Coefficient of friction plotted versus the normal load (Fz) for the cycle load experiments with and without additive. The duration of the experiments is color coded.

The data, processed according to the “tribological significance” were used to plot the coefficient of friction versus the normal load
Results

(Figure 3.37). This time the duration of the experiment is color coded. In both experiments it can be seen that in the beginning the lowest values are observed (dark friction trace). After the first full turn on the disc the COF increases and exhibits a different behavior in the two experiments. In the experiment with ZnDTP, the COF shows the highest values at the smallest loads. It decreases with increasing load and levels off at values between 0.3 and 0.4. In the case of pure PAO, the behavior is the opposite: the highest values are observed in the points of highest normal load. On the other hand in the low-load region, the COF also shows a trend to decrease until at a load of 4 N it increases again. This transition can be seen even better if the friction force is plotted versus the normal load (Figure 3.38). The slope of the friction force increases at 4 N, except for the values on the first turns of the disc. In the experiment with additive, the opposite behavior can be observed. At 2 N load, the slope of the friction force decreases.

![Figure 3.38: The friction force (F_x) is plotted versus the normal load (F_z) for the cycle load experiments with and without additive. The duration of the experiments is color coded.](image-url)
3.4.2 Wear Results

Profilometry The topography of the iron discs was determined by optical profilometry (refer to section 2.3.6). In Figure 3.39 an example of a topographic map of an experiment in pure PAO is presented. The highest loads (10 N) are applied at 0°, 90°, 180° and 270°, in between the lowest loads (1 N) are applied. The smaller the radius of the wear scar, the longer the duration (1-100 Turns). The wear scar width and depth increases for high loads and with increasing duration. The magnified picture in Figure 3.39 (right-hand side) shows approximately one sector of the disc. On both sides of the wear tracks deposited material can be seen. In the wear tracks of 30 and 100 Turns (the two smallest radii) an oscillative pattern in the wear scar depth is observed.

Figure 3.39: Topographic map of an oscillating load test in presence of pure PAO 166. The right-hand side picture represents the area marked on the left-hand side.

Figure 3.40 shows the topographic map of the oscillating wear test in presence of a 1 wt-% solution of ZnDTP (Hitec) in PAO166. In this case the lowest loads were applied at 0°, 90°, 180° and 270°. Also with additive the wear scar width and depth increases with increasing load and longer duration. In the magnified area deposited
material can be seen on both sides of the wear track. In contrast to the pure base oil, no oscillation in the depth of the wear scars can be observed along the wear track.

Figure 3.40: Topographic map of an oscillating load test in presence of a 1 wt-% ZnDTP (Hitec) solution in PAO 166. The right-hand side picture represents the area marked on the left-hand side.

Data was evaluated as described in section 2.3.6. For a number of load/duration pairing, the areas $A_1$ and $A_2$ (see Figure 3.41) were evaluated.

Figure 3.41: Cross-section of a wear scar. The areas $A_1$ (wear scar) and $A_2$ (deposited material) were evaluated for a number of load/duration pairings.

Figure 3.42 shows the cross-sections of the wear scar depending on the applied load and duration. The results are shown for four ex-
Oscillating Load Tests

Experiments (two experiments in pure PAO and two in a 1 wt-% ZnDTP solution). In all four experiments an increase in the worn area can be observed with increasing load and duration. In Figure 3.43 the wear areas of the wear tracks at 30 turns (left) and at 100 turns (right) are summarized. Also in this graph it can be seen that the worn area increases with load but no distinct differences can be observed between the experiments with and without additives.

Figure 3.42: Area $A_1$ (wear scar) in dependence of load and the duration. Two experiments were run in pure PAO (top row) and two in a 1wt-% ZnDTP solution in PAO (bottom row).

Figure 3.43: Area $A_1$ (wear scar) for the 30 turn (left) and the 100 turn (right) experiment.
Figure 3.44 shows the area $A_2$ (see Figure 3.41) in dependence of load and duration for the four experiments. The amount of deposited material increases with load and duration in all experiments. The experiments presented on the right-hand side show much smaller values than the experiment on the left-hand side. It must be assumed that the difference between the sample treatment prior (e.g. polishing) or after (solvent washing, sample handling) the tri-bostress shows more influence on the amount of deposited material than the presence or absence of additive.

Figure 3.44: Area $A_2$ (deposited material) in dependence of load and the duration. Two experiments were run in pure PAO (top row) and two in a 1wt-% ZnDTP solution in PAO (bottom row).
3.5 XPS Analysis of Reference Compounds

All reference compounds were measured as received without any further purification. If the substance was a powder, it was ground with mortar and pestle and pressed into a pellet. This was then mounted on a standard PHI sample holder with a molybdenum mask. Steel discs were mounted on a special sample holder with an inset.

3.5.1 Steel Discs (100Cr6) after Polishing and Ageing in Dry Air

The 100Cr6 steel was characterized after polishing according to the procedure described in section 2.2. It was analyzed in three different states: first it was measured after removing the oxide film with Ar⁺ ion sputtering in the preparation chamber, second it was measured immediately after the polishing procedure, and third after three days in dry air (stored in a desiccator), after the natural oxide film could stabilize. A comparison of the O1s and the Fe2p₃/₂ signal of the three states is shown in Figure 3.45.

**Sputtered Sample**

For the measurement of the substrate without the oxide film, the sample was sputtered with Ar⁺ ions for 5'. The Fe2p₃/₂ signal could be detected at 706.8 eV, it was modeled with a Gauss-Lorenz ratio of 0.85 and a tail function T(0.9).

**Polished Sample**

For the sample analyzed immediately after polishing, three peaks had to be fitted in the O1s spectra. The peak at 530.2 eV was attributed to oxide, a second at 531.8 eV to oxy-hydroxide and a third one at 533.4 eV is probably due to adsorbed water on the surface [8,9].

For the Fe2p₃/₂ signal, four signals had to be used. The contribution at 706.8 eV is due to the metallic iron below the oxide film. An Fe²⁺ peak was found at 709.3 eV, including a shake-up satellite with 8% of the main peak intensity, located 5.5 eV to the higher-binding-energy side. The peak at 711.3 eV was assigned to Fe³⁺.
Results

The third measurement was performed after ageing the steel sample for three days in dry air. This was done to allow the growth of a stable oxide film. The peak assignment of the O1s signal is analogous to the previous sample. The comparison of the Fe2p signal for the freshly polished and aged samples (Figure 3.45) reveals a difference in the Fe$^{2+}$ peak position, as well as in the relative ratio between the Fe$^{2+}$ and the Fe$^{3+}$.

**Figure 3.45:** O1s and Fe2p$_{3/2}$ peaks from the sputtered 100Cr6 disc, the disc immediately after polishing, and the disc aged for three days in dry air.

**Aged Sample** The third measurement was performed after ageing the steel sample for three days in dry air. This was done to allow the growth of a stable oxide film. The peak assignment of the O1s signal is analogous to the previous sample. The comparison of the Fe2p signal for the freshly polished and aged samples (Figure 3.45) reveals a difference in the Fe$^{2+}$ peak position, as well as in the relative ratio between the Fe$^{2+}$ and the Fe$^{3+}$. 
Table 3.10: Peak-fit parameters of the 100Cr6 steel, sputter cleaned, immediately after polishing and after ageing 3 days on dry air. No charge correction has been done since the samples are conducting. The accuracy of the binding energy values is ±0.1 eV.

<table>
<thead>
<tr>
<th></th>
<th>Peak Energy (eV)</th>
<th>Peak Width (eV)</th>
<th>G/L Ratio (%)</th>
<th>Peak Area (eV cts/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>sputter cleaned</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>706.8</td>
<td>1.3</td>
<td>85</td>
<td>-</td>
</tr>
<tr>
<td><strong>immediately after polishing</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
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</tr>
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<td>O1s (oxide)</td>
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<tr>
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<td>1638</td>
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<td>562</td>
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<td>1.3</td>
<td>85</td>
<td>3728</td>
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<tr>
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<td>45</td>
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<td><strong>polished and aged 3 days</strong></td>
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<td></td>
</tr>
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<td>1.53</td>
<td>20</td>
<td>2730</td>
</tr>
<tr>
<td>O1s (oxyhydroxide)</td>
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<td>1.53</td>
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<td>1002</td>
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<tr>
<td>O1s (H2O)</td>
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<td>1.53</td>
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<tr>
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<td>1.3</td>
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<td>715</td>
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<tr>
<td>Fe2p3/2 (II)*</td>
<td>709.4</td>
<td>2.8</td>
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<td>1321</td>
</tr>
<tr>
<td>Fe2p3/2 (III)</td>
<td>711.1</td>
<td>3</td>
<td>45</td>
<td>2214</td>
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</table>

* including a satellite 5.5 eV higher than the Fe²⁺ peak with an intensity of 8% of the main peak
3.5.2 Zinc diisopropyl dithiophosphate (i-ZnDTP)

The purity of the i-ZnDTP molecule was confirmed by elemental analysis (see section 2.1.3), infrared spectroscopy and NMR [10]. A more detailed description of the XPS analysis of i-ZnDTP can be found elsewhere [10].

![Reference spectra from the i-ZnDTP powder. All spectra have been corrected for sample charging.](image)

The XPS results are summarized in Table 3.11. The C1s peak of the i-ZnDTP powder showed two contributions. The main peak was assigned to aliphatic carbon and used for sample-charging correction. This peak was assigned to 285.0 eV, which resulted in a sample charging of 1.71 eV. The second C1s peak was found at 286.9 eV and assigned to the carbon bound to oxygen. The O1s
peak at 533.1 eV is also in agreement with a C-O bond. The FWHM of the P2p peak was found to be 1.94 eV, it was fitted with two peaks according to the spin-orbit splitting. Each contribution had a FWHM of 1.55 eV, the peak position of both peaks were left free to vary, a peak separation of 0.84 eV was found. The FWHM of the S2p peak was found to be 2.25 eV. The peak was modeled according to the spin-orbit coupling with a 2p3/2 and the 2p1/2 contribution (with a FWHM of 1.7 eV each). The peak position was left free to converge and a peak separation of 1.25 eV was obtained. The Zn2p3/2 peak was found at 1022.7 eV, the ZnLMM peak maximum at 987.8 eV (kinetic-energy scale).

Table 3.11: Peak-fit parameters of the i-ZnDTP powder. The sample charging of 1.7 eV has been corrected by referencing the C1s aliphatic peak to 285.0 eV. The accuracy of the binding energy values is ±0.1 eV.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Energy (eV)</th>
<th>Width (eV)</th>
<th>G/L Ratio (%)</th>
<th>Area (eV cts/s)</th>
<th>Concentration (at-%)</th>
<th>Theoretical Concentration (%)</th>
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<td>C1s aliph.</td>
<td>285.0</td>
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<td>30</td>
<td>18800</td>
<td>33</td>
<td>35</td>
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<td>C1s (C-O)</td>
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<td>10300</td>
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<td>17</td>
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<td>O1s</td>
<td>533.1</td>
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<td>20</td>
<td>22400</td>
<td>15</td>
<td>17</td>
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<tr>
<td>P2p3/2</td>
<td>133.8</td>
<td>1.55</td>
<td>45</td>
<td>4200</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>S2p3/2</td>
<td>162.8</td>
<td>1.7</td>
<td>45</td>
<td>12600</td>
<td>19</td>
<td>17</td>
</tr>
<tr>
<td>Zn2p3/2</td>
<td>1022.7</td>
<td>2.0</td>
<td>20</td>
<td>38400</td>
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<tr>
<td>ZnLMM</td>
<td>987.8*</td>
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</tr>
</tbody>
</table>

*Peak maximum, value in the kinetic-energy scale.

The quantitative analysis is in excellent agreement with the theoretical values.
3.5.3 Zinc Sulfide

A sample charging of 3.6 eV was found in the spectra of the zinc sulfide, which was corrected by referencing the C1s signal to 285 eV (adventitious carbon). The S2p peak of the zinc sulfide powder shows a FWHM of 2.3 eV. The peak was fitted with two peaks according to the spin-orbit splitting, each peak had a FWHM of 1.65 eV. The difference between the 2p\(_{1/2}\) and the 2p\(_{3/2}\) peak position was found to be 1.26 eV. The Zn2p\(_{3/2}\) peak position was found at 1022.1 eV, the Zn\(_{LMM}\) peak maximum at 989.0 eV (kinetic-energy scale). Quantitative analysis was in good agreement with the theoretical values (Table 3.12).

![Figure 3.47: Zn2p and S2p spectra of the ZnS powder. The spectra have been corrected for sample charging.](image)

<table>
<thead>
<tr>
<th>Peak</th>
<th>Energy (eV)</th>
<th>Width (eV)</th>
<th>G/L Ratio (%)</th>
<th>Area (eV cts/s)</th>
<th>Concentration (at-%)</th>
<th>Theoretical Concentration (%)</th>
</tr>
</thead>
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<tr>
<td>C1s (ref)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S2p(_{3/2})</td>
<td>162.1</td>
<td>1.65</td>
<td>45</td>
<td>1780</td>
<td>54</td>
<td>50</td>
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<tr>
<td>Zn2p(_{3/2})</td>
<td>1022.1</td>
<td>1.8</td>
<td>80</td>
<td>15200</td>
<td>46</td>
<td>50</td>
</tr>
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<td>Zn(_{LMM})</td>
<td>989.0*</td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

*Peak maximum, value in the kinetic-energy scale.
3.5.4 Zinc Oxide

A sample charging of 1.0 eV was found in the spectra of the zinc oxide, which was corrected by referencing the C1s signal to 285 eV (adventitious carbon). In the O1s spectra two contributions were found. The main peak at 530.2 eV was attributed to oxygen present in the oxide state, while a smaller contribution at 531.9 eV is probably due to hydroxide. The Zn2p peak was found at 1021.3 eV, the $Zn_{LMM}$ peak maximum at 988.6 eV (kinetic-energy scale). The quantitative results (including both oxide and hydroxide) agree with the theoretical values.

![Figure 3.48: O1s and Zn2p spectra of the ZnO powder. The spectra have been corrected for sample charging.](image)

Table 3.13: Peak-fit parameters and quantitative analysis for the zinc oxide powder pressed into a pellet. The sample charging of 1.0 eV has been corrected by referencing the C1s main peak to 285.0 eV. The accuracy of the binding energy values is ±0.1 eV.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Energy (eV)</th>
<th>Width (eV)</th>
<th>G/L Ratio (%)</th>
<th>Area (eV cts/s)</th>
<th>Concentration (at-%)</th>
<th>Theoretical Concentration (%)</th>
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</thead>
<tbody>
<tr>
<td>C1s</td>
<td>285.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O1s oxide</td>
<td>530.2</td>
<td>1.60</td>
<td>40</td>
<td>4565</td>
<td>41</td>
<td>50</td>
</tr>
<tr>
<td>O1s hydroxide</td>
<td>531.9</td>
<td>1.60</td>
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<td>1170</td>
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<td>-</td>
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<tr>
<td>Zn2p3/2</td>
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<td>1.85</td>
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<td>26388</td>
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<td>$Zn_{LMM}$</td>
<td>988.6*</td>
<td></td>
<td></td>
<td></td>
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</tr>
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</table>

*Peak maximum, value in the kinetic-energy scale.
3.5.5 Iron Phosphate

The iron phosphate turned out to be susceptible to sample degradation. Therefore it was measured with a larger aperture (aperture #3, $E_{\text{pass}} = 23.5$ eV, step size = 0.05 eV) to allow faster data acquisition. The sample was cooled with liquid nitrogen during acquisition to reduce outgassing. Peak-fit parameters can be found in Table 3.14

In the O1s signal two peaks had to be fitted. The main peak at 531.7 eV is accompanied by a small contribution (10% of the main peak) at 533.3 eV, which might be due to hydroxides. The P2p peak was found to have a FWHM of 2.05 eV. It was fitted with two peaks with area ratio 2:1 according to the spin-orbit splitting. The FWHM of the two peaks was fixed at 1.65 eV. The position of the 2p$_{1/2}$ peak was found 0.93 eV higher than the 2p$_{3/2}$ peak. Three peaks had to be used for the Fe2p$_{3/2}$ peak. Beside the main peak at 712.2 eV a peak at 716.0 eV (10% peak intensity of the main peak) with unknown origin was found. The third component, found at 709.2 eV, showed an increase with increasing X-ray irradiation.

Figure 3.49: O1s and Fe2p$_{3/2}$ and P2p spectra of the FePO$_4$ powder. The spectra have been corrected for sample charging.
time. It can be assumed that this contribution arises from Fe$^{2+}$, which was reduced from the Fe$^{3+}$ due to the X-ray irradiation.

The quantitative analysis of this sample shows differences from the theoretical values. While the oxygen-to-phosphorus ratio is 2.8 instead of 4, the iron concentration turns out to be smaller than expected. So far no explanation for this discrepancy could be found.

**Table 3.14:** Peak-fit parameters for the FePO$_4$ powder pressed into a pellet. The sample charging of 3.2 eV has been corrected by referencing the C1s main peak to 285.0 eV. The accuracy of the binding energy values is ±0.1 eV.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Peak Energy (eV)</th>
<th>Peak Width (eV)</th>
<th>G/L Ratio (%)</th>
<th>Peak Area (eV cts/s)</th>
<th>Concentration (at-%)</th>
<th>Theoretical Concentration (%)</th>
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<td></td>
<td></td>
<td></td>
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References


In this chapter the results presented in the previous chapter are compared with each other and with results from literature. In the first section the tribological contact between the ball and the disc is analyzed. In section 4.2 the chemical composition of the tribofilm is discussed in respect to the chemical states of the elements and the quantitative analysis. Starting from this, a film-formation mechanism is proposed in section 4.3. Section 4.4 discusses the friction and wear results of the oscillating load test. The general use of the combinatorial tribotests is analyzed in section 4.5.
4.1 Tribological Contact

The actual area of the tribological contact between the ball and the disc is of great importance because it determines the contact pressure during the tribological tests. It is clear that the contact area may change during the test. In order to avoid this, a “running in” period precedes the tests, which creates a reproducible surface on the ball from which to begin the subsequent tests. The results discussed in this section are valid for the tribological contact of a 100Cr6 steel ball on a 100Cr6 steel disc.

4.1.1 Running In

Contact Geometry  
At room temperature, a round worn area can be observed in the contact point between the ball and the disc at the end of the running in (Figure 3.2), which was done in presence of the lubricant-additive solution. This area was worn away during the running in and is assumed to define the apparent contact area in the subsequent test and to be in uninterrupted contact with the counter surface. As a consequence it can be assumed that the normal load is evenly distributed over this area and the resulting contact pressure can be calculated by dividing the applied normal load by this area (Table 4.1).

At elevated temperature (Figure 3.24), no such flat spot or other deformation on the ball or on the disc can be observed at the end of the running in. It can therefore be assumed that the response of the ball and the disc are completely elastic. The elastic contact between a sphere and a plane can be calculated according to the Hertzian theory [1].

Hertzian Contact  
In the Hertzian contact, the contact radius \( a \) can be calculated according to Equation 4.1.

\[
a = \left( \frac{3 \cdot w \cdot r}{4 \cdot E} \right)^{1/3} \quad \text{Equation 4.1}
\]

Here \( w \) is the load, \( r \) is the radius of the sphere, and \( E \) is an elastic modulus which depends on Young’s moduli, \( E_1 \) and \( E_2 \), and on the
Poisson’s ratios, $\nu_1$ and $\nu_2$, for the material of the sphere and of the plane in the following way:

$$\frac{1}{E} = \frac{(1 - \nu_1^2)}{E_1} + \frac{(1 - \nu_2^2)}{E_2}$$

Equation 4.2.

In the present system the sphere and the plane are both made from the same material and typical values for steel were used ($E_1 = E_2 = 210$ GPa and $\nu_1 = \nu_2 = 0.3$). The radius of the ball is 2 mm. The average pressure can be calculated by dividing the applied load by the contact area ($a^2\pi$), the maximum contact pressure is calculated by multiplying the average contact pressure with 3/2. The calculated average contact pressure, maximum contact pressure and contact radius are shown in Table 4.1.

<table>
<thead>
<tr>
<th>Load</th>
<th>Load carried by flat area (room temperature situation)</th>
<th>Contact pressure</th>
<th>Hertzian theory (elevated temperature situation)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Contact pressure</td>
<td>Average contact pressure</td>
</tr>
<tr>
<td>10 N</td>
<td></td>
<td>566 MPa</td>
<td>1’240 MPa</td>
</tr>
<tr>
<td>5 N</td>
<td></td>
<td>283 MPa</td>
<td>985 MPa</td>
</tr>
<tr>
<td>1 N</td>
<td></td>
<td>57 MPa</td>
<td>576 MPa</td>
</tr>
<tr>
<td>0.5 N</td>
<td></td>
<td>28 MPa</td>
<td>457 MPa</td>
</tr>
<tr>
<td>0.1 N</td>
<td></td>
<td>5.7 MPa</td>
<td>267 MPa</td>
</tr>
<tr>
<td>0.05 N</td>
<td></td>
<td>2.8 MPa</td>
<td>212 MPa</td>
</tr>
</tbody>
</table>

**Coefficient of Friction**

The coefficient of friction shows a general behavior during running in for all experiments but the absolute values are different (Figure 4.1). In the beginning, values around 0.2 are found which increase to 0.4-0.6, with a high scatter (indicating stick-slip) in the data. After 20-40 revolutions of the disc the coefficient of friction starts to decrease again and reaches values around 0.2-0.35. Using
higher load (10 N) the drop to lower values is delayed, while at elevated temperatures the drop occurs earlier. At room temperature the formation of the flat spot described above and the behavior of the coefficient of friction can be related to each other.

![Figure 4.1](image)

**Figure 4.1:** Comparison of the friction coefficient during running in of the standard test, the combined spiral and step test and the combinatorial step tests at 25°C and at 150°C.

**Room Temperature**

From Table 4.1 it can be seen that the average contact pressure calculated according to the Hertzian theory is always higher than the apparent contact pressure assuming the load is carried by the flat area. In the beginning of the running in (when the ball is not yet worn), a contact situation similar to the Hertzian model is present. At the high loads (10 N or 5 N) used in the running in, the contact pressure is in the range of 1240 MPa (985 MPa) and the associated high shear forces lead to progressive wear of the ball. With the formation of the flat area the contact pressure decreases to ca. 566 MPa (283 MPa) at the end of the running in.
The behavior of the coefficient of friction during the running in done in presence of the lubricant additive solution (Figure 4.1) can be explained by the formation of this flat spot. In the beginning of the test, the ball and the disc have a native oxide film. This oxide film is only a few nanometers thick and must be worn away during the first period of the running in. At this stage nascent iron is present at the surface of the ball (and probably on the disc), which is causing the high friction values. As wear goes on, the worn area on the ball increases and since the applied load is carried by this area the contact pressure is reduced. The decrease of the contact pressure leads to a decrease in the wear rate and may eventually stop completely. This is supported by the observation that the size of the worn area on the ball does not significantly increase with time after the initial running in period. It must be assumed that when the wear rate decreases, a (protective) film, formed by the lubricant additive present during the running in, covers the iron. This film prevents wear and also reduces the coefficient of friction.

This model is based on the observation of the coefficient of friction and on optical microscopy. Attempts were made to investigate the surface of the ball with XPS to confirm the proposed mechanisms. The small size of the worn area and the curved nature of the ball made it difficult to focus the analyzed area into the area of interest. These influences prevent the interpretation of the measured data.

**Elevated Temperature**

The running in prior to the tribotests performed at 150°C was done in presence of the lubricant additive solution at the same temperature as the latter tests. The initial increase in the coefficient of friction during the running in is also present, but the drop to a low value is observed much earlier than in the room temperature experiments (Figure 4.1). In addition, the flat spot at the bottom of the ball is not present after the tests (Figure 3.24). Since the friction coefficient is not much lower than in the room temperature experiment, the shear forces will also have the same order of magnitude but obviously they are not causing as much wear. In this case the shear plane must be located in between the two surfaces which are protected by the tribofilm.
4.1.2 Tribotests - Room Temperature

During the running in period a flat worn area of ca. 150 µm diameter was formed on the ball (Figure 3.2). All subsequent tribotests start from this geometrical situation. A first consequence of this flat is that the contact pressures at low loads are remarkably lower than in the Hertzian situation (Table 4.1).

The different tribological tests performed (standard-, step-, and spiral test) can be compared at a load of 1 N (contact pressure ca. 57 MPa). The results discussed below are for samples aged 3 days in dry air prior to the tribotest, if not otherwise noted.

**Standard Tests**

The coefficient of friction in the standard tests show an irregular behavior (Figure 3.3). The value is always between 0.2 and 0.3 but it increases and decreases with time. From the coefficient of friction and also from the observations on the tribostressed surfaces (Figure 3.2) it has to be concluded that the conditions present in these experiments cause severe wear. One explanation for the unsteady friction force might be that wear particles may be trapped in and released from the area of contact. Indeed at the end of the tribotest, worn material was observed on the surface of the disc, which was removed by the solvent washing prior to the analysis. On the surface of the ball islands of material can still be detected after cleaning with solvent, which might be wear particles or part of the tribofilm (Figure 3.2). The removal and reaccumulation of this material may eventually cause the unsteady behavior. Unfortunately, as discussed above, it was not possible to investigate the chemical composition of the islands at the bottom of the ball by XPS.

**Spiral Test**

The spiral test shows deep scars with only slight scratching in between (Figure 3.7). The scars are separated by the distance which the radius changes during one turn of the disc. This indicates that only one particular location on the ball is continuously producing this scar. The coefficient of friction shows a value of about 0.22, without large changes during the experiment.

**Step Test**

Step tests show a more reproducible behavior in coefficient of friction than the standard test (Figure 3.8). The radial steps during the test cause a jump to higher values which is followed by a decay to
a “steady state” value. With each step at least one part of the ball is moved to an area which has not been tribologically stressed before. It can be assumed that the increase in the friction force is caused by the higher friction on the non-treated surface. After 3-4 turns of the disc (or “passes” of the ball) the steady state value is reached. After this time a film could develop on the disc surface which reduces friction and protects the surface from wear.

**Enlarging the Tribostressed Area**

On the basis of the coefficient of friction and the optical appearance of the surface it can be stated that the step test produces more uniform tribostress than the spiral test. From this point of view the step test seems to be better suited as a method to enlarge the worn area. However, it has to be verified if the spectroscopic results of the step test can reproduce the results from the standard test. This was done comparing the XPS results of the 1 N standard test with the results from the spiral and step test, which are also produced at 1 N load.

The 1 N wear scar of a standard test has a width of 75 µm, which is smaller than the spot size of the XPS analysis. Thus, it has to be considered that the signal might be a mixture between the wear scar and the non-contact area. Despite this, a very good agreement can be seen between the two experiments. The peak positions (refer to Table 3.1 and Table 3.3) of all elements do not vary within the experimental error. The relative intensities between sulfur, phosphorus, zinc and oxygen are in good agreement for the step test and the standard test but they are smaller in the spiral test (see Table 4.2).

**Table 4.2:** Comparison of elemental ratios of the 1 N standard test, the 1 N step test and the combinatorial step tests.

<table>
<thead>
<tr>
<th>Test</th>
<th>P/S(tot)</th>
<th>P/Zn</th>
<th>O(PO₄)/P</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 N Standard Test</td>
<td>1.6</td>
<td>2.2</td>
<td>4.4</td>
</tr>
<tr>
<td>1 N Step Test</td>
<td>1.7</td>
<td>2.6</td>
<td>4.2</td>
</tr>
<tr>
<td>1 N Spiral Test</td>
<td>1.0</td>
<td>1.8</td>
<td>5.5</td>
</tr>
</tbody>
</table>

This comparison demonstrates that at 1 N load, the step test produces the same tribofilm as in a 1 N standard test. The spiral test shows qualitatively the same results but it seems that the quantity
Discussion

of tribofilm produced (in the analyzed area) is not the same as in the two other experiments.

The results presented above might be explained by the “kinetics” of the film formation. It can be assumed that the tribofilm at one specific location is only formed when the ball is passing by at this location, because only in this moment the thermal and tribological stress is high enough to initiate the reaction of the molecule. Comparing the different tests, it can easily be seen that the “number of passes” of the ball at a specific location is different for the different type of tests. The number of passes in the standard test equals the number of turns (90) because all turns are done at the same radius. In the spiral test the radius at which the test is done changes by 25 µm each turn. Assuming a width of 150 µm for the contact area each spot “sees” six turns of the ball. In the step test five turns of the ball are done prior to the next 25 µm step. Since also in this case the 150 µm flat area covers the area of six subsequent steps at radii separated 25 µm from each other, each spot experiences approximately 30 passes. The spectroscopic results show, that the 30 passes at each spot are enough to produce the same XPS signal as the 90 passes on a standard test but the six passes in the spiral test do not produce the same tribofilm. Therefore, the step test is regarded to be a useful method to enlarge the wear scar and allow the analysis of tribotests performed at low loads, which would otherwise not have been possible.

Step Tests at Different Load

The typical “step test” behavior described above with a jump in the coefficient of friction after the step is only observed at medium load (1 N and 0.5 N). The test done at 0.1 N load shows this behavior of the coefficient of friction only in some parts and is much less pronounced than at 0.5 N and 1 N load. At 5 N load, the coefficient of friction shows only a small variation with time. At low load, limitations of the load cell (see below) make the interpretation of the frictional results difficult.

4.1.3 Tribotests - Elevated Temperature

The tribotests performed at 150°C present a thermal film on the surface of the disc prior to the tribotest. This thermal film has been found to be mainly composed of zinc polyphosphates and polythiophosphates in agreement with the literature [2-4]. The film
thickness, estimated to be >10 nm is also in agreement with literature values (5-25 nm) [5]. The thermal film modifies the tribological response compared to room temperature, but the most striking difference is that no worn area can be observed on the ball (Figure 3.24). The coefficient of friction for the different loads (Figure 4.2) is only slightly lower than at room temperature. Also in these experiments at medium load, the coefficient of friction shows jumps but in contrast to the low-temperature experiments, they go to lower values and the friction increases afterwards to a plateau value. Apparently the thermal film has a low shear strength causing the low friction values after the steps. At this moment one part of the contact is in an area which has not been stressed before and is still covered by the thermal film and thus the friction force is reduced. After a few turns of the disc this film is either removed or modified, which results in a higher friction value. The 5 N load test does not show large variations in the coefficient of friction. It may be that in this case the load is high enough that the thermal film is already removed during the first rotation of the disc.

Since in the elevated-temperature experiment no flat spot is observed, it is assumed that a Hertzian contact is present. The contact radius can be calculated to be 11 μm at 0.1 N and 40 μm at 5 N. This shows that at loads larger than 0.1 N the wear tracks overlap in the step test and the whole contact area is evenly tribologically stressed.

**Comparison 25°C and 150°C Experiments**

Figure 4.2 shows the coefficient of friction summarized for both room temperature and elevated temperature combinatorial step tests. The values presented are the “plateau” values, which is the value reached at the end of a five turn cycle, immediately prior to a step. The error bars represent the error calculated using the error propagation of the resolution of the load cell. For all load and temperatures the coefficient of friction is in the range of 0.2-0.3, which is typical for boundary lubrication [6].
The elevated temperature experiment shows slightly lower values in the coefficient of friction. This might be explained by the presence of the thermal film which probably has a low shear strength. Part of this film might still be present on the surface also after rubbing and leads to a reduction in the coefficient of friction. On the other hand it is shown by XP spectroscopy that the films produced at elevated temperatures and at lower temperatures have different chemical structures, which may also cause a different friction force. In the room-temperature experiments the decrease in the coefficient of friction with increasing load is also accompanied by a change in the chemical composition. The increase in phosphates found at higher loads in the contact area might lead to the lower friction values.

4.1.4 Load Cell

The resolution of the 5 N load cell measuring both frictional force and normal load is ± 5 mN. The experiments at low loads are done at 100 mN and 50 mN, the resolution of the load cell is then 5% or 10% of the applied load. While this might be just accurate enough to produce the wear scar, the friction forces are approximately 20 mN and 10 mN, thus the error for the friction force is on the order of 25-50%. This high error results in a large scatter of the data.
at low loads (see Figure 3.22 and Figure 4.2) and makes the interpretation of the friction results at low loads impossible.

In addition it was observed that at high temperatures the load cell drifts in the order of 10-20 mN during the test. This drift influences the measured forces also during the measurement. This value is in the same order as the measured friction force at 50 mN load and therefore this test was omitted in the experiments performed at high temperatures.
4.2 The Tribofilm

When elastohydrodynamic lubrication in a tribological system has broken down, friction and wear can be reduced if a protective film, the tribofilm, is formed on the rubbing surfaces [7]. Tribofilms are formed due to the presence of anti-wear and extreme-pressure additives in the base oil. ZnDTP, one of the most widespread and deeply investigated additives, has been studied previously by our group [4,8-12] and was also used in this work. Despite innumerable studies that have sought to characterize the ZnDTP tribofilms (see [13] and literature cited therein), the literature has not, to date, reached a consensus on the chemical pathways involved in the process of tribofilm formation. Beside different experimental approaches in the tribofilm formation and different analytical techniques used to characterize the tribofilms, one probable reason for these discrepancies could be that ZnDTP acts as a “smart material” [14], producing tribofilms with different chemical and mechanical properties depending on the prevailing tribological conditions.

In this work the tribological conditions (combinatorial step test, see section 3.3) were chosen such that the same coefficient of friction resulted as in standard tribological ball-on-disc tests but due to the step-wise displacement of the ball the tribofilm was formed on a larger area (Figure 3.11). The larger area (ca. 250µm) allowed the ex-situ analysis of the tribofilms by XPS. Tribofilms formed at different loads, as well as adsorption and chemical reaction of the ZnDTP solution on the steel surface, were studied at room temperature and at 150 °C.

4.2.1 Non-contact Area

In each combinatorial tribotest an area of the surface was not subjected to tribological stress. In this non-contact area adsorption of ZnDTP or of products formed during the film formation and carried in the oil to the non-contact area on the steel disc could be studied at the end of the test (duration 5.5 h).

The non-contact area mainly revealed an iron oxide film on the steel surface (Figure 3.16). The O1s signal at 530.2 ± 0.2 eV is characteristic for oxygen in iron oxide, the high resolution spectra
The Tribofilm

of Fe$_{2p}^{3/2}$ revealed a mixed Fe$^{2+}$/Fe$^{3+}$ oxide film. The Fe$^{2+}$ component in the non-contact area is higher than in the Fe$^{2p}$ signal of the oxide film aged for three days (Figure 3.45). Interestingly, the Fe$^{2p}$ spectrum of a sample immersed into a i-ZnDTP/decane solution for the same time as a tribotest (results not shown), but without tribological stress of the surface did not show the change in the Fe$^{2+}$/Fe$^{3+}$ ratio. This might suggest that chemical species produced during the tribological stress caused the changes of the oxidation state of the steel surface.

The intensities of the XPS signals P$_{2p}$, S$_{2p}$ and Zn$_{2p}$ of the adsorbed additive in the non-contact area are all very low (Figure 3.17), a detailed assignment of the chemical state by curve fitting is thus difficult. However, the binding energies were found the same as in the tribostressed areas (Table 3.5) but different from the pure ZnDTP (Table 3.11).

In-situ ATR FT-IR spectra of ZnDTP additive adsorbed on the iron-coated germanium crystal at room temperature showed no changes in peak position or peak shape compared to the transmission spectra of ZnDTP [4]. Adsorption tests performed up to 96 h confirmed these findings [8]. Thus, it can be reasonably assumed that ZnDTP additive adsorbs on the steel surface at room temperature but no decomposition of the molecule occurs. However, the results from the non-contact area of the tribostressed samples might suggest that the surface changes due to chemical species produced during the tribological stress.

**4.2.2 Tribofilms formed at room temperature**

The chemical composition of the tribofilm can be expected to vary with the severity of the tribological conditions [3], or more specifically, with the contact pressure. Systematic investigations on the influence of the applied load are rare in the literature, mainly due to the time needed when working with standard tribological testing. In the present work, the effect of the applied load on the chemical composition of the surface layer in the contact region (tribofilm) could be studied on a single sample using the combinatorial approach and imaging XPS surface analysis.
**Discussion**

**XPS Imaging** The results clearly show that the tribostressed areas (annuli) are different from the non-contact areas: the oxygen O1s map (Figure 3.14) reveals mainly a “phosphate spectrum” in the areas with tribofilm whereas an “oxide spectrum” is found in the areas without tribostress. The phosphate-type O1s spectrum is dominant in the tribostressed areas at all loads with some indication that higher loads lead to an increase in the surface concentration of phosphate. XPS elemental maps, previously obtained from standard ball-on-disc tribotests with 10 N load, already showed the differentiation between phosphate and oxygen type O1s signal. In addition an increased phosphorus, sulfur and zinc concentration was found in the worn area whereas iron was depleted [12]. The same result for the oxygen map was found in this work in the 1 N and 10 N standard tribotest (Figure 3.4) and in the step test with 1 N load (Figure 3.9). It can be concluded that mapping the O1s signal in the scanned mode allowed to differentiate between areas of non-contact and tribostressed areas even in the case where no signs of wear or tribofilm formation can be detected in the optical microscope.

**Chemical States of the Elements** A more detailed analysis of the chemical state of the elements is possible based on the high-resolution XPS spectra (Figure 3.16, Figure 3.17) and the reference compounds (section 3.5). Of special interest are the chemical states of phosphorus, sulfur and zinc – elements contained in the ZnDTP additive that were proposed to react with the iron oxide film to form the tribofilm [12].

The binding energy of the phosphorus P2p\(_{3/2}\) signals from tribofilms formed at room temperature are found at 133.4 eV - 133.7 eV (Table 3.1, 3.3, 3.5), in agreement with literature values for phosphate (133.4-133.8 eV [15,16]). Based on the binding energies the formation of polyphosphates (BE 134.0 - 135.0 eV [16-19]) can be ruled out. The assignment of the phosphorus peak position to phosphorus bond in a non-bridging phosphate agrees well with the findings from the O1s signal.

The oxygen signals in the O1s high-resolution spectra found at 531.6 - 531.8 eV (Table 3.1, 3.3, 3.5) are in agreement, within experimental error, with the position of the non-bridging oxygen in iron phosphate reference compound (531.7 eV, refer to Table 3.14) and the literature [15]. Iron hydroxides
The Tribofilm

(531.7±0.1 eV) could show the same binding energy [20,21]. At room temperature, the intensity of this oxygen peak at 531.7 eV increases with increasing applied load (Figure 3.5, 3.16), as does the amount of phosphorus (Figure 3.17). The intensity ratios between the “phosphate-type” oxygen and the total phosphorus signal intensity, corrected with the appropriate sensitivity factors, are close to the theoretical values for orthophosphates of 1:4 (Figure 3.19). This supports the formation of a phosphate structure, at least at high loads. At lower loads in addition to the phosphates some hydroxides might also be present, causing a high O(II)-to-phosphorus ratio.

The presence of iron phosphate is further substantiated by the occurrence of a peak at 712.6 eV in the iron Fe2p 3/2 high-resolution spectra, measurements on the reference compound iron phosphate (section 3.5.5) showed a peak position at 712.2 eV, literature values are reported at 712.4 eV-712.6 eV [15]. The intensity of the peak assigned to iron phosphate increases with higher applied load (Figure 3.16) parallel to the increase of the P2p and the O1s “phosphate” intensity. The presence of iron phosphate at high loads is in agreement with the formation of iron phosphate in wear particles, as reported by Martin [3].

The Fe2p component at 706.9 eV, assigned to metallic iron, is always present in these tribofilms. This peak shows the highest intensity in the non-contact area and decreases at high loads (Figure 3.16). This increase indicates that the thickness of the film, which covers the steel substrate, is increasing with increasing loads, assuming that a homogeneous tribofilm is present.

The iron Fe2p 3/2 high-resolution spectra are influenced by the X-ray satellite of the Fe2p1/2 peak and the Fe2+ shake-up satellite. The X-ray satellite was compensated applying the X-ray satellite subtraction routine of the CASA XPS software and the Fe2+ satellite was modeled as an 8% contribution of the Fe2+ main peak [22,23]. Despite this careful curve-fitting model, the inspection of the Fe2p 3/2 peak fit at 1N and 5N load (Figure 3.16) shows a small contribution at ca. 716.0 eV that cannot be matched. The origin of this signal remains unclear.
The chemical state of sulfur based on the binding energy of the S2p peak at 161.9±0.1 eV (Table 3.3, Table 3.5) can be assigned to sulfides. Unfortunately, the peak position of the S2p signal does not provide further information about the cation of the sulfide (zinc sulfide, iron sulfide or organic sulfide). The ZnLMM signal (see below) indicates that on the tribostressed surfaces (with the loads and contact pressures adopted in this work) the presence of zinc sulfides can be ruled out. A second sulfur peak at 163.0 ± 0.1 eV introduced to model the S2p signal (Figure 3.17) was assigned to organo-sulfur species (e.g. thiols). It can be assumed that after the reaction of the phosphorus present in the ZnDTP molecule to phosphate, part of the sulfur reacts to form sulfides. The remaining sulfur may react with alkyl chains to form organo-sulfur species. These species are soluble in the lubricant, and only a small amount would adsorb at the surface or become incorporated in the surface film. This could explain the observed progressive depletion of sulfur compared to phosphorus with increasing load (Figure 3.18).

The chemical state of zinc cannot be assigned based on the Zn2p signal due to the small shift between different compounds. XPS measurements on reference substances (section 3.5.3, 3.5.4) show peak positions at 1021.3 eV for ZnO and 1022.1 eV for ZnS, literature values for the same compounds were found between 1021.5-1022.5 eV for ZnO and between 1021.6-1022.0 eV for ZnS (Table 4.3). The measurements of the reference compounds of the present thesis are in agreement with literature values but a relatively large scatter can be observed in the literature values. This scatter might be explained by different sample-charging correction. The use of the Auger parameter (\(\alpha'\)) [24], which is independent of the sample charging, overcomes this problem and gives less diverging values (Table 4.3).
The Auger parameter for the tribofilms formed at room temperature were found at 2010.5±0.1 eV. The Auger parameter of the tribofilms are in between the values found for ZnO (2010.0±0.1 eV) and ZnS (2011.3±0.2 eV), and close to the value of ZnDTP (2010.4 eV). The most relevant data to identify the chemical state of zinc – that of zinc phosphate – were not available in literature, but this work is in progress [28]. Also the possibility of more than one contribution in the ZnLMM spectra has to be investigated further.

### Table 4.3: Auger parameter $\alpha' (=E_k(Zn_{LMM})+E_k(Zn2p_{3/2})$ for tribofilms, thermal films, and reference compounds (including literature values).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zn$2p_{3/2}$ eV (BE)</th>
<th>Zn$_{LMM}$ eV (KE)</th>
<th>$\alpha'$ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tribofilm 25°C 5 N</td>
<td>1022.4</td>
<td>988.1</td>
<td>2010.5</td>
</tr>
<tr>
<td>Tribofilm 25°C 1 N</td>
<td>1022.4</td>
<td>988.2</td>
<td>2010.6</td>
</tr>
<tr>
<td>non-contact 25°C</td>
<td>1022.5</td>
<td>989.5</td>
<td>2012.0</td>
</tr>
<tr>
<td>Tribofilm 150°C 5 N</td>
<td>1022.6</td>
<td>987.8</td>
<td>2010.4</td>
</tr>
<tr>
<td>Tribofilm 150°C 1 N</td>
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</tr>
<tr>
<td>ZnO (own reference)</td>
<td>1021.3</td>
<td>988.6</td>
<td>2009.9</td>
</tr>
<tr>
<td>ZnO [25]</td>
<td>1021.5</td>
<td>988.6</td>
<td>2010.1</td>
</tr>
<tr>
<td>ZnO [26]</td>
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<td>987.7</td>
<td>2010.2</td>
</tr>
<tr>
<td>ZnS (own reference)</td>
<td>1022.1</td>
<td>989.0</td>
<td>2011.1</td>
</tr>
<tr>
<td>ZnS [25]</td>
<td>1022.0</td>
<td>989.3</td>
<td>2011.3</td>
</tr>
<tr>
<td>ZnS [26]</td>
<td>1022.0</td>
<td>989.7</td>
<td>2011.7</td>
</tr>
<tr>
<td>ZnS [27]</td>
<td>1021.6</td>
<td>989.7</td>
<td>2011.3</td>
</tr>
</tbody>
</table>

The Auger parameter for the tribofilms formed at room temperature were found at 2010.5±0.1 eV. The Auger parameter of the tribofilms are in between the values found for ZnO (2010.0±0.1 eV) and ZnS (2011.3±0.2 eV), and close to the value of ZnDTP (2010.4 eV). The most relevant data to identify the chemical state of zinc – that of zinc phosphate – were not available in literature, but this work is in progress [28]. Also the possibility of more than one contribution in the Zn$_{LMM}$ spectra has to be investigated further.

### Composition

Very little work has been published about the quantitative composition of tribofilms. This is probably due to difficulties in quantification of many of the surface analytical methods (e.g. XANES, AES) used to study tribofilms. In quantitative XPS analysis it has
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to be considered that the surface composition might be inhomogeneous not only in the z-directions but also in the horizontal direction. Therefore, in this work only relative intensities of elements from the tribofilm are presented.

The oxygen-to-phosphorus ratio (Figure 3.19) and the low intensity of the bridging oxygen in the room temperature tribofilms (Figure 3.16) indicate that orthophosphates (and no polyphosphates) are present probably with some organophosphates. In the literature zinc is usually reported to be present as the cation in the (poly)phosphate [13]. For orthophosphates a phosphorus-to-zinc ratio of 0.75 would be expected, but the measured values vary between 1.8-2.8 for the 1 N and the 5 N area. Since the measured phosphorus-to-zinc ratio is higher than 0.75 there are not enough zinc cations to compensate for the negative charges of the phosphate anions. This would support the indication from the Fe 2p spectrum that part of the tribofilm is also composed of iron phosphate.

Lateral Inhomogeneity

The lateral resolution of the imaging XPS technique used in this work was not sufficient to reveal inhomogeneities in the micrometer range. From the optical micrographs (Figure 3.12) and from the scanning Auger maps (Figure 3.21) it can be seen that the wear scars produced during the tribological tests are not homogeneous. This is in agreement with the ToF-SIMS analysis of wear tracks [9] and with literature on tribofilms formed on steel with ZnDTP additive [29]. The consequences of this inhomogeneity are two-fold: first, the XPS measurements in this and other work [16,30] report an average chemical composition over some µm² that might consist of areas with a tribofilm and areas where no tribofilm has been formed, thus the composition and thickness estimated are average values. Second, the calculated contact pressure and the film formation mechanism have to be reviewed. These inhomogeneities indicate that the load is carried by some (microscopic) asperities. The highest tribological and thermal stresses are found in these contact areas, which form the real contact area and in which the tribofilm is formed. The amount and the composition of the tribofilm are therefore dependent on the size and the tribological stress in the real contact area.
4.2.3 Thermal Films

One of the principal questions still open in the friction and wear reducing action of the ZnDTP additives is if the additive reacts thermally (due to the high temperature formed by friction of metal-metal asperities) [31] or if the local pressure and the shear stress induced promote a different reaction pathway. The study of thermal films (formed without tribological stress) was thus frequently used to investigate the effect of high temperatures. In-situ ATR FT-IR tests with an iron-coated germanium crystal in a 20 wt-% ZnDTP/PAO solution showed after 38 h exposure to 150°C a rearrangement of the ZnDTP molecule with the formation of P-O-P bonds and the elimination of alkanes [8,9], thus the formation of polyphosphates. XPS [16] and XANES results [2,32] are in agreement with these findings.

Chemical States of the Elements

The oxygen O1s spectrum on thermally formed films in this work (Figure 3.30) shows a high bridging-oxygen concentration at binding energies of 533.3 eV beside the main peak at 532.0 eV. Literature values for the binding energy of bridging oxygen (P-O-P or P-O-C) are found between 533.1-534.1 eV [16-19]. This supports that the thermal film consists of polyphosphate.

The binding energy of phosphorus at 133.8 eV (Table 3.8) is slightly lower compared to literature values for polyphosphates 134.0 - 135.0 eV [16-19]). Beside problems of correction for sample charging (see Appendix B), only little data has been published about the P2p signal in polyphosphates of various chain length [19]. However, it can reasonably be concluded that thermal films formed at 150°C on steel are composed of long-chain polyphosphates. On the other hand, the phosphorus-to-zinc ratio (0.7) indicates that more zinc than needed in the polyphosphates is present, suggesting that also short chain phosphates are formed.

No iron signal from the substrate is detectable on the thermal film. Clearly, the thermal film is completely attenuating the electrons arising from the substrate, which indicates that the film is thicker than three times the inelastic mean free path of the iron signal, which is approximately 10 nm.
Discussion

The Auger parameter value of zinc for the thermal film is remarkably different from the contact-area values (Table 4.3). In the thermal film the Auger parameter is found at 2009.9 eV, close to the value of ZnO, but the assignment to ZnO would not agree with the O1s signal of the thermal film, where the oxide signal at 530.2 eV is only very weak (Figure 3.30). This indicates that neither ZnO nor ZnS are present in the thermal film. The investigation of zinc phosphate and polyphosphates reference substances are ongoing [28,33].

Two different chemical states of sulfur were found in the thermal film (Figure 3.30): a first at 162.4±0.1 eV which might be assigned to organic sulfides, and a second at 169.3±0.1 eV assigned to sulfate (Table 3.8). The zinc Auger parameter (Table 4.3) indicates that no zinc sulfide is present. Since no other metal cations were identified on the thermal surface, the sulfides are most probably of organic nature.

4.2.4 Tribofilms Formed at Elevated Temperature

Tribotests in the presence of ZnDTP are thought to be most representative at elevated temperatures for the majority of technical applications, because this type of additives is used to reduce wear on sliding steel parts operated at elevated temperatures (e.g. in internal combustion engines). In the elevated temperature experiments PAO was used as lubricant instead of decane. Because of the low boiling point of decane (174°C) it showed significant evaporation at temperatures above 100°C. A commercial, purified ZnDTP was used as additive because of the low solubility of i-ZnDTP in PAO. Previous experiments with in-situ ATR tribometry and ex-situ XPS analysis with the same lubricant-additive system but with 20 wt-% of the additive have shown that at 150°C iron/zinc orthophosphates are formed in the tribostressed areas [16].

Imaging XPS The oxygen O1s map of the combinatorial step test at elevated temperatures (Figure 3.26) shows higher signal intensity in the wear tracks than in the non-contact areas. With the LLS analysis the spectra can be decomposed into signals of the non-contact area and the tribostressed area. The corresponding chemical-state maps (Figure 3.26) were constructed. No other XPS imaging maps were recorded due to the low signal intensity of the other elements.
The oxygen O1s spectra recorded in the tribostressed areas at different loads (Figure 3.27) show three contributions (Table 3.6): The main peak at 531.9 eV is assigned to oxygen in a phosphate or non-bridging oxygen in a polyphosphate. The second O1s peak, which is found at 533.2±0.2 eV, is assigned to bridging oxygen in polyphosphate, which is in agreement with literature values [16-19]. The relative intensity of this peak compared to the intensity of the non-bridging oxygen peak is higher in the tribofilms produced at elevated temperature than in the films formed at room temperature. Also the binding energy at elevated temperature is higher than at room temperature, which is an indication that in the case of the elevated temperatures the signal arises from bridging oxygen, while at low temperatures some water contribution might also be present. In addition the angular-resolved spectra on the elevated-temperature experiment (Figure 3.29) show no change of the relative intensity of this peak compared to the main peak at 531.8 eV at the different angles, indicating a homogeneous tribofilm. The contribution from water (which would adsorb on the outermost layer of the film) can be ruled out as an increase at small angles would be expected.

The phosphorus P2p spectra (Figure 3.28) show only one signal at all loads, the highest intensity being found in the non-contact area. The peak binding energy (Table 3.6) at 133.5±0.1 eV would be in agreement with phosphates (133.4-133.8 eV [15,16]) but low for polyphosphates (134.0 - 135.0 eV [16-19]). As for the O1s signals, a mixture of these two compounds can be assumed to be present in the tribofilm. The phosphorus-to-zinc ratio of the areas produced at elevated temperature is approximately 1 and the phosphorus-to-oxygen ratio is between 4 and 4.5. These values would agree with the presence of a pyrophosphate (Zn₂P₂O₇), if it is considered that part of the oxygen is also bond in the sulfate ion.

Two chemical states were revealed for sulfur in the S2p spectra (Figure 3.28), a first at 162.0±0.1 eV was assigned to sulfide, a second one at 169 eV to sulfate (Table 3.6). It is interesting to note that the highest intensity of sulfide is found in the non-contact region whereas sulfate shows the maximum intensity at high loads.

The chemical state of zinc according to the Auger parameter of 2010.3 eV (Table 4.3) is closer to ZnO than ZnS, the presence of
zinc cations in the phosphate / polyphosphate layer is also possible. It is interesting to note that the zinc intensity (as seen by comparing the Zn3s / P2p ratio in Figure 3.17 and 3.28) is much higher in the tribofilms formed at higher temperatures.

The iron Fe2p contribution is completely absent in the non-contact area (Figure 3.28). This result is in agreement with the pure thermal film where also no iron can be detected with XPS. Apparently, the thermal film is completely attenuating the electrons arising from the substrate, which indicates that the film is thicker than three times the inelastic mean free path of the iron signal, which is approximately 10 nm. In the tribostressed area, the iron signal can be detected and the film thickness must be smaller than 10 nm (or the film is inhomogeneous). However, the signal intensity is much smaller than in the experiments at room temperatures and no metallic iron (706.9 eV) can be observed. The signal intensity increases with increasing load, with the exception of the 5 N area where again a lower intensity was found. Due to the low signal intensity, causing a low signal-to-noise ratio and considering the difficulties in peak assignment in the Fe2p3/2 signal discussed above, no detailed analysis of the peak fit is possible. However, the angular resolved experiments presented in Figure 3.29 indicate that the Fe3+ signal is higher on the outside of the oxide layer, while the Fe2+ signal is higher on the inside. This can be interpreted such that the thermal film oxidizes the surface of the substrate. On the other hand, the oxide surface is not dissolved by the film because no contribution of iron can be found in the pure thermal film.

**Effect of Time in Thermal Film Formation**

A surprising fact is that the tribofilm is not covered again by a thermal film after it has been formed. Especially the tribofilms formed in the beginning of the test remain in the heated solution for a few hours, so it could be expected that these films would be re-covered by a thermal film. This is apparently not the case, because on the thermal film, the iron signal is completely attenuated by the film, while on the tribofilm it can be observed (Figure 3.28). If a thermal film would cover the tribofilm, it would be expected that the iron signal vanishes again. There might be two explanations for this behavior, either the tribofilm is inert to thermal film formation, or all of the additive in the solution has reacted after a certain time and therefore no further thermal film is formed.
This point has been investigated by immersing a tribostressed sample after the XPS analysis into a fresh additive-oil solution for 5.5 hours. The subsequent XPS analysis showed that no iron can be detected in the areas tribostressed before. Thus a new thermal film was formed. This shows, that the tribofilm is not inert for thermal film formation and it indicates that the thermal film is forming during the first period the solution is heated. This explains also why the 5 N area in the combinatorial tribotest at 150°C shows a more “thermal-film-like” composition and does not fit into the series of the other loads. The 5 N area was the first area tribostressed after the running in. Probably at this point still some unreacted additive was left in the solution and the surface was partially covered with a thermal film. The 5 N tribotest is finished 3.5 h after starting the experiment (0.5 h heating up plus 2 h running in and 1 h tribotest at 5 N). Since the 1 N experiment seems not to be affected by an additional thermal film, it can be concluded that the thermal film formation stops after approximately 3 h. Also on the other tribostressed areas no indication for a thermal film was detected.

4.3 Film-formation Mechanism

The film-formation mechanism is different for tribofilms at room temperature and at elevated temperatures. This can be seen from the discussion on the chemical state of the elements present in the film and also the anti-wear performance is different at room temperatures and at elevated temperatures. While on the room-temperature tribofilm, considerable wear is still occurring, although it is significantly reduced compared with measurements without additive [12], the film formed at elevated temperature is strong enough to prevent wear on the surface of the ball and the disc.

4.3.1 Effect of Load

A change in the surface composition with load is observed in tribofilms formed at both room temperature and at elevated temperatures. In the room-temperature experiments with increasing load, more phosphate was formed on the surface. On the other hand, the oxygen signal shows that oxide is always present. The Auger O_{KLL} map of the 1 N region (Figure 3.21) shows areas of high and low oxygen signal, which suggests that phosphates are particularly formed in the areas of the highest tribological stress (resulting in a
strong oxygen signal), while in the areas of low intensity mainly oxides are present. Surface analytical methods with higher spatial resolution would be needed to confirm this assumption and investigate the local chemistry of these areas.

On the elevated temperature tribofilms the dependence of the relative concentration of the elements on load is not as strong as at room temperature. This is probably due to the formation of the thermal film prior to the tribotest. The phosphorus-to-sulfur ratio and the phosphorus-to-zinc ratio show only small changes with increasing load. An increase in the iron signal intensity with increasing load (not considering the 5 N area, see section 4.2.4) can be related to the (partial) removal of the thermal film. Increasing load results in a higher contact pressure and larger contact area and the subsequent increased removal of thermal film. Similar to the differences observed at room temperature, the different intensity ratio in the tribofilms formed at elevated temperatures can be explained by the different amount of tribofilm formed in the contact area due to the increase in the real contact area. Also in this case, the signal measured at low loads is probably a mixture of the tribofilm formed and the remaining thermal film.

### 4.3.2 Effect of Temperature

**Room Temperature**

The proposed mechanism of reaction at room temperature is the following: In the non-contact area a thin, organic layer (including ZnDTP or LI-ZnDTP) is adsorbed. Due to the mechanical and thermal stress during the tribological contact, the adsorbed species and additive molecules from the solution react with the iron oxide to form a protective film. This takes place in the region of highest mechanical and thermal stress. The phosphorus, oxygen, and zinc in the ZnDTP react with oxygen from the oxide and dissolved oxygen in the oil to form an iron phosphate-containing film, while organo-sulfur species are released into the solution. Some of these species may react to form organic sulfides that are incorporated in the film or adsorbed on the surface. The phosphate film is thin (<5nm) and inhomogeneous. The composition and amount of phosphate film formed on the surface depend on the applied load. The higher the load, the more phosphate is found on the surface. This may be explained by the fact that the higher the applied load, the higher the real contact area. The highest tribological and ther-
mal stresses are found in the real contact area and therefore the tribofilm is formed preferentially in these areas. The amount and the composition of the tribofilm are therefore dependent on the size and the tribological stress in the real contact area.

**Elevated Temperature**

A relatively thick film is formed on the sample due to the purely thermal activation. The isomerization of the ZnDTP, which has been proposed by several authors [2,34] cannot be detected directly but would be supported by the depletion of sulfur in the contact areas. The alkyl chains move from the oxygen to the sulfur (refer to reaction (1)-(5) in Chapter 1) and during the reaction of the thiophosphate to poly(thio)phosphate, part of the organo-sulfur species may be released to the lubricant. This reaction is finished after approximately 3 h (see section 4.2.4). The thermal film must be quite soft because it is partially removed while being tribologically stressed. The other part reacts due to the tribological stress to form shorter-chain-length phosphates, probably pyrophosphate. The (partial) formation of iron phosphate (which was reported for severe conditions [3]) can not be excluded, but could also not be confirmed due to the low signal-to-noise ratio of the Fe2p signal. Also a small concentration of sulfate could be detected on the tribo-stressed film.

This mechanism is in agreement with most of the literature. The shortening of the chain length due to the tribological stress would support the model of Martin [35], where the shortening is proposed to be due to the reaction of zinc phosphates with iron oxide (refer to reaction (7) in section 1.3). The tribofilm thickness in the system under investigation (< 10 nm) is in agreement with interferometric measurements (5-25 nm) done in a ball-on-disc configuration (53 N) [5]. A different experimental setup (reciprocating line contact, 220 N) revealed a larger film thickness (40-100 nm), estimated using the P K-edge XANES edge jumps [36].

**4.3.3 Effect of Native Oxide Film**

The air exposure of the sample prior to the tribotest seems to influence the tribological behavior at high loads (refer to Figure 3.22). This may be related to the different oxidation of the surface immediately after polishing and after three days of air exposure. The comparison of the Fe2p spectrum shows that more Fe$^{3+}$ is present.
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in the aged sample. This is can be explained by the formation of Fe$_3$O$_4$ instead of Fe$_2$O$_3$ on the surface [37]. A decrease of the metallic signal in the Fe2p spectrum after 3 days indicates that the thickness of the oxide film increases with time. The relative concentration of Fe$^{2+}$ and Fe$^{3+}$ of the oxide layer of a Fe10Cr steel was found to be stable after 24 h [38]. Therefore, it can be assumed that after three days a stable oxide film is formed. The increased thickness might be the reason for the higher stability of the aged film and the break-down of the non-aged films at 5 N load and the subsequent higher friction coefficient.

4.4 Oscillating Load Tests

Oscillating load tests were used in this study to expand the number of parameters which can be explored in one single experiment. They were used to apply a series of loads spatially separated from each other, which should allow the measurement of wear in dependence of the applied load after the test. Each test consisted of a series of wear tracks and on each wear track a different duration of the test was chosen in order to explore the time-dependence of friction and wear.

4.4.1 Friction

Accuracy of Normal Load

The first point which has to be evaluated is whether the tribometer was able to maintain the programmed load accurately. This can be seen in Figure 3.32 for a particular rotation of the disc. The measured normal load shows an almost triangular shape. Since the load was programmed to have a linear increase and decrease between the minimum and maximum values, this demonstrates that the accuracy of the applied load was very good. In Figure 3.33 and Figure 3.34 at the bottom the normal load averaged over all turns during the test can be seen. Also this shows, that the normal load can be maintained accurately.

Stick-Slip

Figure 3.33 shows, that in the case of the test in pure PAO strong stick-slip is occurring. After approximately 30 turns the stick-slip is always occurring at the same spots on the sample. This can be particularly well observed in the polar plot of the pure PAO experiment (Figure 3.35). In the processed plot, the areas where the “slip” is occurring are always at the same (rotational) position at
each turn. In the experiment with additive a similar behavior can be seen. The “slip” is also occurring at almost the same spot as in the previous turn, but these locations seem to move with the ongoing tests (Figure 3.36). The lower friction force at which the slip is occurring in the test with additive (see Figure 3.38) leads to much smaller distances in between the “sticking” sites. Since the lateral spring constant is the same in both experiments, the disc has to move a much smaller distance to reach the slip force for the experiment with additive than in the case of the pure PAO.

Surface Modification

In Figure 3.39 the magnified area of the tribologically stressed area of the pure PAO experiment shows different wear scar depths along the scars. It can be assumed that the deeper areas form a kind of pocket, where the ball rests and when the tangential force is high enough it jumps to the next pocket. A close look at Figure 3.35 shows, that the highest COF values appear only after the separation of the sticking sites from each other, thus after the formation of these pockets. It can be assumed that part of the measured tangential force in the “slip” moment is due to the force needed to tear the ball out of these pockets.

In Figure 3.40 in the magnified area of the sample produced in presence of additive no such modification of the wear scar can be observed. The open question is, why the “slip” is also occurring at the same locations in these experiments? One explanation might be that these sites are chemically modified due to the tribological stress and the presence of the additive. A very interesting question would then be, what is the chemical composition in the “sticking” sites and which is the composition in between? The analysis of such samples with surface-analytical methods with high spatial resolution may provide a deeper insight into the mechanism of stick-slip.

Coefficient of Friction versus Load

The load dependence of the coefficient of friction is different for the experiments with and without additives. Figure 3.37 shows that in the pure PAO the coefficient of friction increases with increasing load, while in the experiment with additive the coefficient of friction decreases with increasing load. The increase in the pure PAO is probably due to the increased removal of the oxide layer at high load and the contact with the underlying iron. Part of the in-
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crease might also be related to the formation of the pockets discussed above.

The decrease of the coefficient of friction with load in the experiment with ZnDTP agrees with the results from the combinatorial step test, where the same trend was observed. This is probably due to the formation of a phosphate film, which increases with increasing load as was shown in the combinatorial step test. The film prevents contact between the ball and the iron surface which decreases the coefficient of friction. At lower loads less film is formed and the ball might be in partial contact with the iron surface causing higher friction values. It is surprising that at low load the coefficient of friction is higher than in the experiment without additive. So far no explanation for this behavior could be found.

4.4.2 Wear

The cross-section of the wear scars increases with load and with duration for all experiments presented. This shows, that within one experiment the evaluation of the cross-section is a reasonable measure for the wear produced under different stress. On the other hand, as it can be seen in Figure 3.42, two experiments produced under nominally the same conditions do not produce the same absolute results. This is most obvious in comparing the cross-section of the deposited material (Figure 3.44). In between the first and the second experiments, the values vary by a factor of two.

The large differences between the samples produced at the same conditions prevent the possibility to detect a trend between the experiments with and without additive. In the direct comparison of these experiments for the 30 turn and the 100 turn test (Figure 3.43) it can be seen that the wear result seem not to be influenced by the composition of the lubricant.

There are several reasons which may cause the non-reproducible results. The first reason might be that the sample treatment after the test is probably insufficiently reproducible. For instance no defined protocol for solvent cleaning was used. The samples were cleaned multiple times in an ultra-sonic bath (each time with fresh solvent) until all of oil was removed from the surface, but the total time of the cleaning was not defined. This might lead to differenc-
Advantage of Combinatorial Tribotests

es in the amount of material removed from the sides (and probably from inside) of the wear track. Another reason might be that the second two samples were kept for two weeks in dry air prior to the laser profilometric analysis because the system was broken. This might also be the reason for the much smaller amount of deposited material observed on these samples.

A third point may be, that the differences in wear scar depth between the experiment with and without additive may not be large enough. A soft substrate material was used to produce a large wear scar. Apparently also with the lubricant additive the wear scars were large, which indicates that part of this scar might be formed by plastic deformation of the sample, which cannot be prevented by the lubricant additive.

4.5 Advantage of Combinatorial Tribotests

The combinatorial step test in combination with the use of imaging XPS made the analysis of a tribological parameter library possible. Without the use of the step test, the analysis of areas tribostressed at low loads would not have been possible because at low loads the wear scar is smaller than the spot size of the XPS analysis and the measured signal would also contain spectroscopic information from the non-contact area. The comparison of the tribological and spectroscopic results of the step test at 1 N load and the standard test at the same load indicates that the step test is a useful approach to enlarge the worn area. On the other hand, the O_KLL map of the 1 N wear scar produced at room temperature (Figure 3.21) shows that the tribofilm formed is inhomogeneous on the micrometer scale. It can be assumed that the real contact area is an important factor in the tribofilm formation. The optical micrograph of the 1 N and 10 N wear scar of the standard test indicate that also in the standard tests similar inhomogeneities might be present. Spectroscopic techniques with higher lateral resolution might give additional insight in the local chemical composition of the surface.

The combinatorial tribotest requires the spectroscopic mapping of the tribostressed surface. With room-temperature samples, only the wear scars produced at 1 N and 5 N could be detected visually, the other rubbed areas could not be seen. The i-XPS maps clearly show all tribostressed regions and allow the selection of the areas
Discussion

of interest. The small-area XPS analysis in these regions gives detailed information about the chemical state of the elements and the composition of the surface film.

This demonstrates how i-XPS with the ability of mapping of different chemical states in combination with small-area XPS is a useful tool for the analysis of combinatorial samples. However, the time required to map a surface with reasonable spatial and spectroscopic resolution is enormous and is only possible for elements having a strong signal intensity. In addition the information density of the parameter library is limited by the analyzed area, the spatial resolution and the required time for the analysis. These problems may partially be overcome in the future because of the availability of newer XPS instruments, which allow the analysis of surfaces with a resolution of a few micrometers in reasonable times. Also, the use of other surface analytical techniques as ToF-SIMS, Auger Spectroscopy or synchrotron-based spectroscopic methods may be considered.

XPS is a powerful method for analyzing tribostressed surface. However, there are also some problems with the analysis of tribological samples, which have to be considered.

The surface sensitivity of the method and the need of an UHV environment makes the removal of the oil prior to the analysis necessary. This is commonly done by solvent rinsing which also removes part of the tribofilm [14]. In addition the sampling depth of the method is limited to a few nanometers. It has to be borne in mind that thermal films or tribofilms may be tens of nanometers thick and that the surface layer contains only part of the information.

Imaging XPS and small-area XPS require long acquisition times. This implies the danger that the sample is changed due to X-ray irradiation. Therefore, the stability of the sample under X-ray irradiation has to be analyzed to validate the results.

**Oscillating Load Test**

The oscillating load test produces valuable information about the tribological behavior of a lubricant-additive system under a series of conditions. This experimental setup allows the measurement of the coefficient of friction and wear as a function of the normal load
and the duration of the test. The friction results were in good agreement with friction results from the combinatorial step test.

Wear was found to increase with increasing load and duration. However, in the setup used in this work, the interpretation of the wear results is difficult. A redesign of the experiment with different materials to reduce plastic deformation and a standardized sample treatment may result in a useful method to analyze friction and wear in dependence of a set of experimental conditions.
Discussion

References


Discussion
CHAPTER 5

CONCLUSIONS AND OUTLOOK

In the final chapter of this thesis the most important conclusions that can be drawn from this work are presented. Open questions and proposes experiments for their clarification are also addressed, as well as ideas for the further development of the tribological combinatorial approach.
5.1 Conclusions

The development of new lubricant additives (necessary due to more severe environmental regulations and increasing demands from industry) has been a very time consuming procedure: single ball-on-disc tests have to be performed for every combination of the tribological parameters (load, velocity) and the lubricant additive formulation. The goal of this thesis was to develop a new type of tribotest based on the combinatorial approach that should markedly reduce the time of lubricant additive testing. In addition not only tribological data (coefficient of friction) but also the tribofilms formed under different conditions were to be analyzed with imaging and small-area XPS.

Two types of combinatorial tests (based on the traditional ball-on-disc test) were developed and successfully tested. Each of them was designed to investigate a different aspect of the relationship between friction, tribofilm formation and wear produced during this friction process:

- The combinatorial step test was designed to produce several tribologically stressed areas (annuli) with different loads applied on a single disc. The tribologically stressed areas were then analyzed by imaging and small-area XPS analysis after the tribotest. The parameters studied in this test are load (0.05 – 5 N) and temperature (25 °C and 150°C). The tests were performed in presence of a solution containing ZnDTP additive.

- The oscillating load test was designed to gather results of friction and wear in dependence of the applied load and the test duration on a single sample. Results from tests performed in pure PAO and in a solution of a commercial purified ZnDTP in PAO were compared. In these tests no surface analysis was performed.

Combinatorial Step Test

The principle of this new test, a stepwise displacement of the wear track by 25 µm every 5 turns of the disc in order to create tribostressed areas sufficiently wide for XPS analysis, was found to be successful. The coefficient of friction obtained was similar to the standard ball-on-disc test. Imaging XPS surface analysis showed that the oxygen O1s signal was especially sensitive to changes in
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the chemical environment (oxide type or phosphate type) in the tribofilm, and thus by LLS curve fitting of the i-XPS maps the tribostressed areas could be clearly identified even if they were not visible in the optical micrographs.

The load dependence of the tribofilm composition and the chemical state of the elements in the tribofilm were investigated by imaging XPS and small-area XPS. At room temperature, where only a few papers have been published to date on tribofilm formation, new insight into the generation of tribofilms was obtained. It was shown that an increasing amount of phosphate was formed with increasing load and that part of the phosphate is iron phosphate. In non-tribostressed areas the XPS surface analysis results showed the adsorption of some species originating from the additive and a change in the oxidation state of the iron.

At elevated temperature the current understanding of tribofilm formation and the film composition could be confirmed. It was shown that the formation of the thermal film prior to tribological stress plays an important role in the tribofilm formation. The thermal film formed showed long-chain polyphosphates and the length of these chains decreased with increasing load during the tribotest.

Due to the spot size of the XPS analysis (120 µm) used in this study (determined by the XPS instrument used) the wear tracks had to be quite wide to be analyzed (produced by stepping the ball) and lateral inhomogeneities of the micrometer scale could not be analyzed. Thus, the results have to be considered as average values at a given load.

Oscillating Load Test

In the oscillating load test the friction and wear behavior was analyzed in a two-dimensional parameter library (load, duration). The oscillating load test was run in pure PAO and in a solution of ZnDTP in PAO at room temperature. Clear differences could be observed in the coefficient of friction between the two experiments. While in the pure PAO the coefficient of friction increased with increasing load, it showed a decrease with increasing load in the experiment with ZnDTP.

After the tribotest the sample topography was analyzed by laser profilometry in order to obtain information on the depth of the
Conclusions and Outlook

wear tracks and the amount of worn material as a function of the applied conditions (load, duration). An increase of wear with both increasing load and duration could be observed. However, the absolute wear values measured on the samples showed a low reproducibility, which prevents the comparison of the experiments with and without additives. This might partly be due to plastic deformation of the disc that is independent of the wear and cannot be reduced by a lubricant additive.

These examples demonstrate that with the combinatorial tribotests a parameter library can be produced and evaluated with respect to different aspects (chemical composition, friction behavior, wear).

5.2 Outlook

The successful use of the combinatorial approach in tribotesting has been demonstrated by the production of parameter libraries on a single disc. However, the combinatorial approach could be optimized regarding the parameters varied, the information density in the library and the reproducibility in the creation of the parameter library.

Parameter Library

The parameters varied in the presented experiments are load, duration and the presence and absence of a lubricant additive. Other (new) lubricant additives could thus be tested in the same way. Beside load and test duration the relative velocity between the two sliding bodies should be explored as new parameter. By changing the sliding velocity the contact temperature is expected to change which might influence the film-formation mechanism. This could be done with the combinatorial step test at constant load but varying sliding velocity in the different annuli or in combination with the oscillating load test.

Information Density

The information density (number of annuli produced in the combinatorial step test) of the parameter library is limited due to the limited lateral resolution of the i-XPS instrument used in this study. This problem may be overcome in the future by the use of new XPS instruments with a spatial resolution down to a few micrometer, which can acquire high-resolution spectra within a reasonable time. Other surface analytical methods (e.g. ToF-SIMS, AES or synchrotron-based methods (XANES, PEEM)) with spatial resolu-
tion in the sub-micrometer range can provide additional information about the presence of lateral inhomogeneities in the tribofilm and their importance in tribofilm formation.

**Tribofilm**
There are also still open questions regarding the tribofilm composition and structure, which could not be solved in the current study. For instance, the role of sulfur is still not clear. From the presented results it can only be said that part of the sulfur is present as a sulfide but it could not be determined which cation is present or if it is an organic sulfide. The two-dimensional chemical-state plot of sulfur might in this case give further information about the chemical bonding of sulfur. It is also not yet fully understood how the quantitative results can be matched with the spectroscopic results. The relative intensity of phosphorus, zinc and oxygen cannot be explained completely with the proposed model. Further work also needs to be done in this respect.

**Reproducibility**
It has been observed in the oscillating load test that the reproducibility of the wear results was a critical point. A standardized protocol for sample handling before and after the generation of the parameter library is needed. In respect to the materials selection it would be necessary to increase the hardness of the substrate material to avoid plastic deformation. In this selection it has to be considered that it is necessary to locate the wear on the disc and to avoid wear on the sliding ball. This is important because otherwise the wear from the ball gives a contribution to the total wear which cannot be measured in dependence of the applied conditions. A possible combination would be a steel with a medium hardness (e.g. non-hardened 100Cr6) in combination with hardened 100Cr6 balls.

**Screening of Additives**
Once an appropriate experiment is found, the results should be verified with conventional experiments. The friction coefficient and the wear results of the oscillating load test should be compared with results from standard ball-on-disc experiments where the same parameters are systematically modified on different samples, to verify if the dependence on the parameters is the same as observed in the combinatorial experiment. Further, it might be interesting to try to simulate the tribological conditions of different industrial applications on a parameter library and to see if the performance corresponds to the results form the tribological test. If
Conclusions and Outlook

this is successful, the performance of an unknown lubricant additive could be screened for the use in different applications and promising candidates selected for further investigations.
In this appendix the detailed peak-fit parameters of the data presented in Chapter 3 will be shown. The data is structured in the same order as it appears in the results section.
### A.1 Single Wear Track 1/10 N and non-contact area

**Table A.1**: Peak-fit parameters of the 10 N region

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<tr>
<th>Name</th>
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<th>Line Shape</th>
<th>R.S.F.</th>
<th>Area</th>
<th>corr. Area</th>
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<td>CPS*eV</td>
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### Table A.3: Peak-fit parameters of the non-contact region

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### A.2 Comparison Step Test and Spiral Test

**Table A.4: Peak-fit parameters of the step test region**

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**Table A.5: Peak-fit parameters of the spiral test region**

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## Table A.6: Peak-fit parameters of the non-contact region

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<th>Line Shape</th>
<th>R.S.F. CPS*eV</th>
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### A.3 Combinatorial Step Test Ambient Temperature

**Table A.7:** Peak-fit parameters of the 5 N region

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<th>Energy (eV)</th>
<th>FWHM (eV)</th>
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<th>Area (CPS*eV)</th>
<th>corr. Area (CPS*eV)</th>
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<th>Line Shape</th>
<th>R.S.F. (CPS*eV)</th>
<th>Area corr. (CPS*eV)</th>
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### Table A.9: Peak-fit parameters of the 0.5 N region

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## Peak-Fit Parameters

### Table A.10: Peak-fit parameters of the 0.1 N region

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### Table A.11: Peak-fit parameters of the 0.05 N region

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ZnLMM (kinetic-energy scale)

Fe(0) met 706.95  1.30  GL(85)T(0.63)  24.6  1006  40.8
Fe(II) 709.35  2.80  GL(45)T(3)  24.6  2839  115.4
Fe(III) 710.95  3.00  GL(45)T(3)  24.6  1640  66.7
FePO4 712.6  3.00  GL(45)T(3)  24.6  687  27.9
Table A.12: Peak-fit parameters of the non-contact region

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<td>209.5</td>
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<td>1.90</td>
<td>GL(30)</td>
<td>3.08</td>
<td>75</td>
<td>24.4</td>
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<td>2023</td>
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<td>GL(45)T(3)</td>
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### A.4 Combinatorial Step Test 150°C

#### Table A.13: Peak-fit parameters of the 5 N region

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<th>Energy (eV)</th>
<th>FWHM (eV)</th>
<th>Line Shape</th>
<th>R.S.F. (CPS*eV)</th>
<th>Area (CPS*eV)</th>
<th>corr. Area (CPS*eV)</th>
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<td>3.08</td>
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<td>271.5</td>
</tr>
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<td>1.76</td>
<td>GL(30)</td>
<td>3.08</td>
<td>163</td>
<td>52.8</td>
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<td>GL(20)</td>
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<td>GL(20)</td>
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<td>GL(20)</td>
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<td>509</td>
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<td>GL(45)</td>
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<td>305</td>
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<td>GL(45)</td>
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<td>GL(45)</td>
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#### Table A.14: Peak-fit parameters of the 1 N region

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<th>Line Shape</th>
<th>R.S.F. (CPS*eV)</th>
<th>Area (CPS*eV)</th>
<th>corr. Area (CPS*eV)</th>
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<td>1.62</td>
<td>GL(30)</td>
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<td>1.79</td>
<td>GL(20)</td>
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<td>8.09</td>
<td>286</td>
<td>35.3</td>
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<td>162.1</td>
<td>1.65</td>
<td>GL(45)</td>
<td>3.57</td>
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<td>GL(45)</td>
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<td>GL(45)</td>
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Table A.15: Peak-fit parameters of the 0.5 N region

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Table A.16: Peak-fit parameters of the 0.1 N region

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<td>7.7</td>
</tr>
<tr>
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<td>133.45</td>
<td>1.65</td>
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<td>(kinetic-energy scale)</td>
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Table A.17: Peak-fit parameters of the non-contact region

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<th>Area corr. (CPS*eV)</th>
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<td>1.65</td>
<td>GL(45)</td>
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<tr>
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<td>GL(30)</td>
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<tr>
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<td>GL(30)</td>
<td>3.67</td>
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</tr>
<tr>
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<td>1.96</td>
<td>GL(20)</td>
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<td>(kinetic-energy scale)</td>
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</table>

A.5  Thermal Test at 150°C

Table A.18: Peak-fit parameters of a thermal film (5.5 hours, 1 wt-% ZnDTP (Hitec) solution at 150°C). The sample charging has been compensated by referencing the main C1s contribution to 285.0 eV, which resulted in a sample charging of 0.96 eV. The values presented are corrected for sample charging.

<table>
<thead>
<tr>
<th>Name</th>
<th>Energy (eV)</th>
<th>FWHM (eV)</th>
<th>Line Shape</th>
<th>R.S.F. (CPS*eV)</th>
<th>Area corr. (CPS*eV)</th>
</tr>
</thead>
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</tr>
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<td>1.89</td>
<td>GL(30)</td>
<td>3.08</td>
<td>1912</td>
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<td>1.90</td>
<td>GL(20)</td>
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</tr>
<tr>
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<td>533.25</td>
<td>1.90</td>
<td>GL(20)</td>
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<tr>
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<td>1.65</td>
<td>GL(45)</td>
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<td>1.65</td>
<td>GL(45)</td>
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<td>890</td>
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<td>(kinetic-energy scale)</td>
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<td>1.65</td>
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<td>2.57</td>
<td>2519</td>
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</table>
This appendix deals with special details which one has to consider during XPS analysis of parameter libraries and tribofilms. These are the stability of the sample under X-ray irradiation and the charge correction methods applied.
B.1 Stability of Tribofilms During X-Ray Irradiation

Imaging and small-area XPS require long acquisition times during which the sample is constantly exposed to X-ray irradiation and radiational heat originating from the X-ray source. It is important that the analyzed sample is stable under this radiational impact, otherwise the acquired spectra are not representative of the surface state prior to the analysis, but are artifacts of the X-ray analysis. Therefore, the stability of tribofilms and the non-contact area under X-ray irradiation has been investigated.

B.1.1 Ambient Conditions

**Non-contact Area**

A non-contact area of a tribological sample (standard test, 1 N load, 3 hours) was analyzed immediately after the introduction of the sample into the analysis chamber and after 24 hours of X-ray irradiation. To minimize the irradiation effect during the first analysis, a large aperture (#4, 0.8 mm) and a pass energy of 46.95 eV was chosen for this comparison, to keep the analysis time as short as possible. The C1s and the O1s spectra are shown in Figure B.1. The C1s spectra shows a decrease in signal intensity. Two peaks were used to fit the peak, the peak position of both peaks moving slightly to lower binding energy after the X-ray exposure.
The O1s signal is also affected by the X-ray irradiation (Figure B.1 and Table B.1). Three peaks were used to fit the signal. The total signal intensity of the O1s signal increases and the relative intensities of the two most intense signals changes between the two spectra.

Due to the low concentration of molecules from the additive on the surface and the short analysis time, the signal-to-noise ratio of the elements phosphorus, sulfur and zinc was very low. Despite the low signal-to-noise ratio, a shift to lower binding-energy values in the phosphorus (from 133.4 to 132.9 eV) and the sulfur signal (from 162.2 to 161.8 eV) could be found. The signal intensity of these signals increases with X-ray exposure.

Figure B.1: C1s and O1s spectra of the non-contact area of a tribostressed sample in the beginning and after 24 hours of X-ray irradiation. A change in both signals can be seen.
Considerations for XPS Analysis

Table B.1: C1s and O1s peak positions in the non-contact area of a tribostressed sample in the beginning and after 24 h of X-ray irradiation.

<table>
<thead>
<tr>
<th>Peak</th>
<th>B.E. (eV)</th>
<th>FWHM (eV)</th>
<th>Area (cps*eV)</th>
<th>B.E. (eV)</th>
<th>FWHM (eV)</th>
<th>Area (cps*eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s (0 h)</td>
<td>284.8</td>
<td>2.3</td>
<td>7.2 \times 10^4</td>
<td>288.3</td>
<td>2.4</td>
<td>2.4 \times 10^4</td>
</tr>
<tr>
<td>C1s (24 h)</td>
<td>284.7</td>
<td>2.3</td>
<td>4.9 \times 10^4</td>
<td>287.8</td>
<td>2.5</td>
<td>1.0 \times 10^4</td>
</tr>
<tr>
<td>O1s (0 h)</td>
<td>529.8</td>
<td>1.7</td>
<td>2.8 \times 10^5</td>
<td>531.3</td>
<td>1.7</td>
<td>1.7 \times 10^5</td>
</tr>
<tr>
<td>O1s (24 h)</td>
<td>529.9</td>
<td>1.6</td>
<td>3.3 \times 10^5</td>
<td>531.4</td>
<td>1.6</td>
<td>1.2 \times 10^5</td>
</tr>
</tbody>
</table>

**Contact area** The contact area of a standard tribotest (1 N, 3 hours) was analyzed after 30 minutes and after 24 hours of X-ray exposure. The first spectra were acquired after 30 minutes of X-ray irradiation because it was necessary to localize the wear track with i-XPS and to select the point to be analyzed. In this case, the standard analysis conditions (Aperture #2 (0.12 mm), $E_{pass} = 46.95$ eV) were used.

The C1s and O1s spectra are shown in Figure B.2. The C1s signal shows a slight decrease in the signal intensity. The peak position of the C1s spectra moves from 284.9 to 284.6 eV. The O1s signal shows only small changes due to the X-ray irradiation. Peak positions are constant, the signal intensity of the peak at 531.4 eV shows a slight decrease, while the intensity of the peak at 529.9 eV shows a small increase.
The C1s and O1s spectra reported above are measured on the same spot on the sample. No direct comparison (on the same sample) of other spectral regions was done but analysis of wear tracks produced under the same conditions analyzed after short (<1 h) and long (>24 h) X-ray irradiation revealed no significant shift in peak position or relative intensities.

**Figure B.2**: C1s and O1s spectra of the 1 N wear track of a standard test after 0.5 hours and after 24 hours of X-ray irradiation. A change in both signals can be seen.

The C1s and O1s spectra reported above are measured on the same spot on the sample. No direct comparison (on the same sample) of other spectral regions was done but analysis of wear tracks produced under the same conditions analyzed after short (<1 h) and long (>24 h) X-ray irradiation revealed no significant shift in peak position or relative intensities.

**Table B.2**: C1s and O1s peak positions in a 1 N wear scar in the beginning of the analysis and after 24 h of X-ray irradiation. All values are in binding-energy scale (eV) and not corrected for sample charging.

<table>
<thead>
<tr>
<th>Peak</th>
<th>B.E. (eV)</th>
<th>FWHM (eV)</th>
<th>Area (cps*eV)</th>
<th>B.E. (eV)</th>
<th>FWHM (eV)</th>
<th>Area (cps*eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s (0.5 h)</td>
<td>284.9</td>
<td>2.3</td>
<td>768</td>
<td>288.2</td>
<td>2.6</td>
<td>169</td>
</tr>
<tr>
<td>C1s (24 h)</td>
<td>284.6</td>
<td>2.4</td>
<td>670</td>
<td>288.1</td>
<td>2.8</td>
<td>200</td>
</tr>
<tr>
<td>O1s (0.5 h)</td>
<td>529.9</td>
<td>1.6</td>
<td>3287</td>
<td>531.4</td>
<td>1.6</td>
<td>2350</td>
</tr>
<tr>
<td>O1s (24 h)</td>
<td>529.9</td>
<td>1.6</td>
<td>3450</td>
<td>531.4</td>
<td>1.6</td>
<td>2290</td>
</tr>
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</table>
B.1.2 Elevated Temperature

Thermal Film

The surface of a thermal film (produced by immersing the sample for 5.5 h into a solution of ZnDTP (Hitec) at 150°C) was investigated immediately after the introduction of the sample into the analysis chamber and the changes in the signals were observed for 12 hours.

The C1s and the O1s peak are shown in Figure B.3. While in the C1s peak mainly a shift to lower binding energy can be observed, the O1s peak shows differences in the peak shape. In Table B.3 the peak positions of the main peaks observed on the sample are shown. After 12 h of analysis the C1s main peak moves from 285.7 eV to 284.5 eV. Also all other peak positions move to lower binding-energy values. The shift of the other components are lower (between 0.8-1.0 eV) than in the C1s signal. An exception can be seen in the second O1s peak, which moves only 0.4 eV.

Figure B.3: C1s and O1s spectra of a thermal film acquired immediately after the introduction into the analysis chamber and after 12 h of X-ray irradiation.
In Figure B.3 a difference in signal intensity can also be seen. While the C1s intensity is reduced with time, all other signals show an increase with acquisition time.

<table>
<thead>
<tr>
<th>Contact Area</th>
</tr>
</thead>
</table>
| The stability of the tribofilm in the contact area was investigated on a sample tribostressed with a step test. The step test was done with 41x25 µm steps at 5 N load in a 1 wt-% ZnDTP (Hitec) solution heated to 150°C. A tribostressed area of 1 mm was produced. Spectra were acquired after 10’ and 70’ of X-ray irradiation. The acquisition of the spectra was done on the same sample but not on exactly the same spot, assuming that the sample is homogeneous. Due to this only peak positions can be compared and not absolute signal intensities. In Figure B.4 the C1s and the O1s spectra are presented. In the C1s spectra a slight shift to lower binding-energy can be seen, the shape of the signal does not change noticeably. In the O1s signal no significant changes can be seen.

### Table B.3: Binding Energy of the main peak positions of a thermal film during X-ray irradiation. All values are in binding-energy scale (eV) and not corrected for sample charging.

<table>
<thead>
<tr>
<th>X-ray exposure:</th>
<th>0 h</th>
<th>1 h</th>
<th>12 h</th>
<th>Δ (B.E.(12h)-B.E.(0h))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s (main)</td>
<td>285.7</td>
<td>285.2</td>
<td>284.5</td>
<td>-1.2</td>
</tr>
<tr>
<td>O1s (I)</td>
<td>532.5</td>
<td>532.3</td>
<td>531.7</td>
<td>-0.8</td>
</tr>
<tr>
<td>O1s (II)</td>
<td>533.7</td>
<td>533.6</td>
<td>533.3</td>
<td>-0.4</td>
</tr>
<tr>
<td>P2p3/2</td>
<td>134.4</td>
<td>134.0</td>
<td>133.5</td>
<td>-0.9</td>
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<tr>
<td>S2p3/2</td>
<td>163.0</td>
<td>162.7</td>
<td>162.0</td>
<td>-1.0</td>
</tr>
<tr>
<td>Zn 3s</td>
<td>141.2</td>
<td>140.9</td>
<td>140.4</td>
<td>-0.8</td>
</tr>
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</table>
The binding-energy values of the main peaks are shown in Table B.4. The binding energies either stay constant between the two acquisitions, or move slightly to lower binding energies. The shifts are strongest in the C1s, S2p and the Zn3s signals.

Figure B.4: C1s and O1s spectra of a thermal film acquired after the 10' and after 70' of X-ray irradiation.
On the same sample no spectra were acquired after a longer X-ray exposure time. Comparison of these data with spectra acquired on tribostressed areas produced under the same conditions show that additional X-ray exposure leads to an additional shift in the C1s peak to approximately 284.6 eV. Also the S2p (sulfide) peak shifts 0.2 eV but no additional shift can be observed in the other peaks.

### Table B.4: Binding Energies of the main peak positions of a tribological film produced at elevated temperatures during X-ray irradiation. All values are in binding-energy scale (eV) and not corrected for sample charging.

<table>
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<tr>
<th>X-ray exposure:</th>
<th>10'</th>
<th>70'</th>
<th>( \Delta (\text{B.E.}(70')-\text{B.E.}(0')) )</th>
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</thead>
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<tr>
<td>C1s</td>
<td>285.0</td>
<td>284.8</td>
<td>-0.2</td>
</tr>
<tr>
<td>O1s(I)</td>
<td>530.2</td>
<td>530.2</td>
<td>0</td>
</tr>
<tr>
<td>O1s(II)</td>
<td>531.8</td>
<td>531.7</td>
<td>-0.1</td>
</tr>
<tr>
<td>O1s(III)</td>
<td>532.1</td>
<td>532.1</td>
<td>0</td>
</tr>
<tr>
<td>S2p_{3/2}</td>
<td>162.5</td>
<td>162.2</td>
<td>-0.3</td>
</tr>
<tr>
<td>S2p_{3/2}</td>
<td>168.9</td>
<td>168.9</td>
<td>0</td>
</tr>
<tr>
<td>P2p_{3/2}</td>
<td>133.5</td>
<td>133.4</td>
<td>-0.1</td>
</tr>
<tr>
<td>Zn3s</td>
<td>140.6</td>
<td>140.4</td>
<td>-0.2</td>
</tr>
</tbody>
</table>

B.1.3 Discussion

**Thermal Film and Non-Contact Area**

The C1s signal intensity and peak position of the thermal film and the non-contact area of the tribotest performed at room temperature are affected by the irradiation. In both cases a decrease of the C1s signal intensity can be observed, which may be explained by the evaporation of carbon containing molecules. The structure of these molecules could not be determined but they may be adsorbed lubricant, additive or fragments of the additive. Mass spectroscopy of the residual gas in the analysis chamber might help in better understanding the degradation process but was not possible with the instrument used. With the decrease of the C1s signal intensity an increase of the intensity of the other elements was observed. This would be in agreement with the removal of a carbon containing overlayer.
Considerations for XPS Analysis

No further changes were observed in the non-contact area of the room-temperature experiment but the peak position and peak shape (especially the O1s signal) on the thermal film exhibited strong change due to the irradiation. The shift in the binding energies of the elements may arise from changes in the chemical structure of the surface due to degradation of the present compounds or from changes in the conductivity of the surface. All peak positions measured on the thermal film shift to lower binding energy by approximately 0.9 eV, therefore the assumption can be made that at least part of the shifting arises from changes in the conductivity. The change in the conductivity is of course also related to changes in the chemical structure of the tribofilm. The non-contact area of the sample tribostressed at elevated temperature is considered to be very similar to the thermal film. The analysis of this non-contact area was done after the analysis of the other areas, which was after approximately 50 h. It has to be considered that after this long X-ray irradiation the surface is already degraded and signals from this measurement should be interpreted with care.

Contact Area

The tribostressed areas were much less sensitive to X-ray irradiation than thermal films and the non-contact areas of tribologically stressed samples. The peak position of the C1s signal shifts to lower values and the intensity is slightly reduced but no significant change in the other signals could be observed. This indicates that on the rubbed surface a thin carbon film is present, probably due to adsorbed lubricant, which is evaporated due to the irradiation or the radiational heat from the X-ray source. The underlying tribofilm seems to be chemically stable enough that no degradation occurs. This gives good confidence that the results are representative for the surface films formed immediately after the tribotest.
B.2 Charge Correction

If a sample measured by XPS is non-conductive, peak positions shift to the high-binding-energy side due to the positive charging of the surface. Therefore, a crucial point in the determination of binding energies is the charge correction applied. A common practice is to reference the main carbon peak to adventitious carbon at 285.0 eV (values between 284.5 and 284.8 eV are also used) and shift the whole spectrum.

In the literature, charge correction on tribofilms from ZnDTPs is treated differently. Some authors reference their spectra to adventitious carbon (285.0 or 284.8 eV) [1-4], some report that no charge correction was necessary because no charging was observed on the sample [5] and in some work charge correction is not mentioned [6-8].

In this work no charge correction was done in the tribostressed areas. The C1s main peak was found either at or below 285 eV. Assuming that this contribution arises from aliphatic carbon, no charging of the surface can be observed because this would lead to a shift to higher binding energies. Also the peak position of oxide in the O1s peak was found always close to 530.2 eV, which is in agreement with values from literature [9] and confirms that no sample charging occurs. On thermal films and in some reference compounds sample charging was observed and corrected by referencing the C1s main peak position to 285 eV.

It is shown in the experiments where the stability of the tribofilms during X-ray irradiation is investigated that in all of the experiments the C1s peaks shift to lower values during the analysis (see above), while other peaks are not (e.g. tribostressed areas, Table B.2) or less (e.g. thermal films, Table B.3) affected. If in this case a shifted C1s peak would be used for referencing, it would result in a too high binding energy for the other peaks.

This might explain that some of the peak positions reported in this work (e.g. P2p$_{3/2}$ or bridging O1s) are lower than values found in the literature. Assuming that literature measurements are done on tribofilms which are non-conductive (unfortunately this point is rarely reported), and the same X-ray degradation processes occur...
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on these samples, and shifted C1s peaks are used as reference, the reported values would be too high.
References


Considerations for XPS Analysis

Part of this thesis have been or will be published in the following articles:

“A Combinatorial Approach to Elucidating Tribochemical Reactions”
M. Eglin, A. Rossi, and N. D. Spencer, Tribology Letters (in press).

“X-Ray Photoelectron Spectroscopy Analysis of Tribostressed Samples in the Presence of ZnDTP: A Combinatorial Approach”
M. Eglin, A. Rossi, and N. D. Spencer, Tribology Letters (in press).

“Surface Analytical Studies of Surface-Additive Interaction by Means of in Situ and Combinatorial Approaches”

“Additive-Surface Interaction in Boundary Lubrication: A Combinatorial Approach”

“Zinc Diisopropyl Dithiophosphate by XPS”
# Curriculum Vitae

## Personal

<table>
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<tr>
<th>Name</th>
<th>Michael Eglin</th>
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<tr>
<td>Date of Birth</td>
<td>May 27, 1973</td>
</tr>
<tr>
<td>Nationality</td>
<td>Swiss</td>
</tr>
<tr>
<td>Marital Status</td>
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## Languages

German (native speaker), English (fluent), French (fluent)

## Education

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<td>May 1999 - March 2003</td>
<td>Ph.D. thesis at the Laboratory for Surface Science and Technology (LSST); Swiss Federal Institute of Technology (ETH) Zürich; Switzerland</td>
</tr>
<tr>
<td>1999</td>
<td>Diploma in Materials Science, Department of Materials; ETH Zürich</td>
</tr>
<tr>
<td>1993-1999</td>
<td>Study of Materials Engineering; ETH Zürich</td>
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<tr>
<td>1989-1993</td>
<td>Gymnasium (Mathematics and Natural Science); Baden</td>
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## Award

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<td>2002</td>
<td>Gordon Research Conference on Tribology: Poster Award</td>
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### Work Experiences and Placements

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<th>Period</th>
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<tr>
<td>October 1999 - July 2002</td>
<td>Teaching assistant for undergraduates at the Department of Materials; ETH Zürich</td>
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<tr>
<td>June - September 1999</td>
<td>Course at the National Synchrotron Light Source (NSLS); Brookhaven National Lab (BNL); Upton NY (USA): Training of the basics of synchrotron radiation experiments</td>
</tr>
<tr>
<td>October 1998 - April 1999</td>
<td>Diploma Thesis: Thermoplastic Processed Photoluminescent Polarizers; Polymer Technology Group (Prof. P. Smith); ETH Zürich</td>
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<tr>
<td>April - July 1998</td>
<td>Semester Thesis: Electrochemical Characterization of Titan in Halide Containing Solutions; Group for Metallic High Performance Materials (Prof. S. Virtanen); ETH Zürich</td>
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<tr>
<td>October 1997 - January 1998</td>
<td>Semester Thesis: Finite Element Calculations of Ceramic Dental Bridges; Institute for Nonmetallic Inorganic Materials (Prof. L.J. Gauckler); ETH Zürich</td>
</tr>
<tr>
<td>November 1996 - April 1998</td>
<td>Employee (part time) at the Laboratory for Surface Science and Technology; ETH Zürich</td>
</tr>
<tr>
<td>May - September 1996</td>
<td>Trainee Position: ABB Atom; Nuclear Fuel Division; Västerås; Sweden</td>
</tr>
<tr>
<td>April 1995 - April 1996</td>
<td>Employee at I.P.S. Software, Würenlos; Switzerland: Visual Basic programming</td>
</tr>
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My warmest thanks go to Antonella Rossi who did a great job in supervising my thesis. In the beginning, her thorough introduction to the world of surface analysis was the fundament where I could base my work on. Later it was her indefatigable support, the valuable suggestions and thorough questions which improved the quality of my work.

I would like to thank Hugh Spikes for the interest in my work and accepting of being co-examiner of this thesis.

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I also thank the whole crew of the LSST. Special thanks go to Manfred Heuberger, Irene Klingenhuss and Tomas Bartos who shared the office with me. Federica Piras shared not only the supervisor with me but we had also many interesting discussions about the related topic of our theses. With Vinzenz Frauchiger and Roger Michel I spent not only a great time during our studies and at the LSST but our friendship reaches much further than science.

Finally, I would like to thank all my family for their support and Irene for her motivating words, her confidence in me and her always open arms for me.