Doctoral Thesis

Combinatorial study of the tribochemistry of anti-wear lubricant additives

Author(s):
Heuberger, Roman Christian

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Combinatorial Study of the Tribochemistry of Anti-Wear Lubricant Additives

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presented by
Roman Christian Heuberger
Dipl.-Ing. ETH
born November 4th, 1976
citizen of Kirchberg (SG), Switzerland

accepted on the recommendation of
Prof. Dr. Nicholas D. Spencer, examiner
Prof. Dr. Antonella Rossi, co-examiner
Prof. Dr. Wilfred T. Tysoe, co-examiner

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Abstract

The formation, the anti-wear properties and the renewal of the surface film of two metals rubbing against each other under boundary lubrication conditions, are governed by many factors, such as the composition of the counterparts, the contact pressure, the temperature, the composition of the lubricant oil and the sliding speed.

The most frequently used lubricant additives are zinc dialkyldithiophosphates (ZnDTPs), but they have the disadvantage of containing large amounts of phosphorus and sulphur, which impair the environment. Alternatives are thus badly needed, and ashless phosphorothionates are possible substitutes. However, while much effort has been put into understanding the reaction mechanism of ZnDTPs, so far, few results are available that correlate the anti-wear properties of films formed in the presence of metal-free additives, such as the class of phosphorothionates.

The present work is a combined tribological and XPS surface analytical study of the reaction mechanism of ZnDTP and a series of alkylated triphenyl phosphorothionates with different alkyl chains. The additives were tested in combinatorial ball-on-disc tests with varying contact pressures at different temperatures. Three kinds of tests were performed: First, the combinatorial step test with different contact pressures at different annuli, whereby tribostressed regions were produced by a stepwise change of the radius. Second, the combinatorial oscillating-load test, where different contact pressures were applied in dependence of the angular position on one annulus and third, the wear test, where different contact pressures were tested in dependence on the angular position of the annulus, with several sliding speeds on different annuli. The last experiment was also performed with a ceramic ball instead of the steel ball, investigating the effect of different tribopairs.

In oils blended with ZnDTP, lower friction and wear coefficients were obtained at lower temperatures, with higher contact pressures, higher sliding speeds and when applying the ceramic-steel contact instead of the steel-steel contact. The elemental composition of the tribofilm and the thermal film as well as their chemical state and thickness were determined from the XPS results and a subsequent application of a multilayer model to the processed data.
At higher temperatures, thicker iron/zinc poly(thio)phosphate tribofilms were formed. With increasing contact pressure, shorter chains were obtained, resulting in harder and tougher films. The thermal decomposition of ZnDTP was activated above 130°C, resulting in thick thermal poly(thio)phosphate films. Longer phosphate chains were obtained at higher temperatures, up to cross-linked phosphates at 180°C.

In oils blended with phosphorothionates similar effects on friction and wear were obtained as with ZnDTP. The films were thinner and enriched in sulphur, which was even more pronounced with longer additive alkyl chains. Higher temperatures led to the oxidation of the sulphide to sulphate, while with higher contact pressures less sulphate was formed. The activation temperature of the phosphorothionates is higher compared to that of ZnDTP; thicker thermal films were not observed until the temperature was above 150°C.

The anti-wear mechanisms of both types of additives are similar: Both start with the adsorption of a phosphorothionate, which are dialkyldithiophosphate and reacted species in the case of ZnDTP and the complete molecule in the case of phosphorothionates. At higher temperatures, thermal degradation products also adsorb on the surface. Under the frictional heat and the shear forces present in the tribological contact, the adsorbed molecules react to form short-chain poly(thio)phosphates and the released sulphur reacts with the metal to form zinc sulphides in the case of ZnDTP and iron sulphides for the phosphorothionates.

This work contributes to the study of the anti-wear films under boundary lubrication conditions. The combinatorial approach was enhanced and designed for high resolution XPS, analysing both the balls and discs. A parameter library was successfully produced for different anti-wear additives in dependence of temperature, contact pressure, sliding speed and tribopair. The correlation found between the tribological data and the surface-analytical results provides a scientific base, both for the understanding of the influence of the different mechanical test conditions on the tribological film formation and modification, as well as for the choice of the additives that may be used to prevent wear and reduce friction between steel counterparts under extreme conditions.
Kurzfassung

Die auf der Oberfläche zweier Metalle unter Festkörperreibung gebildeten Schichten und deren Verschleisseigenschaften hängen stark von den Bedingungen wie Kontaktdruck, Temperatur und der chemischen Zusammensetzung der Metalle und des Schmiermittels ab.

Der häufigste und wirksame Antiverschleisschmiermittelzusatz ist Zink Diakylthiophosphat (ZnDTP); dies ist jedoch wegen den hohen Anteilen von Zink, Schwefel und Phosphor schlecht umweltverträglich. Für die dringend benötigten metallfreien, schwefel- und phosphorarmen Zusatzstoffe sind Phosphorthionate eine mögliche Alternative. Während sehr viel Arbeit in die Erforschung von ZnDTP investiert wurde ist bisher nur wenig über metallfreie Zusatzstoffe wie Phosphorothionate bekannt.


In Schmiermitteln mit ZnDTP wurden bei tieferen Temperaturen, höheren Kontaktdrücken und höheren Gleitgeschwindigkeiten oder bei Verwendung keramischer statt metallischer Kugeln tiefere Reibungs- und Verschleisskoeffizienten erzielt. Unter diesen Bedingungen wurden Eisen/Zink Poly(thio)phosphatschichten mit kürzeren Kettenlängen gebildet, was härteren und zäheren Filmen entspricht. Bei höheren Temperaturen wurden dickere Eisen/Zink Po-
ly(thio)phosphat Schichten gebildet. Die thermische Zersetzung von ZnDTP setzte oberhalb von 130°C ein, was zu dicken thermischen Zink Poly(thio)-phosphat Filmen auf der nicht beanspruchten Oberfläche führte. Bei höheren Temperaturen waren auch in diesem Fall die Phosphatketen länger, wobei bei 180°C ein vernetzter Phosphatfilm gebildet wurde.

In Phosphorthionathaltigen Lösungen wurden ähnliche, tendenziell leicht höhere Reibungs- und Verschleissseffekte erzielt wie mit ZnDTP-haltigen Lösungen. Die gebildeten Filme waren jedoch dünner und enthielten mehr Schwefel. Bei erhöhter Temperatur fand eine Oxidation des Schwefels statt, was einen erhöhten Sulfatgehalt zur Folge hatte. Andrerseits führte ein höherer Kontakt- druck zu weniger Sulfaten. Die Aktivierungstemperatur war mit 150°C höher als bei ZnDTP, erst ab 150°C wurden dickere thermische Filme gebildet.


Abbreviations

In this work, the following abbreviations are used:

μ  friction coefficient
AES Auger electron spectroscopy
AFM atomic force microscopy
ARXPS angle-resolved X-ray photoelectron spectroscopy
BO bridging oxygen
b-TPPT butylated triphenyl phosphorothionate
CAE constant analyser energy
EA emission angle
fwhm full width at half maximum
GL Gaussian-Lorentzian peak shape
IMFP inelastic mean free path
LA asymmetry function
MEM maximum entropy method
NBO non-bridging oxygen
n-TPPT nonylated triphenyl phosphorothionate
PAO poly-a-olefin
RR retard ratio
SEM scanning electron microscopy
Tof-SIMS time-of-flight secondary ion mass spectroscopy
TPPT triphenyl phosphorothionate
XANES X-ray absorption near edge spectroscopy
XPS X-ray photoelectron spectroscopy
ZnDTP zinc dialkyldithiophosphate
This chapter starts with the aims of the thesis, followed by a short introduction into tribology and its subfields friction, wear and lubrication. Special attention is dedicated to the anti-wear films produced with the lubricant additives used in this work: zinc dialkyldithiophosphate and ashless phosphorothionates. In the third section, the analysis of anti-wear films is elucidated and the principles of X-ray photoelectron spectroscopy and laser profilometry explained. In the last section, tribological testing is described both generally and in detail for combinatorial testing.
1.1 Aim of the Thesis

Lubricants for engines and machines contain a large variety of additives, including those to minimize friction and wear for saving energy and increasing the lifetime of the machines [1]. These additives involve metals, phosphorus and sulphur, which are directly problematic for the environment and indirectly problematic due their poisoning of automobile catalysts. The replacement of the additives by environmentally more acceptable alternatives is difficult because the most common additive zinc dialkyldithiophosphate (ZnDTP) is very efficient under a wide range of conditions [2]. Nevertheless, in order to replace ZnDTP with ashless additives, an understanding of the mechanisms of ZnDTP and its alternatives is necessary.

The Main Goals

• Develop a robust combinatorial tribotest that can benefit from the high-resolution capabilities of the new XPS instruments, for high-throughput additive characterisation.

• Understand the role of contact pressure and temperature on the adsorption/reaction behaviour and tribological performance of ZnDTP.

• Understand the role of contact pressure, temperature and substituent structure on the adsorption/reaction behaviour and tribological performance of ashless phosphorothionate additives.

Experimental Approach

This work is based on the studies performed by Dr Michael Eglin [3-7], who developed a combinatorial test for testing ZnDTP at room temperature and at 150°C. In his work, the contact region had to be enlarged (step-test) due to the limitations of the XPS instruments (minimum analysed area of 120 μm) for later X-ray photoelectron spectroscopy (XPS) analysis. The new generation of XPS spectrometers is able to focus a monochromatic X-ray beam down to 5-10 micrometers, and this allows imaging and small-area XPS measurements on single wear tracks of a ball-on-disc experiment to be performed. One of the aims of this work is to set up a combinatorial test that can be effectively applied at a large temperature range using different additives. Thus more practical significance can be achieved with longer tribostress on the wear track. By varying the load in dependence of the angular position within a tribotrack, different loads
can be tested within one experiment without changing the wear track and thus not allowing purely thermal reactions to modify the tribofilm.

By performing experiments at different temperatures and with various additives, a library of friction behaviour, wear and tribofilm composition is created for different loads and temperatures both for ZnDTP and ashless phosphorothionates with different chain lengths. By analysing the composition of the tribofilm formed on the ball, additional information about the permanent contact area and the area near the contact is obtained. All this information will be combined to understand the mechanisms of the anti-wear additives under a variety of different conditions.
1.2 Tribology

Tribology is defined as “the science and technology of interacting surfaces in relative motion”, and covers the fields of friction, wear and lubrication, including the interactions between solids, liquids and gases. The word tribology comes from the Greek word τρίβωμα, which means rubbing or attrition [1].

1.2.1 Fundamentals

Friction

The friction force is the resistance encountered, when one body is moved over another [1]. The friction coefficient is defined as the ratio between the friction force $F$ and the normal load $L$:

$$\mu = \frac{F}{L}$$

Equation 1.1

Normally the values encountered for $\mu$ are between 0.1 and 1, but can range from 0.001 for lightly loaded rolling bearings to 10 for clean metals in vacuum [1].

Leonardo da Vinci was the first to discover the laws of friction at the end of the 15th century. 200 years later, Guillaume Amontons rediscovered these laws and presented them to the Royal Academy of Sciences in Paris in 1699 [1, 8]. Nowadays these laws are called Amontons’s laws:

1. The friction force is proportional to the normal load.
2. The friction force is independent of the apparent area of contact.
3. The friction force is independent of the sliding velocity.

In 1785, Charles Augustin de Coulomb discovered a third law [1, 8]:

These three laws are valid for a large variety of tribosystems including metals or wood, under both dry and lubricated conditions, but they are limited, especially if dealing with polymers [1].

Wear

In DIN 50320, wear is defined as the loss of material of a solid, caused by the mechanical stress of bodies in motion. There are several categories of wear, but often a clear differentiation is not possible in practice.
In *adhesive wear*, the two counterparts are in direct contact via asperities, which adhere to each other, possibly by microwelding. Due to the shearing off of the junctions upon further motion of the bodies, these bonds break and material is torn out of the surface, producing cavities in the surface and wear particles, which may lead to abrasive wear in a next step [1, 9, 10]. *Abrasive wear* takes place when hard particles or counterparts remove material of a softer material, resulting in scratches and furrows. The hard particles can originate from a different material, e.g. carbides in grinding or diamonds in polishing, or metal oxides from one of the two counterparts. The process of abrasive wear involves both plastic flow and brittle fracture [1, 10]. *Erosive wear* is related to abrasive wear and occurs due to impacting particles, carried by a gas stream or a flowing liquid [1, 10]. *Surface fatigue* occurs if cyclic loading damages the structure of the surface, resulting in cracks, small cavities or delamination [10]. *Corrosive wear* takes place, if the material suffers oxidation or corrosion by the surrounding medium in addition to the tribostress. This might lead to the formation of oxide layers on the surface, which are often destroyed by adhesive wear [10].

**The Wear Equation**

In an adhesive asperity contact in unlubricated conditions, a spherical particle with the volume $\delta V$ is removed [11]. Then the total worn volume is the total of all wear particles $\Sigma \delta V$, giving $V = A \cdot l$, where $A$ is the real contact area and $l$ the sliding distance [11]. Because in reality, the experienced wear is much smaller, only a proportion $K$ of the asperities produces wear, while the others do not, thus [11]:

$$V = K \cdot A \cdot l$$

Equation 1.2

Under plastic deformation, assuming that the real contact area is equal to the load divided by the hardness of the softer material (Vickers hardness in Pa), the worn volume becomes:

$$V = K \cdot l \cdot \frac{L}{H}$$

Equation 1.3

This equation is called *Holm-Archard wear equation* and $K$ is called *Archard coefficient* or *wear coefficient* and is dimensionless [1, 10]. Although this equation was introduced for adhesive wear without lubrication, it is successfully applied for different kinds of tribological systems. In practical applications, the quantity $K/H$ is often more useful since the hardness is not always known. This quantity is the *dimensional wear coefficient* $k$, given in $[m^3/Nm]$ [1, 10]:

$$k = \frac{K}{H} = \frac{V}{L \cdot l}$$

Equation 1.4
The values for $k$ range from $10^{-18}$ m$^3$/Nm for very low wear up to $10^{-14}$ m$^3$/Nm in very severe conditions [10]. In practical work, $k$ is often given in [mm$^3$/Nm] [1].

**Lubrication**

To reduce friction and to prevent wear, the surfaces of the counterparts in motion are often separated by a lubricant film. This is in most cases an oil-based solution, but water-based lubricants are gaining in importance. For lubricated systems, the friction force depends mainly on the viscosity $\eta$, the velocity $v$ and on the normal load $L$. These parameters are taken together to form the Sommerfeld number $S$ [1]:

$$S = \frac{\eta \cdot v}{L}$$

Equation 1.5

The Stribeck curve describes the dependence of the friction coefficient on the Sommerfeld number (see Figure 1.1). Three regimes can be distinguished: In the *hydrodynamic lubrication* regime at high Sommerfeld numbers, the surfaces are completely separated by a thick lubricant film. Therefore the friction coefficient is low and arises from the shear forces in the viscous lubricant [1]. In the *mixed or elasto-hydrodynamic lubrication* regime at intermediate Sommerfeld numbers, the lubricant films are thin and the local pressures so high that an elastic deformation of the counterparts occurs [1]. In the *boundary-lubrication regime* at low Sommerfeld numbers, the lubricant film is squeezed out of the contact area and the whole load is carried by the asperities in contact. This typically results in high friction coefficients and high wear [1].

*Figure 1.1: Stribeck curve: Dependence of the friction coefficient on viscosity, speed and load for a lubricated sliding system.*
1.2.2 Lubricant Additives

In most cases, the base oil is a mineral oil with 20-30 carbon atoms. Either straight or branched chains are used, sometimes contain aromatic or aliphatic rings. Synthetic oils are more expensive and used for more demanding applications, where for example insulating, thermally or chemically resistant lubricants or low flammability are required. Organic esters, polyglycols or silicones are used in such applications [1, 10].

To modify the properties of the lubricant, a large variety of additives are added. Polymers are added to change the viscosity of the oil and to improve the flow properties in cold lubricants, decreasing the pour-point by decreasing the order and thus decreasing the crystallisation temperature [1].

Corrosion inhibitors protect the surfaces from reactive or oxidative species in the solution by adsorbing onto the surface and sterically hindering the reactive species' interaction with the surface [10]. Detergents and dispersants, e.g. amphiphiles, attach to oxidative or degradation products or to dirt particles, which results in oil-soluble species. This prevents deposition on the surface.

The oil might oxidize by thermally activated dissociation of a hydrogen atom from the hydrocarbon chain or be induced by the presence of nascent iron [10]. The resulting radical carbon-chain reacts with dissolved oxygen to form peroxides, which in turn, induce further radical formation and further oxidation. This leads to a higher acidity and lower viscosity of the lubricant. To prevent these effects, anti-oxidants like metal deactivators, radical inhibitors or peroxide decomposers are added [10].

Silicone polymers are added in very low amounts to minimize foaming by decreasing the surface tension [10].

The friction and wear modifiers are probably the most important additives. In the boundary-lubrication regime the asperities are in direct contact and thus high friction and wear occurs. To reduce the direct contact of the surfaces, protective films should thus be formed on the surface [1, 10]. There are three kinds of additives:

The friction modifiers, also called adsorption or boundary additives, are used to inhibit stick-slip by physical adsorption on the surface and herewith forming thin layers, thus preventing adhesion and microwelding. Usually amphiphiles with polar head-groups such as alcohols, esters, unsaturated and saturated acids bound on aliphatic chains are used. They adsorb on the surface and prevent the direct contact of the tribopartners. Usually these additives only work under low loads and at temperatures below 80°C. At higher temperature the additives
desorb upon thermal activation [10, 12]. Another group of friction modifiers is that of organomolybdenum compounds (e.g. MoDTC).

In the mixed and boundary-lubrication regimes, *anti-wear additives* are used to react with the surface to form a protective layer, which ensures that sporadic asperity contacts do not lead to severe wear. Typically, these additives are phosphorus based, zinc dialkyldithiophosphates (ZnDTPs) being the most frequently used in engine oils and thus one of the major sources of phosphorus and sulphur in engine oils. Other additives are tricresylphosphate and other phosphate esters or phosphorothionates [10].

Under severe boundary-lubrication conditions, *extreme-pressure additives* react with the surface to prevent microwelding, for example in slowly moving and heavily loaded gears. These additives are sulphur based, including dibenzylidisulphide, phosphosulphurised isobutene, trichloroacetone or molybdenum disulphide [10, 12].

**Zinc Dialkyldithiophosphates**

Initially introduced in the 1940s as antioxidants, ZnDTPs impart excellent anti-wear properties by forming protective films on the rubbing surfaces [2, 13] and are the most common additives in engine oils [10]. ZnDTPs work under anti-wear conditions and at mild extreme-pressure conditions but not under severe extreme-pressure conditions [10].

There are three groups of ZnDTPs according to the side chain of the phosphates. The primary ZnDTPs have single carbon chains bound on the oxygen atoms, the secondary ZnDTPs branched chains and the aryl ZnDTPs an aromatic ring bound on the oxygen atom, on which an aliphatic chain is bound (see Figure 1.2). The properties and wear protection strongly depend on the side chain (see Table 1.1).

<table>
<thead>
<tr>
<th>Structure</th>
<th>Thermal Stability</th>
<th>Hydrolytic Stability</th>
<th>Oxidation Protection</th>
<th>Wear Protection</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary ZnDTP</td>
<td>good</td>
<td>satisfactory</td>
<td>satisfactory</td>
<td>satisfactory</td>
</tr>
<tr>
<td>Secondary ZnDTP</td>
<td>moderate</td>
<td>good</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>Aryl ZnDTP</td>
<td>very good</td>
<td>bad</td>
<td>moderate</td>
<td>bad</td>
</tr>
</tbody>
</table>
**Introduction**

Primary ZnDTP

![Chemical formula of primary ZnDTP](image1)

Secondary ZnDTP

![Chemical formula of secondary ZnDTP](image2)

Aryl ZnDTP

![Chemical formula of aryl ZnDTP](image3)

*Figure 1.2: Chemical formulae of primary, secondary and aryl zinc dialkylidithiophosphates (ZnDTPs).*

**Anti-oxidant Mechanism**

As mentioned in section 1.2.2, reactive radicals are formed by thermal dissociation. These create peroxides, which in turn lead to further oxidation. Antioxidants should stabilize the radicals in order to inhibit the oxidation process. ZnDTP has the ability to decompose hydroperoxides and peroxi-radicals and thus is effective in two ways [2, 14-17]. In addition, both the original additive and the reacted species are able to neutralize radicals (see Figure 1.3) [2, 15].

**Thermal Degradation of ZnDTP**

Temperature has a significant influence on the course of the reaction and was studied intensively [18-24]. The current understanding is that thermal degradation of ZnDTP begins with the migration of the carbon chain from the oxygen atom to the sulphur atom at temperatures as low as 60°C [18, 19, 25]. This is a two-step process, where first an alkyl chain reacts with another molecule to form a trialkylidithiophosphate, as was found by Jones and Joy by $^{31}$P-NMR [19]. In a second step the re-alkylation of the monoalkylidithiophosphate takes place on the P-S$^-$ rather than on the P-O$^-$:
ZDTP: zinc dialkyldithiophosphate; [(RO)₂P(S)S]₂Zn
HDT: dithiolic acid; (RO)₂P(S)SH
BZDTP: basic ZDTP; [(RO)₂P(S)S]₄Zn₄O
DS: (RO)₂P(S-SP(S)(RO); DS⁻: (RO)₂P(S)S⁻

Figure 1.3: Antioxidant reaction scheme of ZnDTP after Willermet et al. [15].

Once a finite amount of trialkyldithiophosphates is present in the solution, the alkylation of sulphur is autocatalytic and does not depend on the presence of dianions. The charge over the terminating oxygen and sulphur atom in the O,S-dialkyldithiophosphate anion is actually delocalized, so that the alkylation of further sulphur atoms continues to produce S,S-dialkyldithiophosphate anions [19].

According to Luther et al., some of the alkyl chains are released into the solution, which increases its acidity [21]. In acidic media (presence of negatively charged nuclei Nu⁻), the formation of thiols is likely [19, 21]:

Equation 1.7

The resulting thiol will further react with other alkyl chains to form dialky sulphides [19]. Another possible pathway to form dialky sulphides is the reaction of phosphoryl groups with each other to form pyrophosphates, which starts below 100°C:
At higher temperatures (above ~150°C) this involves the presence of higher concentrations of fragments available in the lubricant oil and the formation of longer chains called poly(thio)phosphates can occur [2, 13, 26].

**Metal-free Additives**

**Sulphur Carriers**

Molecules containing sulphur chains with several sulphur atoms in the centre and with alkyl chains on both ends to render them oil-soluble are used as sulphur carriers. For severe extreme-pressure conditions, these chains contain up to 5 sulphur atoms, while for less severe conditions the amount of sulphur is lower [12, 27].

The film composition in the presence of several organosulphurs depending on the applied load was investigated by Najman et al. [28]. They found sulphate in the non-contact areas, iron disulphide and sulphate in tribofilms formed under moderate conditions, while under extreme pressure mainly iron sulphide was formed.

**Phosphate Esters**

Ashless phosphate esters (formula see Figure 1.4) are mainly used in non-flammable hydraulic and turbine oils. Applying quantum chemical molecular dynamics, it was found that the molecule adsorbs with the oxygen atoms in P=O and one P-O-R group to metallic iron, where the first oxygen forms a covalent and the second an ionic bond [29]. Under tribostress, a scission of the double bond is likely [29]. The resulting phosphite molecule decomposes by a scission of the P-O or the O-C bond [30]. Another possible pathway is the thermal decomposition of the phosphate, which starts with a scission of the P-O bond [31]. In both cases phosphoryl groups are created, which link together to form polyphosphate chains similar to those observed for ZnDTPs [2].
Similar mechanisms are supposed to take place for arylphosphates deposited in gas turbines via vapour-phase lubrication, where a phosphate film containing graphite particles is formed [32].

Najman et al. investigated the thermal film formation at 70, 100 and 150°C; mono- and diphenylphosphate esters formed films of similar thicknesses at all temperatures while triphenyl phosphates formed thick layers only at 150°C [33].

**Amine Phosphates**

Amine phosphates (formula see Figure 1.4) are organic salts and thus very polar. Therefore they adsorb strongly onto metallic surfaces. They are mainly used in circulating oils, anti-wear fluids, gear oils and greases. Thicker films are formed using amine phosphates compared to films of phosphate esters or phosphorothionates under the same conditions, because the counter ion for the polyphosphate film is already present in the molecule [33]. The drawback is that non-soluble salts can be formed, which may lead to blockages of tubes.

**Phosphorothionates**

Ashless phosphorothionates (formula see Figure 1.4) are used as anti-wear additives for metalworking fluids, hydraulic fluids and greases. Long alkyl chains are used if a high solubility in oil is required, for example in cutting fluids, which may contain up to 10% of nonylated triphenyl phosphorothionate.

For phosphorothionates, similar decomposition mechanisms are supposed to take place, starting with the cleavage of the P=S bond [34], but no clear mechanisms have been described in the literature. Dithiophosphates were found to be more reactive and form thicker layers than monothiophosphates [33]. For phosphorus- and sulphur-containing solutions, the formation of iron sulphide was favoured at higher contact pressures while iron disulphide and iron sulphate were formed at lower contact pressures [35].

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**Figure 1.4:** Chemical formulae of phosphate ester, amine phosphate and phosphorothionate. The number of alkyl chains might vary from the given formulas.
1.2.3 Anti-Wear Films

Anti-wear additives react with the surface to form a protective layer, which is much more durable than that formed by the adsorbed boundary additives. The reactivity of the additive is crucial: if an additive is not sufficiently reactive, then no film can be formed before the parts become severely damaged, and if the additive is too reactive, then the additive loses its function after a short time [27] or may lead to corrosive attack on the surface. While natural esters are reactive at low temperatures, increasing temperatures are needed to activate the additives in the following order: natural esters, synthetic fatty acids, chloroparaffins, phosphorus-containing additives, sulphur-containing additives, free sulphur [27]. Not only does the additive’s properties define its reactivity in real applications, the reactivity also depends on the base oil, on the presence of other additives and on the metal and its surface [27]. The usual level of the anti-wear additives in lubricants lies between 1 and 3 wt.% [10].

As mentioned above, the most frequently used additives are ZnDTPs, which contain large amounts of phosphorus, sulphur and zinc, which impair the environment directly and also indirectly by poisoning exhaust catalysts. Therefore international regulations are limiting the concentration of phosphorus and sulphur in engine oils: alternatives to ZnDTP and therefore an understanding of the working mechanisms of both ZnDTP and its possible alternatives are badly needed. In contrast to ZnDTPs [2-4, 18-26, 36-51], only little work has been carried out dealing with alternatives such as organosulphurs [12, 28], phosphates [12, 32, 33, 52-54], phosphorothionates [33-35, 54-57] or dithiophosphates [33, 34, 54-56, 58].

Usually, anti-wear additives are used in engines and machines made of steel. In recent decades, lighter metals such as aluminium or magnesium or thermally and mechanically more stable ceramics have been used as engineering parts, often in combination with conventional steel. Lubricants, designed for steel, do therefore come into contact with other materials. For ceramics, this leads in some cases to a decrease of friction and wear [59-62], sometimes has significant side-effects [59, 60] or wear might even be enhanced [60]. Generally, there are only few molecules adsorbed on ceramic surfaces [63] and the additives are less effective in reducing wear than for metallic tribopairs [60, 62, 64].

**Phosphate Glasses**

In anti-wear films, phosphate glasses are usually formed, together with other compounds. In such a (poly)phosphate (see scheme in Figure 1.5), there are two types of oxygen atoms that can be distinguished by XPS: the bridging oxy-
Figure 1.5: Scheme of zinc polyphosphate with the chain length n. The oxygen atoms linking two phosphorus atoms together (bold) are called bridging oxygen (BO), while the terminal oxygen atoms in the phosphate groups are called non-bridging oxygen (NBO) [65].

Table 1.2: Names and chain lengths of phosphate glasses [2, 65].

<table>
<thead>
<tr>
<th>Name</th>
<th>Chain Length n</th>
<th>BO/NBO</th>
<th>Charge/P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orthophosphate</td>
<td>1</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>Pyrophosphate</td>
<td>2</td>
<td>1/6</td>
<td>2</td>
</tr>
<tr>
<td>Polyphosphate</td>
<td>&gt;3</td>
<td>1/6&gt;x&gt;1/2</td>
<td>2&gt;x&gt;1</td>
</tr>
<tr>
<td>Metaphosphate</td>
<td>infinite</td>
<td>1/2</td>
<td>1</td>
</tr>
<tr>
<td>Ultraphosphate</td>
<td>crosslinked</td>
<td>&gt;1/2</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

gen (BO) links two phosphate groups together (P-O-P) and the non-bridging oxygen (NBO) terminates the phosphates (-PO₄) [65]. The binding energy of NBO was found between 531.5 and 532.0 eV [4, 66-68] while BO was between 533.1 and 534.4 eV [4, 66-69]. The ratio of BO to NBO allows the chain length n of the (poly)phosphate to be calculated, and therefore provides important information on the structure of the formed film (see Table 1.2). Another method to characterize the (poly)phosphate is to compare of the phosphorus binding energy of the anti-wear films with the binding energies acquired in reference compounds [70].

Depending on the chain length of the phosphate, different names are used: Single phosphate groups are called orthophosphates, two phosphate groups linked together are pyrophosphates and if there are longer chains, these are called polyphosphates. For infinite chains, the name metaphosphate is used, and if the chains are cross-linked, the term ultraphosphate is used. The number of charges decreases with longer chains (see Table 1.2) and thus the number of cations decreases.

Tribochemistry of Zinc dialkyldithiophosphates

Much effort has been expended to understand the mechanism of ZnDTP anti-wear films. Films were investigated using numerous tools such as atomic force microscopy (AFM) [36-39], nano-indentation [39-42], XPS [4, 42-44], X-ray
absorption spectroscopy (XANES) [26, 44, 45] and in situ attenuated total reflection infrared spectroscopy [46, 47].

It has been suggested that during a ball-on-disc tribological contact similar reactions occur on both counterparts, already starting at room temperature [3, 4, 48]. While it has been proven that the tribofilm composition changes on the disc with the test temperature from a zinc phosphate at low temperature to a zinc polyphosphate at higher temperature [42, 44, 46, 47] only very little work was done so far regarding the ball [49, 50].

Different groups have investigated the influence of the load on the tribofilm composition. While Bird and Galvin found only small effects within the experimental uncertainties [43], at room temperature, Eglin et al only observed the formation of orthophosphates at high loads [4, 5] and Yin et al found higher formation rates and longer polyphosphate chains with higher loads at 80°C [51]. A comparison of the applied loads is difficult because often only the load is given but neither the contact pressure nor the contact area are reported.

Changes in elemental concentrations and chain length of the phosphate chains with depth have been observed by means of XANES (sampling depth 5 nm or 50 nm, depending on the applied mode) [44, 51, 71] as well as by depth profiling by means of argon-sputtering [44].

It has been proposed that wear particles made of iron oxide are digested by the zinc (poly)phosphate, in accordance with the chemical-hardness approach [72, 73], where iron and phosphates are hard Lewis acids and bases, respectively, and zinc and oxides are soft. Therefore a cation exchange is taking place resulting in the formation of iron-zinc (poly)phosphates and zinc oxide [72].

![Figure 1.6: Scheme of ZnDTP anti-wear film after Gellman et al. [32.]]
cause of the higher charge brought into the system with the Fe$^{3+}$ instead of the Zn$^{2+}$ cation, the polyphosphate chain becomes shorter [72].

Gellman and Spencer suggest the formation of a layered structure with an iron oxide film containing sulphides on top of the steel substrate (see Figure 1.6). On that a film of short-chain phosphates is formed with a long-chain poly-(thio)phosphate on top. Oxide and sulphide particles are incorporated in the phosphate film and thus do not contribute to abrasive wear. On top there is an adsorbed soft alkylphosphate film, which is easily washed away [32].

Although much effort has been made to understand the reaction mechanism of ZnDTP, there remain many open questions concerning the reacting species, the film formation and its kinetics [2, 13].

**Tribofilms in the Presence of metal-free Additives**

Tribofilms produced in lubricants containing metal-free anti-wear additives have been analysed by means of X-ray photoelectron spectroscopy (XPS) [53, 54, 56], absorption spectroscopy (XANES) [33-35], scanning electron microscopy (SEM) [32, 55, 56] and atomic force microscopy (AFM) [28, 56] among others. With AFM and SEM typically pad-like structures were found on the tribofilms [28, 55, 56].

Matsumoto investigated the chemical composition of the tribofilms produced with amine phosphate with XPS and found both at room temperature and at 150°C iron phosphate and iron oxide in the wear tracks, whereas with higher contact pressures thicker films containing more phosphorus were obtained [54]. On tribotrails formed at 100°C in the presence of phenylphosphates, Najman et al. found iron(II)polyphosphates, whereas with longer sliding time similar films but with shorter chains were formed due to the diffusion of iron into the reaction layer [33].

Rossi et al. determined the chemical composition of tribofilms produced at 100°C in the presence of tributyl thiophosphates to be made of phosphates and sulphates [53]. Najman et al. found in tribotests performed at 100°C with phosphorothionates films made of short chain iron(II)polyphosphates together with iron sulphides and sulphates, whereas with increasing sliding time the amount of iron sulphate increased until after six hours comparable amounts of phosphates and sulphates were present in the film [34]. Under extreme pressures, they detected the formation of iron sulphide, in moderate conditions iron disulphide and sulphate while in the non-contact area only sulphates were formed [28, 58]. Similar results were obtained with lubricants containing phosphates and sulphur: again the formation of iron sulphide was favoured at higher contact
pressures while iron disulphide and iron sulphate were formed at lower contact pressures [35]. Dithiophosphates were more reactive and formed thicker layers than monothiophosphates [33].

Najman et al. also performed experiments in triphenyl phosphorothionates (TPPT) solution at 100°C with a sliding speed of approximately 0.35 m/s and a contact pressure of 540 MPa (estimated using the contact pressure given in [58]) [55, 56]. The tribofilms were composed of short-chain polyphosphates with sulphates [56] with a phosphorus-to-sulphur ratio of 13:1 [55]. Unfortunately they observed zinc contamination in these films originating from former experiments [55, 56].
1.3 Analysis of Tribofilms

Anti-wear films are formed on the surface of both sliding partners. To understand the processes of film formation, these films were investigated mainly with surface-analytical tools. One can classify the analytical approaches into three main groups [ref]: the in vivo analysis allows data acquisition in the tribological contact during the experiment: inside the wear scars and inside the contact, the in situ analysis which analyse the sample without demounting it, i.e. inside the scar but outside the contact and the ex situ techniques, which analyse the sample after the experiment in a different environment. The advantage of in vivo techniques is that information on the tribological contact itself is provided during the experiment but the information and resolution is often limited. For in situ measurements often the experiment has to be interrupted, but it provides information of the sample in its environment. For ex situ investigations a large variety of techniques with high potential are available, but the sample might have been oxidised, contaminated or modified during cleaning after the experiment or during exposure to air prior to the analysis.

In vivo information is gained by measuring the friction force, which depends on the tribological system including the tribofilm. Plotting the friction coefficient in dependence of the position and number of turns allows lateral inhomogeneities or time dependences to be detected [3, 74]. Optical methods have been used to follow the triboemission of charged particles [75], to measure local temperatures [75] or to determine the film thickness between the tribopartners [48, 76, 77].

A radionuclide technique has been used to monitor wear in situ. The pin was marked radioactively and the radioactive signals in the oil solution converted into wear rates [78, 79]. This is a very laborious technique but provides valuable information about the ongoing wear. Attenuated total reflection infrared spectroscopy was performed by Piras et al. to investigate the chemical interaction of additives with metallic substrates with and without tribostress [6, 46, 47, 53, 68]. This method allowed the identification of the formation of polyphosphates as a consequence of the thermal reaction and of orthophosphates during sliding even if the measurements had to be performed after cooling the ATR crystal and very high additive concentrations had to be used due to the limited sensitivity, and the crystal was cooled down to room temperature to perform the measurement. Martin et al. performed the tribological experiment in the ultra-high vacuum environment of an Auger spectrometer, which is usually used for ex
situ measurements [49, 50]. This allows the sample to be analysed without air exposure but can be damaging for the ultra-high vacuum in the spectrometer.

Many different techniques have been applied to investigate tribostressed samples ex situ. Different kinds of microscopes have been used to analyse for example the widths of wear tracks or the morphology of the tribofilms. This includes optical microscopy, SEM [32, 55, 56] and AFM [28, 36-39, 56]. The mechanical properties of the films have been investigated with AFM and nanoindentation [39-42, 80]. The chemical compositions of the films were investigated with time-of-flight secondary ion mass spectrometry (ToF-SIMS) [81, 82], Auger spectroscopy, XPS [4, 42-44, 53, 54, 56], XANES [26, 33-35, 44, 45] or SEM equipped with EDX, sometimes in combination with focussed ion beam (FIB) milling [80]. Among the spectroscopic techniques, XPS and Auger spectroscopy can be performed in a quantitative way, while this is very difficult with the other techniques. With Auger spectroscopy, Tof-SIMS and SEM areas in the nanometre range can be analysed whereas with XPS or XANES the spatial resolution is in the micrometre range. With Tof-SIMS, the very top layer of the sample is analysed while XPS, Auger and XANES in the total electron yield (TEY) mode probe the top 5 nm. With XANES in the fluorescence yield (FY) mode, the top 50 nm can be analysed, thus obtaining depth-dependent data if performed in both modes. For SEM-EDX the sampling depth is difficult to estimate because X-rays are emitted from a large, bulb-shaped region beyond the activated area. Combining XPS or Auger spectroscopy with ion bombardment, depth profiling can be performed, but selective sputtering and degradation effects might affect the composition.

In this work, optical microscopy, XPS and laser profilometry were used to investigate the surface and composition of the tribostressed samples. The principles of the latter two techniques are introduced shortly in the following sections, for more detailed descriptions of XPS the following books are recommended [83-85].

1.3.1 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), was one of the first vacuum surface-analytical technique to be developed [86]. Among the surface-analytical techniques it is the one that is more popular in tribology because it is relatively easy to collect the data and it provides not only elemental information of all the elements of interest (except H) but also allows the oxidation state of the elements
to be assessed and provides quantitative information and thicknesses of multi-layer films in the nanometre range. The latest X-ray spectrometers allow a spatial resolution of few micrometers to be reached with superior energy resolution.

In XPS, samples are irradiated with monoenergetic soft-X-ray photons. Usually the Ka irradiation of magnesium at 1253.6 eV or aluminium at 1486.6 eV is used. Monochromatic irradiation, produced by diffraction using a Bragg’s lattice, has the advantages that the X-ray energy width is narrower (reduced from 0.9 to 0.25 eV for AlKa) and that satellite peaks and the bremsstrahlung radiation are removed. In addition, monochromatic beams can be focused using an ellipsoidally shaped Bragg’s lattice (see Figure 2.10) and together with less radiant heat the degradation of the sample is minimized [83]. The X-ray penetrates the surface, is absorbed by an electron with a certain binding energy and if the energy of the photon is greater than the binding energy, the electron is emitted (see Figure 1.7). This process is called photoemission and in the simplest case, the energy distribution of the photoelectrons should reflect the energy distribution of electron states in the solid surface.

The kinetic energy $E_{\text{kin}}$ of the electrons is measured with the analyser of the spectrometer. This energy is equal to the energy of the incident photons minus the binding energy $E_B$ and the spectrometer work function $\phi_s$, which is the energy loss when an electron goes from the Fermi level into the vacuum:

$$E_{\text{kin}} = h\nu - E_B - \phi_s$$  

Equation 1.9

By collecting electrons over a certain range of kinetic energies and converting them into binding energies, XPS spectra are acquired. Electrons that are not scattered or scattered elastically, contribute to the characteristic photoelectron peaks while electrons that undergo inelastic scattering, contribute to the background of the spectrum.

The peaks are a direct representation of the electron distribution in an atom:

Figure 1.7: The XPS photoemission of a 1s electron (left) and the relaxation process with the emission of a $KL_{2,3}L_{2,3}$ Auger electron (right) [83, 87].
the core-level notation is \( nlj \) where \( n \) is the principal quantum number (\( n = 1, 2, 3... \)), \( l \) is the orbital angular momentum quantum number and \( j \) is the total angular momentum quantum number; \( j = l + m_s \) where \( m_s \) is the spin angular momentum quantum number (±\( \frac{1}{2} \)). Thus when \( l \) is 1, 2... there are two possible states and thus two signals in the XP-spectrum. For example, an electron with the quantum numbers \( n=2 \) and \( l=1 \) and with a positive spin is called \( 2p_{\frac{3}{2}} \).

The difference in the energy of these two states reflects the "parallel" or "antiparallel" nature of the spin and of the angular momentum vectors of the remaining unpaired electron after the photoemission. This effect is called spin-orbit coupling. The relative population of electrons with the two spins is given by the ratio of their respective degeneracies \( (2j+1) \), therefore the intensity ratio of the \( 3/2 \) to the \( 1/2 \) peak is \( 2:1 \) given by \( \frac{(2*3/2+1)}{(2*1/2+1)} = 4/2 = 2:1 \) [83].

**Auger Electrons**

The core hole resulting from the photoemission process (1s or K orbital in Figure 1.7) is filled with an electron of an outer shell (2p or L\(_{2,3}\) in Figure 1.7). The gain in energy is transferred to another electron (2p or L\(_{2,3}\) in Figure 1.7), which is emitted if the energy is larger than its binding energy. This electron is called KL\(_{2,3}\)Auger electron. In the case of heavier atoms, not always Auger electrons are emitted.

The kinetic energy of the Auger electrons is approximately the difference in the binding energies of the orbitals involved. For a KL\(_{2,3}\)electron:

\[
E_{KL_{2,3}} \approx E_K - E_{L_{2,3}} - E_{L_{2,3}}
\]

Equation 1.10

The kinetic energy of Auger peaks does not depend on the X-ray source and thus the peaks are shifted on the binding energy scale if the X-ray source is changed. Auger signals provide additional information about the chemical state of an element because they depend on the chemical environment of ionized atoms [88]. The sum of the binding energy of the photoelectron peak of an element and the kinetic energy of the element's Auger peak gives the modified Auger parameter \( \alpha' \) [88].

**Angle-resolved XPS**

Because photoelectrons interact strongly with the atoms in the substrate, they usually travel only a small distance (attenuation length) before undergoing inelastic scattering. The intensity of the photoelectron signal \( I \), as a function of sample depth \( z \), can be approximated as:

\[
I = I_0 e^{-z/\lambda \cos \theta}
\]

Equation 1.11
Figure 1.8: Scheme of the information depth in dependence of the emission angle \( \theta \) for angle-resolved XPS measurements (left). Scheme of elastically scattered electrons in angle-resolved XPS, where such electrons contribute significantly to the signal at high emission angles (right).

\( I_0 \) is the intensity at the surface, \( \lambda \) the characteristic attenuation length of the photoelectrons and \( \theta \) their emission angle, measured from the sample normal.

Spectra acquired near normal emission may be representative of the average composition to a depth of \( \sim 3 \lambda \), while spectra acquired at angles nearly parallel to the surface sample are representative of the outermost layers.

The acquisition of XPS spectra at different emission angles \( \theta \) (angle between the surface normal and the lens axis) allows the measurement of samples with different surface sensitivities:

Elastic scattering can change the trajectory of an electron: Electrons actually emitted from the bulk material can be scattered near the surface and emit at higher emission angles (see right). These effects become important for emission angles higher than 60° and dominant at larger emission angles. Therefore only angles up to 60° should be considered for quantitative analysis [83, 89, 90].

**Roughness in XPS**

The roughness of the samples (polished disc: \( R_a = 4 \) nm, tribostressed region on ball: \( R_a = 0.7 \) \( \mu \)m, see Section 3.2.3) is larger than the information depth of the XPS. Gunter et al. showed for rough surfaces that at low emission angles the intensity of the overlayer is higher than it would be for atomically flat surfaces, while at high emission angles lower intensities are obtained for the rough surface [91, 92]. In between, at a 'magic' angle of 40 to 45°, roughness effects are minimal and the accuracy of calculated layer thicknesses depends more on
peak fitting and modelling parameters than on the roughness of the sample [90, 91].

1.3.2 Laser Profilometry

With the oscillating-load tests, the experienced wear rate depends on the angular position of the wear track. Therefore the height over a large area of the disc has to be measured quantitatively. Laser profilometry is the ideal method, providing the height profile with reasonable resolution and accuracy on the desired area.

Principle

A semiconductor laser (wave length: 780 nm, power 0.2 mW) emits light, which is incident onto the sample. The backscattered light is detected by an array of four photodiodes and a feedback circuit controls a height-adjustable lens to roughly focus the beam. The sensor has a window that allows other optical paths to be coupled in; this is white light for a light microscope and two krypton laser beams (407 and 413 nm, 20 mW) for the final adjustment of the lens. The reflected laser beams are measured with a high-resolution CCD camera and the optimal focus is adjusted by comparing the spot diameters of both beams [93].

Roughness

Besides the profile of the wear tracks, the roughness of the surfaces was also analysed using laser profilometry. The average roughness $R_a$ is defined by

$$ R_a = \frac{1}{L} \int_0^L z(x) dx, $$

Equation 1.12

where $z$ is the height of the surface above the mean line with the length $L$ [1]. The root mean square roughness $R_q$ is defined as [1]

$$ R_q^2 = \frac{1}{L} \int_0^L z^2(x) dx. $$

Equation 1.13

Effect of Glassy Overlayers

The ideal situation in laser profilometry is when the light is reflected from a mirror-like metal surface. In tribological systems there is a glassy overlayer formed on a rough surface, which might change the focal point of the laser profilometer what could affect the accuracy of the measurement.
Most of the laser beam will be reflected from the metallic substrate, after having passed through glassy layer. The optical path length increases proportionally to the refractive index, which is around 1.5 for glasses. As will be shown later, the film thickness of the overlayer is usually less than 10 nm, which results in an optical path length of less than 15 nm. Therefore the difference of the path lengths of glass vs. air is less than 5 nm, which is below the accuracy of the profilometer of 10 nm.

In comparison with the surface roughness of the non-contact area of less than 10 nm the glassy overlayer might contribute to the noise of the measurement, but for the wear tracks with depth in the range of 0.1 to 1 μm for the hardened steel discs or even deeper for the wear tests performed with non-hardened discs, the effect of the glassy overlayer on the accuracy of the wear is below 5% for small wear tracks and below 0.5% for the deep ones and can thus be neglected.
1.4 Tribological Testing

In automobile engines, the oil temperature varies considerably over the course of a typical journey. It begins at ambient temperature when starting the engine and increases to 80-100°C under normal use. At higher engine loads, the temperature can locally increase up to 150°C or even higher [94, 95]. In addition, very high contact pressures are present in an engine, which render lubrication challenging, e.g. 1-2 GPa in the case of cam and follower [94, 96, 97]. To cover these and other conditions, there are a large diversity of tribotests. Tests in the laboratory are carried out for understanding tribological processes or to test and simulate different materials and conditions for real applications. The advantage of laboratory tests is that they are cheap, the experimental parameters can be easily controlled and good monitoring possibilities allow the behaviour to be tracked. The parameters should be chosen to be close to real conditions in order to produce meaningful results. On the other hand, practical tests in real machines or in test benches are more expensive but more meaningful for the application. The drawback is that it is difficult to control the conditions and to monitor the experiment [1, 7].

For the laboratory tests, there is a large variety of geometries, where balls, pins, cylinders, flat blocks or pyramids are slid on balls, flat bodies, discs or on the perimeter of cylinders. In symmetrical tests, both areas are tribostressed in the same way, for example in disc-on-disc tests, where both discs are rotated against each other. Most tests are asymmetrical, which means that the involved sliding partners are differently tribostressed. The contact can be conformal, when for example a flat pin is sliding on a flat disc or when a curved surface is sliding on a cylinder with the same curvature. In counterformal contacts, the contact areas do not fit together, for example in a ball-on-disc experiment [1].

A large range of loads and contact pressures are tested [1]. Usually the load is adjusted with weights, but also springs or magnetic forces can be used. The applied speeds range from mm/min up to hundreds of meters per second and the bodies might be sliding, rolling or a combination of both. There are two types of movement, rotation or reciprocating drives, where the sample is moved back and forth. The experiments might be performed in a lubricant or in dry conditions. The applied temperature influences the mechanical properties of the counterparts, the kinetics of ongoing reactions and the viscosity of the lubricant. The environment plays an important role, since water vapour or oxygen might initiate or change the chemical reactions taking place [1].
In most apparatuses the friction force is determined continuously by measuring the tangential force or the torque of a rotating device. This helps understanding the sliding behaviour, for example the running-in of the system or the breakdown of oxide layers or lubricant films. Wear can be measured in situ with electrical or mechanical transducers or ex situ by measuring the dimension of the wear scars or by weighing. The electrical resistance over two counterparts is a measure of film thicknesses of present oxide films, lubricant films or formed anti-wear films [1].

Some of these experiments are standardised by ASTM, DIN or other standards, in order to produce comparable results within different laboratories [1, 7].

1.4.1 Combinatorial Testing

Combinatorial testing is frequently used in the pharmaceutical industry for screening many different samples at once. In tribology, friction and wear strongly depend on various experimental parameters such as the material of the tribopairs, their surface roughness and their geometry, the lubricant composition and the test conditions as the contact pressure, sliding speed and temperature [1, 8, 32]. The investigation of all these parameters is time consuming and laborious: the set up of an experiment where a set of spatially separated areas is tested under different conditions, i.e. the development of a combinatorial approach in tribology, allows for high throughput in lubricant additive testing.

An example of a "combinatorial" test in tribology is the scratch test where a diamond tip is slid over a surface with increasing load [98]. Hogmark et al. invented a crossed sample configuration with varying load over the sample [98, 99]. Both tests are used to screen load effects on hard coatings [98]. Eglin et al. developed a combinatorial approach for ball-on-disc experiments scanning different loads on different radii on one disc [3-5]. Tribological libraries have been generated by varying the parameters with respect to the geometrical position on the sample using a ball-on-disc tribometer capable of changing program load, radius and rotational speed during operation. Two different types of combinatorial experiments were successfully applied: a first approach focuses on the surface-analytical investigation of parameter libraries and a second one on the tribological results (friction, wear). This approach seems to be very effective and useful at low temperatures even if to overcome the problem of a lateral resolution of 120 μm of the X-ray photoelectron spectrometer used for these studies, several tracks close to each other had to be produced in order to get a tribostressed area large enough for small-area XPS. Another disadvantage was
evidenced by the temperature-controlled tests: in some cases at high temperature, the ongoing thermal reactions may change the chemical composition of the tribofilm produced on another radius at the beginning of the experiment.
Chapter 2

Materials and Methods

In this chapter, information on the materials and sample preparation are provided and the different tribological experiments described in detail. The spectrometers and measuring conditions used for X-ray photoelectron spectroscopy are described, followed by a description of the data processing and the modelling for quantitative analysis. The protocol for the interferometric measurements is also given, together with the details of the optical microscopes.

Supporting information on the routines used for processing tribological, interferometric and XPS data is reported at the end of the thesis in the Appendix.
2.1 Materials

2.1.1 Balls and Discs

The balls (diameter 4 mm, Hydrel GmbH, Romanshorn, Switzerland) and discs (CSEM SA, Neuchâtel, Switzerland) were made of a common bearing steel, 100Cr6 (AISI 52100, DIN 1.3505). According to EN ISO 683-17, this steel contains 1.0% carbon, 1.5% chromium, 0.25% silicon and 0.35% manganese (all percentages by weight). Usual tolerances are ±0.1% and both sulphur and phosphorus have to be lower than 0.025%. The steel is hardened by heating it to 800-830°C and a subsequent cooling in water or oil. In this work, hardened balls and discs were used for the combinatorial step tests and the combinatorial oscillating-load tests (see sections 2.3.1 and 2.3.3) and non-hardened balls and discs were used for the wear tests (see section 2.3.2), together with zirconium dioxide balls (ZrO₂, zirconia, diameter 6 mm, P/N: 30307-6.0, Saphirwerk Industrieprodukte AG, Brügg, Switzerland).

The hardness of the hardened discs was measured to be 740±20 HV10 and that of the non-hardened discs was 99±2 HV10.

In the case of the hardened balls, two batches were used; the older batch for the combinatorial step test and the first experiments of the combinatorial oscillating-load test (two experiments in ZnDTP at each temperature and one experiment in pure oil (PAO) at each temperature) while the newer batch was used for all the other experiments of the oscillating-load test. Metallographic investigations on balls of the two batches showed fewer, bigger carbide precipitates on the old balls compared with the new balls, where more, finer dispersed carbides were found [100]. The hardness was tested by micro indentation; it was 562±16 HV0.1 for the old balls and 614±12 HV0.1 for the new balls [100].

2.1.2 Lubricant Oil

As a base oil, poly-α-olefin (PAO, see Figure 2.1, Durasyn 166, Tunap Industries GmbH. & Co., Mississauga, Canada) was used. This is a synthetic oil that can be heated up to 200°C without degradation effects. The physical properties are a density of 830 kg/m³ and a viscosity of 43 mPas at 25°C, 4.8 mPas at 100°C and 2.3 mPas at 150°C [7].
2.1.3 Additives

Two groups of commercial additives were used: a secondary zinc dialkyldithiophosphate (ZnDTP) and three phosphorothionates with increasing chain length.

**Zinc dialkyldithiophosphate**

The commercial secondary ZnDTP HiTEC®7169 (see Figure 2.2, alkyl chains: C₃H₇ + C₆H₁₃; Afton Chemical Corporation, Richmond VA, USA) was used. The additive was purified by liquid chromatography [101]. The additive is a yellowish oily liquid with a melting point below 0°C and a boiling point above 300°C. The density is 1100 kg/m³ (at 15°C) and the flash point is at 110°C [101]. A solution of 1 wt.% in PAO was prepared, with shaking, at room temperature.
Phosphorothionates

The series of differently alkylated triphenyl phosphorothionates TPPT, partially butylated TPPT (b-TPPT) and partially nonylated TPPT (n-TPPT) (Ciba Specialty Chemicals, Basel, Switzerland, purified with liquid chromatography) was tested to investigate the anti-wear performance of ashless additives in dependence of the alkyl chain length. The general chemical formula is given in Figure 2.3; the alkyl chain R changes in the series of the additives as reported in the first row of Table 2.1. The table also lists the physical and chemical properties of the additives. The concentrations used for blending the oil were calculated so that the same phosphorus concentration of 0.08 wt.% was present in all phosphorothionate solutions. The solutions were made weighting the amount of additive. b-TPPT and n-TPPT was dissolved in the base oil by shaking at room temperature (checked by eye). For the crystalline TPPT it was necessary

![Figure 2.3: Chemical structure of the triphenyl phosphorothionates (TPPTs), in which the alkyl chain R changes from H (TPPT) to a mixture of H and tert. butyls (b-TPPT) to a mixture of H and p-nonyl (n-TPPT).]

Table 2.1: Physical and chemical properties of the phosphorothionates [103].

<table>
<thead>
<tr>
<th></th>
<th>TPPT</th>
<th>b-TPPT</th>
<th>n-TPPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial name</td>
<td>Irgalube®TPPT</td>
<td>Irgalube®232</td>
<td>Irgalube®211</td>
</tr>
<tr>
<td>Alkyl chain</td>
<td>R=H</td>
<td>R=H, tert. butyl</td>
<td>R=H, p-nonyl</td>
</tr>
<tr>
<td>Appearance</td>
<td>crystalline white flakes</td>
<td>light yellow liquid</td>
<td>amber liquid</td>
</tr>
<tr>
<td>Melting point</td>
<td>52°C</td>
<td>-39°C</td>
<td>&lt; -50°C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>not measured</td>
<td>432°C</td>
<td>533°C</td>
</tr>
<tr>
<td>Density (at 20°C)</td>
<td>1190 kg/m³</td>
<td>1160 kg/m³</td>
<td>1000 kg/m³</td>
</tr>
<tr>
<td>Flash point</td>
<td>&gt; 200°C</td>
<td>162°C</td>
<td>108°C</td>
</tr>
<tr>
<td>Solubility in mineral oil</td>
<td>2 wt.%</td>
<td>2 wt.%</td>
<td>&gt; 5 wt.%</td>
</tr>
<tr>
<td>Phosphorus content in the molecule</td>
<td>9.1 wt.%</td>
<td>7.7 wt.%</td>
<td>4.3 wt.%</td>
</tr>
<tr>
<td>Sulphur content in the molecule</td>
<td>9.4 wt.%</td>
<td>7.8 wt.%</td>
<td>4.6 wt.%</td>
</tr>
<tr>
<td>Concentration used for blending the oil</td>
<td>0.85 wt.%</td>
<td>1.00 wt.%</td>
<td>1.82 wt.%</td>
</tr>
</tbody>
</table>
to use the ultrasonic bath about five times for 10 minutes for dissolving it in the base oil. The temperature of the lubricant solution remained below 40°C during the ultrasonic bath treatment.
2.2 Sample Preparation

Before a tribotest, the discs were ground with silica paper (grit sizes of 320, 1200 and 2400). Subsequent polishing was performed using diamond paste with grain diameters of 3, 1 and ¼ μm. Ethanol (p.a.) was used for cooling, lubricating and for cleaning the samples. The average roughness of the polished disc was 3.5±0.6 nm determined with a stylus profilometer or smaller than 10 nm determined with a laser profilometer (accuracy 10 nm). The disc surfaces were checked for contamination by XPS and stored in aluminium foil in the hood for 2-3 days prior to the experiment. The balls were cleaned in the ultrasonic bath using first petroleum ether for three minutes and then ethanol (p.a.) for three minutes.

All parts used for the experiment were first cleaned with soap under tap water and then rinsed with deionised water. Later they were ultrasonically cleaned in petroleum ether (technical grade) and ethanol (p.a.) and finally dried under a nitrogen (N₂) stream.

At the end of the experiment, the oil present on discs and ball surfaces was removed by flushing with ethanol (p.a.), followed by ultrasonically cleaning in ethanol for approximately 1 min. The samples were dried under a nitrogen (N₂) stream and immediately introduced into the XPS.
2.3 Tribological Tests

Three kinds of tribotests were performed. The *combinatorial step test* was applied in experiments involving surface analysis with the old generation of XPS spectrometers. A large tribostressed region had to be produced on the sample surface to allow the analysis of the tribological films, avoiding contributions of the elements present in the non-contact areas to the XP-spectra.

The *wear test* was carried out using the non-hardened discs. In this way severe wear conditions were achieved, allowing the comparison of the anti-wear performance of different additives at various sliding speeds and loads together with different sliding partners (zirconia-steel vs. steel-steel contact).

The *combinatorial oscillating-load test* was performed to investigate the tribofilm composition as a function of the applied load with the new generation of XPS spectrometers, which allow a lateral resolution down to 5 μm and therefore the analysis of single wear tracks.

All tribotests were performed in a ball-on-disc arrangement using the CETR UMT-2 tribometer (see Figure 2.4, Center for Tribology, Campbell CA, USA). The contact was always pure sliding without any rolling of the ball. The disc is mounted on a sample holder inside a cup that is filled with 6 ml of oil, so that both the ball and the disc are fully immersed in the lubricant oil during the test [7]. The carriage of the tribometer can be moved up and down in the z-direction, while a horizontal slider allows movements along the x-axis. A rotational drive turns the disc. All motors are under computer control and the positions are determined with an encoder and sent back to the computer. The ball is pressed on

![Figure 2.4: Picture and schematic of a CETR tribometer.](image)
to the disc via a spring and the y/z-load cell measures the resulting friction force and load. The computer then compares the measured load with the nominal load and corrects the applied load by moving the carriage up or down.

There are two load cells with different force ranges, one for forces up to 5 N and another for forces up to 20 N. The resolution is 1/1024th of the maximum load. The 5 N load cell was used for the step tests in ZnDTP while the 20 N load cell was used for the other tests. The load cells were regularly calibrated using a test weight (for details see Appendix).

The tribotests are programmed in test procedures. In such a procedure, a sequence of experiments can be programmed by setting the load, speed, radius and time for each experiment. In addition, the load can be cycled several times over one turn (linear increase and decrease of the load in dependence on the position of the rotational drive). The friction force, the load, the position of the encoders (x, z and rotation) and the time are recorded during an experiment.

Prior to an experiment, the planarity of the disc was checked in order to have constant conditions all over the disc. A stylus was pressed down on the sample with a certain load during one turn of the disc. The z-values of the carriage during this turn determine the planarity of the sample. By placing aluminium foil between the sample holder and the rotational drive, the planarity was adjusted until it was better than ±5 μm on a radius of 7.5 mm.

The tribometer can be equipped with a heating unit (Center for Tribology, Campbell CA, USA) that allows us to heat the oil up to 180°C. A feedback loop measuring the air temperature in the heating unit controls the heating. To prevent an overheating of the oil, the oil temperature was measured and the set-temperature of the air-sensor-feedback-loop was slowly increased by hand. Having reached the final oil temperature, it was constant within ±3°C during an experiment. The forces measured by the load cell drifted due to the high temperatures. Therefore the ball was approached to the surface of the disc when the heating was started and kept there for another hour after the final temperature was reached. The sensor was zeroed before the experiment and after each sequence of a tribotest.

### 2.3.1 Combinatorial Step Test

The step tests were performed to produce a large tribostressed area for the subsequent XPS analysis with the PHI 5700 spectrometer. Therefore the radius was incrementally decreased during the experiment. Eglin et al. developed the tribological test protocol for performing step tests with 5 different loads of 5, 1,
0.5, 0.1 and 0.05 N, where the radius was decreased 11 times by 0.25 μm every 5 turns [3, 5]. They performed tests at 25 and 150°C [4, 7].

In this work, only three different loads were tested, in order to minimize the residence time in the solution after each tribological experiment: This allows the thermal film formation on the tribostressed area to be minimized. A scheme of a typical experiment performed in ZnDTP solution is shown in Figure 2.5; the main parameters are given in Table 2.2. For the tests performed in b-TPPT solution, the parameters given in Table 2.3 were applied. Prior to the actual test, a running-in of the ball on an outer radius of the disc was performed for 2 hours. This was done to flatten the ball, in order to have constant contact conditions during the following step tests. In the step test, the radius is decreased by 25 μm every 5 turns. This step size is much smaller than the average contact area of ~100 μm and therefore the whole area was tribostressed.

![Figure 2.5: Scheme of a sample tribostressed in a step test.](image)

**Table 2.2: Parameters for the step test performed in 1 wt.% ZnDTP.**

<table>
<thead>
<tr>
<th>Load [N]</th>
<th>Radius [mm]</th>
<th>Sliding Speed [mm/min]</th>
<th>Time [min]</th>
<th>Turns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Running-in</td>
<td>5</td>
<td>5.5</td>
<td>31.4</td>
<td>120</td>
</tr>
<tr>
<td>5 N step test</td>
<td>5</td>
<td>4.5±0.125</td>
<td>31.4</td>
<td>11x4.5</td>
</tr>
<tr>
<td>1 N step test</td>
<td>1</td>
<td>4.0±0.125</td>
<td>31.4</td>
<td>11x4.0</td>
</tr>
<tr>
<td>0.2 N step test</td>
<td>0.2</td>
<td>3.5±0.125</td>
<td>31.4</td>
<td>11x3.5</td>
</tr>
</tbody>
</table>

**Table 2.3: Parameters for the step test performed in 1 wt.% b-TPPT.**

<table>
<thead>
<tr>
<th>Load [N]</th>
<th>Radius [mm]</th>
<th>Sliding Speed [mm/min]</th>
<th>Time [min]</th>
<th>Turns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Running-in</td>
<td>10</td>
<td>5.5</td>
<td>31.4</td>
<td>120</td>
</tr>
<tr>
<td>10 N step test</td>
<td>10</td>
<td>4.5±0.125</td>
<td>31.4</td>
<td>11x4.5</td>
</tr>
<tr>
<td>5 N step test</td>
<td>5</td>
<td>4.0±0.125</td>
<td>31.4</td>
<td>11x4.0</td>
</tr>
<tr>
<td>1 N step test</td>
<td>1</td>
<td>3.5±0.125</td>
<td>31.4</td>
<td>11x3.5</td>
</tr>
</tbody>
</table>
Tests in 1 wt.% ZnDTP were performed at 25, 60, 90, 100, 110, 130, 150 and 180°C (all ± 3°C). At room temperature the test procedure was the same as reported by Eglin et al. [5]. According to this protocol, scars were generated applying five different loads of 5, 1, 0.5, 0.1 and 0.05 N on average radii from 5.5 down to 3.5 mm. A control experiment was carried out applying the same load of 5 N at 130°C three times. This was done to check if there was a time dependence of film formation. Samples investigated with the Theta Probe were stressed with only 3 tracks instead of 11 because the Theta Probe allows measurements with a beam diameter of 30 μm.

The tests in 1 wt.% b-TPPT were carried out at 25, 100, 125, 150 and 180°C (all ± 3°C). Again, a control experiment with 5 N load for all three tribostressed areas was done at 150°C to check the time dependence of film formation.

The relative humidity was always between 23 and 44%.

### 2.3.2 Wear Test

The wear test was performed to test different additives and tribopairs at different temperature under different sliding speeds and loads (see Figure 2.6). Eglin introduced a similar test for investigating different sliding time on the different radii [7] while the tests were performed analogously to the procedure described in the following by Spori [104].

![Figure 2.6: Scheme of a sample tribostressed in a wear test (above) and the load dependence on the angular position on the disc (bottom).](image-url)
Table 2.4: Parameters for the wear test.

<table>
<thead>
<tr>
<th>Load [N]</th>
<th>Radius [mm]</th>
<th>Sliding Speed [mm/min]</th>
<th>Time [min]</th>
<th>Turns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Running-in</td>
<td>10</td>
<td>6.5</td>
<td>30</td>
<td>30.0</td>
</tr>
<tr>
<td>V1000</td>
<td>1-10</td>
<td>6.0</td>
<td>1000</td>
<td>3.1</td>
</tr>
<tr>
<td>V398</td>
<td>1-10</td>
<td>5.5</td>
<td>398</td>
<td>7.0</td>
</tr>
<tr>
<td>V158</td>
<td>1-10</td>
<td>5.0</td>
<td>158</td>
<td>16.0</td>
</tr>
<tr>
<td>V63</td>
<td>1-10</td>
<td>4.5</td>
<td>63</td>
<td>36.0</td>
</tr>
<tr>
<td>V25</td>
<td>1-10</td>
<td>4.0</td>
<td>25</td>
<td>80.5</td>
</tr>
<tr>
<td>V10</td>
<td>1-10</td>
<td>3.5</td>
<td>10</td>
<td>176.0</td>
</tr>
</tbody>
</table>

Prior to the actual test, a running-in of the ball was performed with a load of 10 N at an outer radius for half an hour. During the actual wear test, the load was cycled four times per turn from 1 to 10 N according to the scheme on the bottom of Figure 2.6. Different sliding speeds were applied on the different radii (see Figure 2.6 and Table 2.4).

These tests were performed at room temperature and at 150°C in pure oil (PAO), in ZnDTP solution and in a solution of the butylated phosphorothionate. In order to produce measurable wear during the applied 80 turns, non-hardened discs (100Cr6) were used for these tests. As a counter part, balls made of non-hardened 100Cr6 or zirconia were used.

Very high wear was observed at the steel-steel contact samples tri-bostressed at 150°C. Therefore the spacing between the tracks was increased from originally 0.5 mm to 0.7 mm (radii ranging from 6 to 2.5 mm) in order to have well separated tribotracks with a good background between the wear tracks for later data processing of laser profilometer data.

2.3.3 Combinatorial Oscillating-Load Test

Tests with the butylated phosphorothionate showed thermal deposition on the tribotracks (see section 3.1.2). Therefore the multi-track approach from the step and the wear tests is critical for XPS analysis of films produced with such additives. In addition, the new generation of XPS machines allowed measurements on single wear tracks. Therefore a new combinatorial oscillating-load test was designed to test load effects on one sample by varying the load on two cycles per turn (see Figure 2.7 and Table 2.5).

From tribological results of the wear tests and in agreement with Taylor et al. [76], the sliding speed could be increased up to 300 mm/min without leaving the boundary lubrication conditions. This allows having a higher number of turns in order to perform the experiments in more realistic conditions compared to the
combinatorial step test, where only 5 turns were done per radius and therefore the initial state of the tribofilm formation was studied.

The tests were performed at 30, 80 and 150°C in pure oil (PAO) and in PAO blended with the additives ZnDTP or with the phosphorothionates with increasing chain length of the side groups (non-alkylated, butylated and nonylated phenyl ring). These tests were performed at 30°C in contrast to the step tests carried out at room temperature because the rotational drive produced more heat at 300 mm/min than at lower speeds.

The coordinates of an area stressed with a certain load were calculated using the applied load in dependence of the encoder position of the rotational device and comparing it with a reference on the disc. The length of the area tribostressed with a certain load (accuracy of ±0.1 N) was 165 µm and the width of the wear scar was ~150 µm.

![Figure 2.7](image)

**Figure 2.7:** Scheme of a sample tribostressed in a oscillating-load test (above) and the load dependence on the angular position on the disc (bottom).

**Table 2.5:** Parameters for the oscillating-load test.

<table>
<thead>
<tr>
<th></th>
<th>Load [N]</th>
<th>Radius [mm]</th>
<th>Sliding Speed [mm/min]</th>
<th>Time [min]</th>
<th>Turns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Running-in</td>
<td>10</td>
<td>5.0</td>
<td>300</td>
<td>125.7</td>
<td>1000</td>
</tr>
<tr>
<td>Oscillating test</td>
<td>0.5-10</td>
<td>5.0</td>
<td>300</td>
<td>104.7</td>
<td>1000</td>
</tr>
</tbody>
</table>
2.3.4 Data Processing

During a tribological experiment, the friction force, the load, the position of the encoders (x, z and rotation) and the time was written into a data file, which was converted into an ascii file by the program Viewer.exe (Center for Tribology, Campbell CA, USA). The ascii file was read and processed with Matlab 7.1 software (The MathWorks, Inc., Natick, MA, USA).

If, after a sequence of an experiment, a drift of the forces was observed, the forces were corrected assuming the drift had increased linearly with time. These drifts were always smaller than 100 mN for the running-in and smaller than 50 mN for the following tests. At lower temperature, smaller drifts were observed. The friction coefficient $\mu$ was calculated by dividing the corrected friction force by the corrected load.

From the tribological data, the average friction coefficient of all data points, the friction coefficients for several loads in dependence on the number of turns, and the friction coefficients for a certain number of turns in dependence on the applied load were calculated, including standard deviations.

Colour Plots

Using the encoder position of the rotational drive, the friction coefficient was represented in colour plots (see Figure 2.8). The digit in front of the comma of the encoder position specifies the number of turns (x-axis of the plot), the digit after the comma times 360° determines the angular position on the disc (y-axis of the plot) and the corresponding friction coefficient results in the colour at those coordinates. To decrease the noise and the number of data points for these plots (originally up to 600'000 data points), an average of 10 points was plotted per pixel.

Figure 2.8: Colour plot of the friction coefficient during the running-in (left plot) and during the oscillating-load test for a sample tribostressed at 80°C in ZnDTP solution. (Shown here as it is obtained running the Matlab program.)
Materials and Methods

If a constant load was applied (step test or running-in), the height of the ball (encoder position of the z-value) was plotted as a function of the angular position on the left side of the colour plot to check the planarity of the sample again (Figure 2.8 left). If a test with an oscillating load was performed, the applied load was plotted in dependence of the angular position on the left side of the colour plot (Figure 2.8 right). The code for the program is given in the Appendix.

Stick-Slip

Stick-slip was observed at low sliding speeds in the steel-steel contact during wear tests (see Figure 2.9). In G40-05 ASTM, stick-slip is defined as a cyclic fluctuation in the magnitudes of friction force and relative velocity between two elements in sliding contact, usually associated with a relaxation oscillation dependent on the elasticity in the tribosystem and with a decrease of the coefficient of friction with the onset of sliding or with the increase of sliding speed. This phenomenon appears when the sliding contacts stick to each other. As a next step, the contacts slip a certain distance until they stick together again. In such a case the average friction coefficient is not calculated because the sticking condition is not relevant to the friction. The only important value is the applied shear force to release the sticking contact and activate the slipping. This value represents a static friction coefficient rather than a kinetic friction coefficient, but nevertheless is the only useful information that can be obtained [7, 105]. Therefore if stick-slip was observed (numerical criterion determined with numerous examples: standard deviation of 6 following friction coefficients >0.005), the maximum value of each stick-slip step was taken for calculating the friction coefficient.

![Friction Coefficient μ vs Rotation [°]](image)

**Figure 2.9:** Stick-slip of a steel-steel contact in a wear test at 150°C in ZnDTP at a sliding speed of 10 mm/min. One load cycle from 1 to 10 to 1 N was applied during the 90° rotation shown in the plot.
2.4 X-Ray Photoelectron Spectroscopy

The surface chemistry of the tribostressed samples was investigated with X-ray photoelectron spectroscopy (XPS), analysing both the tribostressed and non-contact areas. The first series of experiments was performed using a PHI 5700 spectrometer. The X-ray source of that instrument illuminates the entire sample surface. Using an aperture allows limited areas (diameter of 120 μm in this work) to be analysed. Therefore, tribostressed areas larger than 120 μm were necessary for the analysis of the tribofilms.

The second series of experiments was carried out with the PHI Quantera and the Theta Probe. With both instruments, the electrons are excited with microfocussed X-ray beams, which allow spectra to be measured on single wear tracks of a ball-on-disc experiment. While the PHI Quantera exhibits excellent sensitivity and imaging capabilities with small beam sizes, the Theta Probe allows the simultaneous acquisition of angle-resolved spectra.

All spectrometers were operated at residual pressures below 5 x 10^-7 Pa and were calibrated according to ISO 15472:2001. The accuracy in binding energy was better than ± 0.05 eV.

2.4.1 PHI 5700

The PHI 5700 (Physical Electronics, Chanhassen MN, USA) is equipped with an Al/Mg Kα twin source and a monochromatic AlKα source. The electrons emitted from the sample are focused and slowed down using an Omnifocus IV lens system. An aperture is included in the lens system and allows the size of the analysed area to be chosen between 0.03 and 0.8 mm. The emission angle (angle between surface normal and the lens system of the analyser) is 45° and the source-to-analyser angle 54°. The electrons are analysed with a concentric hemispherical electron analyser and measured with a 16-channel detector. This detector allows measurements to be made in the scanned and in the snapshot mode. In the scanned mode, the energy range of a spectrum is scanned through, and in the snapshot mode, electrons with different energies are collected in different channels, which allows complete spectra to be measured simultaneously, but with a limited energy range and resolution.
For imaging XPS, the analysed area is scanned over the surface by adjusting the settings of the lenses. In each spot of the image complete spectra are acquired using the snapshot mode.

The PHI5700 is further equipped with an argon ion gun (PHI 04-303 A) for sputtering and with a cooling stage for cooling or even freezing outgassing samples with liquid nitrogen via a copper braid.

The samples were focussed by hand using the focal point of a live camera. The positions on the sample were examined by means of imaging XPS and the points of interest for later small-area XPS were selected.

**Experimental Settings**

Measurements were typically performed using non-monochromatic AlKα with a power of 350 W. The analysed area was limited to a diameter of 120 µm by the aperture of the lens system. The analyser was operated in the scanned constant-analyser-energy mode (CAE) (also called fixed-analyser-transmission mode (FAT)) with a pass energy of 46.95 eV for detailed spectra (full-width-at-half-maximum (fwhm) for Ag3d_{5/2} = 1.1 eV) and 187.85 eV for the survey spectra, the step size was 0.1 and 1 eV respectively.

XPS images were typically measured on a 2-2.8 mm² area with a resolution of 64x64 pixels in the snapshot mode with a pass energy of 46.95 eV. Normally only O1s maps were acquired during 4 to 6 hours for obtaining a good signal to noise ratio. These maps were processed with the linear-least-squares algorithm (PHI Multipak V6.0) for differentiating areas with bigger oxide peaks from those with higher intensities of oxygen originating from the phosphate groups.

### 2.4.2 PHI Quantera

The X-ray source of the PHI Quantera (Physical Electronics, Chanhassen MN, USA) is monochromatic AlKα. A scheme of a monochromator as it is used in the PHI Quantera is shown in Figure 2.10. A focussed electron beam impinges on the aluminium anode (X-ray target). The emitted X-rays are monochromatised on an ellipsoidal shaped monochromator in order that a focussed X-ray beam with the slightly higher diameter as the electron beam illuminates the sample surface. Beam diameters between 5 and 200 µm were achieved.

The emitted electrons were collected and retarded with an Omega lens system at an emission angle of 45°. The source-to-analyser angle was also 45°. After passing the hemispherical analyser, the electrons were detected by a 32-channel detector.
For performing imaging XPS or measuring line scans, the electron beam is scanned over the anode by means of the deflection plates (see Figure 2.10). Because the X-rays are now produced at different spots of the anode, the monochromatised X-ray beam is focussed at corresponding spots on the sample surface. By scanning the electron beam on the anode, the X-ray beam is therefore scanning over the sample surface. Adjusting the lens system allows the electrons that originate from other spots than from the centre of the image to be collected.

The system is furthermore equipped with a high-performance floating column ion gun for sputtering, depth profiling and charge compensation (angle ion gun-to-sample normal: 45°). There is an electron neutralizer for optimizing charge compensation or for charge compensation on slightly insulating samples where the ion gun was unnecessary. Outgassing samples can be cooled down with liquid nitrogen.

The Quantera is equipped with a fully automatic sample handling system including two parking areas. The samples were moved from the intro chamber to the sample stage or the parking areas by drag-and-drop on the computer screen. The samples were automatically focussed using the intensity at a binding energy of 530 eV. The unambiguous identification of the tribologically stressed areas was performed by means of the sample-positioning station (SPS), which allows photographs of the sample surface to be acquired outside the instrument. The SPS, in combination with a scanning X-ray image (SXI), facilitates rapid location of the desired analysis region and correlation with the coordinates calculated using the angular position from the tribological test. The positions of the points were double-checked using imaging XPS and line scans.
Experimental Settings

Small-area XPS spectra were collected with a beam diameter of 20 μm with a power of 4.25 W in the CAE mode applying a pass energy of 69 eV and a step size of 0.125 eV. Charging of the sample was minimized using the electron neutralizer. The resulting fwhm for Ag3d5/2 was 1.3 eV under these measuring conditions. Survey spectra were acquired with 280 eV pass energy and a step size of 1 eV. The whole set of spectra (detail and survey spectra) was acquired within 40 to 60 min/spot.

Imaging XPS was performed with a beam size of 10 μm with a power of 2.3 W and a pass energy of 140 eV in the snapshot mode, allowing the simultaneous measurement of spectra with a binding energy range of 15.5 eV. The spectra of all elements of interest were measured on an area of typically 800-600 μm² (lateral resolution normally 10 μm) within 6-8 hours of acquisition. Line scans were acquired with the same settings as for imaging XPS on lines of 800-1000 μm length (resolution between 3.3 and 10 μm) over typically 40 min. For fast checks of the positions of the tribotrack, line scans of selected elements were acquired with a beam size of 20 μm (resolution 10 or 20 μm) within 5 to 10 minutes.

2.4.3 Theta Probe

The Theta Probe (Thermo Fisher Scientific, Waltham MA, USA) is equipped with an Al/Mg Kα twin source and a monochromatic AlKα source with beam diameters ranging from 15 to 400 μm. The emitted electrons are collected with a radian lens with 60° acceptance angle, ranging from 23 to 83° emission angle. For the average emission angle of 53°, the source-to-analyser angle is 67.38°. For the full range of emission angles, the source-to-analyser angle ranges from 43.1 to 93.7°. After passing a hemispherical sector analyser, the electrons are collected on a two-dimensional detector with 112 energy channels and 96 angular channels.

For performing imaging XPS, the sample is moved under the X-ray beam. This takes more time for the acquisition, but the conditions are the same for all points measured.

Further equipment is an ion gun (angle ion gun-to-sample normal: 45°), a combined low-energy electron/ion flood gun for charge compensation and a cooling stage.

In the Theta Probe, the points of interest on the samples were found and focussed using a high-resolution camera. The system offers a probe light where a
light beam is focussed onto the anode and then it is following the same path to the monochromator and the sample surface as the X-ray beam. Focusing using the photoelectron intensity is also possible. The position, intensity and the diameter of the X-ray beam were checked with a phosphor screen and the position on the sample was checked with imaging XPS.

**Experimental Settings**

Angle-resolved XPS measurements were performed using a monochromatic X-ray beam of 30 μm diameter with a power of 6 W in CAE mode, a pass energy of 200 eV and a step size of 0.2 eV. The resulting fwhm for Ag3d$_{5/2}$ was 1.3 eV. The angular information was summed up into 8 channels for better signal-to-noise ratios.

Angle-resolved imaging XPS was performed measuring the O1s spectra on an area of 500·500 μm$^2$ (17·17 points) at 16 angles over approximately 10 hours. This resulted in a total of 4624 spectra.

**2.4.4 Data Processing**

**Peak Fitting**

High-resolution spectra taken on the small areas of choice were processed with CasaXPS Software (V2.3.12, Casa Software Ltd., UK). In the case of Fe2p$_{3/2}$ measured with non-monochromatic AlKα, the satellite originating from the Fe2p$_{1/2}$ peak was subtracted with the CasaXPS software.

The region for fitting the spectra were typically chosen to be 1 eV wider on each side than the peaks of the signal (see $E_1$ and $E_2$ in Figure 2.11). To decrease the influence of the noise to the background, the average of the intensi-

![Figure 2.11: XPS detailed spectrum of Fe2p$_{3/2}$ with the region ranging from $E_1$ to $E_2$ and with an iterated Shirley background applied.](image-url)
ties from typically 11 points was taken to determine the height of the background on each side.

An iterated Shirley background was applied. The intensity of the background $S(E)$ at each binding energy $E$ was calculated taking into account the peak area before that energy and the total peak area [107]:

$$S(E) = I(E_1) - I(E_2) \cdot \frac{\text{Area}_{E_2}^E}{\text{Area}_{\text{tot}}}$$  \hspace{1cm} \text{Equation 2.1}

$I(E_1)$ and $I(E_2)$ are the intensities of spectrum at the edges of the fitted region (see Figure 2.11), $\text{Area}_{E_2}^E$ the area under the peak between $E$ and $E_2$ and $\text{Area}_{\text{tot}}$ the total area of the signal. Because the area under the peaks depends on the shape of the background, the background has to be calculated again on the basis of the new areas; this was repeated 20 times.

The peaks were fitted with a product of the Gaussian and Lorentzian line shapes, in case of the metallic iron and Fe(III) peaks together with an asymmetric tail. The following formulas are used in CasaXPS:

Gaussian:

$$G(E : E_0, \text{fwhm}, m) = \exp^{-\frac{4\ln 2 \cdot \left(1 - \frac{m}{100}\right) \left(E - E_0\right)^2}{\text{fwhm}^2}}$$  \hspace{1cm} \text{Equation 2.2}

Lorentzian:

$$L(E : E_0, \text{fwhm}, m) = \frac{1}{1 + \left(\frac{m}{100}\right) \left(E - E_0\right)^2}$$  \hspace{1cm} \text{Equation 2.3}

Tail:

$$T(E : E_0, \text{fwhm}, k) = \begin{cases} \exp^{-\frac{E - E_0}{\text{fwhm}}} & E \leq E_0 \\ 1 & E > E_0 \end{cases}$$  \hspace{1cm} \text{Equation 2.4}

$$GL(m) = G(E : E_0, \text{fwhm}, m) \cdot L(E : E_0, \text{fwhm}, m)$$  \hspace{1cm} \text{Equation 2.5}

$$GL(m)T(k) = GL(m) + (1 - GL(m)) \cdot T(E : E_0, \text{fwhm}, k)$$  \hspace{1cm} \text{Equation 2.6}

$E$ is the binding energy at each data point, $E_0$ the binding energy of the peak, $\text{fwhm}$ the full-width-at-half-maximum, $m$ the percentage of the Lorentzian function in the product and $k$ the asymmetry parameter.

Curve-fitting parameters were determined from reference spectra acquired under the same analysis conditions; the parameters for spectra acquired with the PHI Quantera are given in Table 2.6. The references are given in section 3.1 and by Eglin et al. [4]. For measurements performed with the PHI 5700 the same parameters were used with the exception of carbon 1s (fwhm 1.6-2 eV), iron 2p$_{3/2}$ (metallic iron: GL(85)T(0.63), fwhm 1.3 eV; Fe(III): GL(45), fwhm 2.8 eV; other iron peaks: GL(45), fwhm 3 eV) and zinc 2p (GL(80)) [4]. For performing angle-resolved XPS with the Theta Probe, the fwhm of phosphorus,
**Materials and Methods**

*Table 2.6: XPS peak-fitting parameters for spectra acquired with the PHI Quantera. If one value is given, this is the parameter used for the peak fitting. If a range is given, the parameter is constrained to be within this range. If a formula (e.g. \(=P(I)+0.85\)) is given, the parameter is linked to be 0.85 higher than the one of the \(P(I)\) peak.*

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>Line Shape</th>
<th>Position [eV]</th>
<th>FWHM [eV]</th>
<th>Area [Cps-eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2p3/2</td>
<td>P(I)</td>
<td>GL(30)</td>
<td>132-136</td>
<td>1.4-1.8</td>
<td>=P(I)2</td>
</tr>
<tr>
<td>P2p1/2</td>
<td>P(II)</td>
<td>GL(30)</td>
<td>=P(I)+0.85</td>
<td>=P(I)</td>
<td></td>
</tr>
<tr>
<td>S2p3/2</td>
<td>S(I)</td>
<td>GL(45)</td>
<td>160-164</td>
<td>1.4-1.8</td>
<td>=S(I)/2</td>
</tr>
<tr>
<td>S2p1/2</td>
<td>S(II)</td>
<td>GL(45)</td>
<td>=S(I)+1.25</td>
<td>=S(I)</td>
<td>=S(I)/2</td>
</tr>
<tr>
<td>S2p3/2</td>
<td>S(III)</td>
<td>GL(45)</td>
<td>166-170</td>
<td></td>
<td>=S(I)</td>
</tr>
<tr>
<td>S2p1/2</td>
<td>S(IV)</td>
<td>GL(45)</td>
<td>=S(I)+1.25</td>
<td></td>
<td>=S(III)/2</td>
</tr>
<tr>
<td>C1s</td>
<td>C(I)</td>
<td>GL(30)</td>
<td>284-286</td>
<td>1.6-1.8</td>
<td>=C(I)</td>
</tr>
<tr>
<td></td>
<td>C(II)</td>
<td>GL(30)</td>
<td>286-287</td>
<td></td>
<td>=C(II)</td>
</tr>
<tr>
<td></td>
<td>C(III)</td>
<td>GL(30)</td>
<td>288-290</td>
<td></td>
<td>=C(III)</td>
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<td>C(IV)</td>
<td>GL(30)</td>
<td>283-283.5</td>
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<td>=C(IV)</td>
</tr>
<tr>
<td>O1s</td>
<td>O(I)</td>
<td>GL(20)</td>
<td>530-530.3</td>
<td>1.6-1.8</td>
<td>=O(I)</td>
</tr>
<tr>
<td></td>
<td>O(II)</td>
<td>GL(20)</td>
<td>531.6-532</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>O(III)</td>
<td>GL(20)</td>
<td>533.4</td>
<td></td>
<td>=O(III)</td>
</tr>
<tr>
<td></td>
<td>O(IV)</td>
<td>GL(20)</td>
<td>534-536</td>
<td></td>
<td>=O(IV)</td>
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<tr>
<td>Fe2p3/2</td>
<td>Fe(met)</td>
<td>GL(85)T(0.63)</td>
<td>706.7-706.9</td>
<td>0.7-1.1</td>
<td>=Fe(II)0.07</td>
</tr>
<tr>
<td></td>
<td>Fe(II)</td>
<td>GL(0)</td>
<td>709.3-709.6</td>
<td>2.4-2.8</td>
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</tr>
<tr>
<td></td>
<td>Fe(III)</td>
<td>GL(55)T(1.6)</td>
<td>710.9-711.0</td>
<td>2.6-3.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe(OOH)</td>
<td>GL(45)</td>
<td>713.5</td>
<td>3-5.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe(PO4)</td>
<td>GL(45)</td>
<td>=Fe(II)+5.5</td>
<td>=Fe(II)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe(Ilsat)</td>
<td>GL(0)</td>
<td>=Fe(II)+5.5</td>
<td>=Fe(II)</td>
<td></td>
</tr>
<tr>
<td>Zn3s</td>
<td>GL(30)</td>
<td>138-144</td>
<td>2-3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn2p3/2</td>
<td>GL(60)</td>
<td>1020-1026</td>
<td>1-3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnLMM</td>
<td>ZnLMM(I)</td>
<td>GL(30)</td>
<td>490-505</td>
<td>2-4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ZnLMM(II)</td>
<td>GL(30)</td>
<td>490-505</td>
<td>2-4</td>
<td></td>
</tr>
</tbody>
</table>

Sulphur, carbon and oxygen was allowed to be wider due to the high pass energy applied, with a maximal width of 2 eV each. The binding energy and the fwhm of each peak was set equal for all angles in order to have constant fitting conditions for all angles.

The spectra were fitted with a linear-least-squares algorithm. If the ratio of the fwhm of the peaks on the sample to the fwhm of the reference spectrum was higher than 1.20 (a number derived from statistical fwhm analysis of over fifty spectra), then this was taken as an indication that an additional peak should be introduced in the curve synthesis.

**Sample Charging**

The binding values reported in this work were corrected for the sample charging, when it was detected, by referring all binding energies to the aliphatic carbon C1s signal at 285.0 eV. It has to be noted that the values in section
3.1.1 slightly differ from them of [108], where the binding energy values were referred to 284.8 eV, the aliphatic carbon taken at 150°C.

For an area analysed with angle-resolved XPS, the carbon 1s spectra acquired at emission angles from 23° to 64° were summed up and fitted. All spectra at all angles were then referred to the aliphatic carbon of this sum at 285.0 eV. The binding energy of aliphatic carbon of the corrected spectra was then at 285.0±0.1 eV.

Angle-resolved XPS

Angle-resolved spectra were fitted with the parameters described above and peak intensities in dependence of the emission angle obtained. Under the assumption of a homogenous compound, the atomic concentrations were calculated in dependence of the emission angle. The applied model compounds are given in Table 2.7 and mentioned for all data presented.

3D-Plots

Angle-resolved imaging XPS spectra of O1s were fitted with VG Avantage 3.19 software by constraining the binding energy of the oxide peak to be between 530.2 and 530.3 eV. The binding energy of the non-bridging oxygen (NBO) peak was fixed to be 1.6 eV above the oxide peak, and the bridging oxygen (BO) peak to be 3.1 eV above the oxide. The percentages of the individual oxygen peaks with respect to the sum of all oxygen peaks were plotted colour coded in 2D-maps, which were then used to create 3D-plots with Adobe Illustrator CS2 (Adobe Systems Inc., San Jose, CA, USA).

2.4.5 Quantitative XPS Analysis

The tribostressed samples were inhomogeneous in composition as a function of depth. Layered structures were present, as shown in the results section by means of angle-resolved XPS. The thickness and composition of the layers were calculated applying a multi-layer model, which is based on a first-principles model.

First-Principles Model

In this section, the general approach for the case of a homogeneous surface irradiated by X-rays is presented in order to summarize the main points of the approach. The basis of quantitative XPS analysis is the following equation [109, 110]:

\[ \text{Energy} = \text{Constant} + \text{Binding Energy} \]
$I_A = \sigma_A(h\nu) \cdot D(E_A) \cdot \int_{\gamma=0}^{2\pi} \int_{\phi=0}^{\pi} L_A(\gamma) \int_{x=0}^{\infty} \int_{y=0}^{\infty} J_0(xy) \cdot \sec \delta \cdot T(xy, \phi, E_A, E_p) \cdot \int_{z=0}^{\infty} N_A(xyz) \cdot e^{-\frac{1}{\lambda M(E_A)} \cos \delta} d\gamma d\Phi dx dy dz$

Equation 2.7

$I_A$ is the measured area under the peak (in Cps·eV) of the element A in the matrix M. Electrons emitted from the subshell $i$ of the element A following the X-ray-solid interaction have a kinetic energy $E_A$. For the photoionization cross-section $\sigma_A(h\nu)$, values calculated by Scofield were used [111]. $D(E_A)$ is the detector efficiency. Figure 2.12 from Seah [109] shows the scheme of the angles in XPS, which are defined in the following: $\gamma$ is the angle formed between the X-ray source and the analyser (or more precisely the axis of the lens system, in the figure labelled as “e- Spectrometer”), $\phi$ is the angle between the surface normal projected on the plane perpendicular to the X-ray beam and the e- spectrometer projected on that plane (see Figure 2.12), $\delta$ is the angle formed between the X-ray source and the surface normal and $\theta$ is the emission angle (angle between surface normal and the analyser). $L_A(\gamma)$ is the angular asymmetry function [112, 113], $x$ and $y$ are the lateral coordinates on the sample while $z$ is the depth of the sample (see Figure 2.12). The photoelectrons are emitted from a given $ni$ (or $nij$) subshell of atoms A contained in a differential volume element of thickness $dz$ at a distance $z$ below the specimen surface. $J_0(xy)$ is the X-ray flux on the sample at the characteristic energy $h\nu$ and $T(xy, \phi, E_A)$ the transmission function [114]. $N_A(xyz)$ is the atom density of the atom A at $(xyz)$ in atoms/unit volume. $\lambda_M(E_A)$ (in nm) is the inelastic mean free path (IMFP) of the

Figure 2.12: Scheme of the coordinates and angles in XPS. (Modified on the basis of [109].)
electrons in the matrix \( M \) and was calculated according to Tanuma et al. [115, 116]. Details on the factors are given in the subsection Sensitivity Factor on page 56.

The instruments used in this study were operated in the constant-analyser-energy mode and thus the energy of the electrons entering the multiplier of the detector is equal to the pass energy \( E_p \). In all instruments used in this work, a range of kinetic energies is measured simultaneously using multi-channel detectors or 2D-detectors. This requires small deviations in the pass energies and therefore it is questionable if the assumption that \( D(E_a) \) becomes \( D(E_p) \) is still valid for these instruments.

A second issue is the area of analysis: While for the PHI 5700 the assumption of a uniformly illuminated surface and a small entrance aperture is valid, the new generation of instruments works with small beam sizes, which leads to illuminated areas similar to Auger electron spectroscopy. Taking into account these two considerations, the étendue was introduced as it is defined for Auger electron spectroscopy [109]:

\[
G(E_a) = \text{area}_{\text{analysed}} \cdot T(E_a) \cdot D(E_a)
\]

Equation 2.8

Since only small areas were analysed, a lateral homogeneity is assumed. Under the assumption of a small angle of detection (several angles in the case of the Theta Probe), Equation 2.7 can be written as:

\[
I_a = \sigma_a(h\nu) \cdot L_a(\gamma) \cdot G(E_a) \cdot J_0 \cdot \sec \delta \cdot \int_0^\infty N_a(z) \cdot e^{-z/\lambda_u(E_a) \cdot \cos \theta} dz
\]

Equation 2.9

There are three special cases for the integral over \( z \): for a homogenous material over the whole depth analysed it becomes \( N_a \cdot \lambda_M(E_a) \cdot \cos \theta \), it is \( N_a \cdot \lambda_M(E_a) \cdot \cos \theta \cdot (1 - e^{-z/\lambda_u(E_a) \cdot \cos \theta}) \) for a homogenous overlayer with the thickness \( z_1 \), and it is \( N_a \cdot \lambda_M(E_a) \cdot \cos \theta \cdot e^{-z_2/\lambda_u(E_a) \cdot \cos \theta} \) for a substrate with an overlayer of the thickness \( z_2 \).

If an overlayer with different material properties attenuates the signal, the IMFP changes as well. The intensity \( I_a \) of the signal \( I_a(z) \) originating from the depth \( z \) can then be calculated according to the Beer-Lambert law:

\[
I_a = I_a(z) \cdot e^{-z/\lambda_u(E_a) \cdot \cos \theta}
\]

Equation 2.10

For the case of several different overlayers with the thicknesses \( z_i \), there is a product of the exponential parts with the thicknesses \( z_i \) and \( \lambda_u(E_a) \).
The Three-Layer Model

In general, substrate and layers are multi-component and the thickness of the different layers as well as their composition is unknown. This general situation has been resolved applying the so-called "three-layer model" [54, 117-119]. This model assumes a contamination layer on the top of a multi-component oxide layer formed on a multi-component substrate. The assumption are that each layer is homogeneous in thickness and composition, that there is no mixing between the layers and that the electrons are attenuated by the overlayers according the Beer-Lambert law (see Equation 2.10). The equations were written in parametric form and were solved numerically applying the Newton-Raphson method. The thickness and composition of the oxide layer and of the substrate are calculated simultaneously. The three-layer model has successfully been applied to tribostressed steel [54, 108], amorphous metals [117, 118], stainless steels [119], minerals [120] and also to model systems such as PLL-g-PEG and ODP SAM on Ta2O5 substrates [121, 122].

The Multilayer Model

Having a substrate covered with three layers, the system of equations changes because an additional overlayer has to be taken into account. In this work the substrate was iron, covered initially with an air-formed iron oxihydroxide layer. During the tribological experiment, a reaction layer was formed at the surface, covered with an organic layer. Details on the model compounds used for calculating the material properties of the different layers are given in Table 2.7.

For this system a multilayer model was developed based on Equation 2.9 and Equation 2.10 and on independent information from angle-resolved XPS data. Instead of the atom density $N_{\alpha}$, the mass fraction $w_{\alpha}$ times the density of the compound $\rho_{M}$ divided by the atomic weight of the atom $A_{\alpha}$ is used. The product $J_0 \cdot \sec \delta$ is unknown but is independent of the elements measured. Taking the ratio of the intensities of two elements, it can be eliminated [89]. The equation for aliphatic carbon was chosen as divisor because this element is present in the uppermost layer and therefore the equation is the simplest, which simplifies obtaining a numerical solution.

The product $\sigma_i(h\nu) \cdot L_i(\gamma) \cdot G(E_i) \cdot \lambda_{i,M} \cdot \cos \theta \cdot \frac{\rho_M}{A_i}$ is substituted by the sensitivity factor $S_{i,M}$ and depends on the element and the compound the electron is originating from. Details and numbers on the sensitivity factor and its components are given on page 56.
If metallic iron was detected with at least 5% of the intensity of the overlayer peaks [89], then a four-layer model with metallic iron as a substrate (Equation 2.11) was used. \( d_{ox}, d_r \) and \( d_{org} \) are the thicknesses of the oxide, reaction and carbon layers.

\[
\frac{I_{i,\text{met}}}{I_{C(\text{aliphatic}),org}} = \frac{S_{i,\text{met}} \cdot e^{-d_{ox}/\lambda_{\text{ox},\cos\theta}} \cdot e^{-d_r/\lambda_{r,\cos\theta}} \cdot e^{-d_{org}/\lambda_{\text{org},\cos\theta}}}{S_{C(\text{aliphatic}),org} \cdot w_{C(\text{aliphatic}),org} \cdot (1 - e^{-d_{org}/\lambda_{\text{org},\cos\theta}})}
\]

Equation 2.11

The thickness of the oxide layer was finite if the intensity of iron was higher than 5% (Equation 2.12) or treated as semi-infinite if not (Equation 2.13). The sum of all \( w_{i,ox} \) is 1. If less than 5% intensity from iron oxide in relation to the overlayer intensity was detected, neither of the two equations was used.

\[
\frac{I_{i,ox}}{I_{C(\text{aliphatic}),org}} = \frac{S_{i,ox} \cdot w_{i,ox} \cdot (1 - e^{-d_{ox}/\lambda_{\text{ox},\cos\theta}}) \cdot e^{-d_r/\lambda_{r,\cos\theta}} \cdot e^{-d_{org}/\lambda_{\text{org},\cos\theta}}}{S_{C(\text{aliphatic}),org} \cdot w_{C(\text{aliphatic}),org} \cdot (1 - e^{-d_{org}/\lambda_{\text{org},\cos\theta}})}
\]

Equation 2.12

\[
\frac{I_{i,ox}}{I_{C(\text{aliphatic}),org}} = \frac{S_{i,ox} \cdot w_{i,ox} \cdot e^{-d_r/\lambda_{r,\cos\theta}} \cdot e^{-d_{org}/\lambda_{\text{org},\cos\theta}}}{S_{C(\text{aliphatic}),org} \cdot w_{C(\text{aliphatic}),org} \cdot (1 - e^{-d_{org}/\lambda_{\text{org},\cos\theta}})}
\]

Equation 2.13

The thickness of the reaction layer was again finite if metallic iron or iron oxide is present (Equation 2.14) or treated as semi-infinite if not (Equation 2.15). The sum of all \( w_{i,r} \) is 1.

\[
\frac{I_{i,r}}{I_{C(\text{aliphatic}),org}} = \frac{S_{i,r} \cdot w_{i,r} \cdot (1 - e^{-d_{org}/\lambda_{\text{org},\cos\theta}}) \cdot e^{-d_r/\lambda_{r,\cos\theta}} \cdot e^{-d_{org}/\lambda_{\text{org},\cos\theta}}}{S_{C(\text{aliphatic}),org} \cdot w_{C(\text{aliphatic}),org} \cdot (1 - e^{-d_{org}/\lambda_{\text{org},\cos\theta}})}
\]

Equation 2.14

\[
\frac{I_{i,r}}{I_{C(\text{aliphatic}),org}} = \frac{S_{i,r} \cdot w_{i,r} \cdot e^{-d_{org}/\lambda_{\text{org},\cos\theta}}}{S_{C(\text{aliphatic}),org} \cdot w_{C(\text{aliphatic}),org} \cdot (1 - e^{-d_{org}/\lambda_{\text{org},\cos\theta}})}
\]

Equation 2.15

For the carbon layer there is only one equation since the intensity of the reaction layer was high enough to apply at least the two-layer model. The sum of all \( w_{i,org} \) is 1.

\[
\frac{I_{i,org}}{I_{C(\text{aliphatic}),org}} = \frac{S_{i,org} \cdot w_{i,org} \cdot (1 - e^{-d_{org}/\lambda_{\text{org},\cos\theta}})}{S_{C(\text{aliphatic}),org} \cdot w_{C(\text{aliphatic}),org} \cdot (1 - e^{-d_{org}/\lambda_{\text{org},\cos\theta}})}
\]

Equation 2.16
For \( n \) peaks, this results in a system of \( n+3 \) equations for the four-layer model with a substrate of metallic iron, \( n+2 \) equations for a three-layer model with a semi-infinite oxide layer as a substrate and \( n+1 \) equations for the two-layer model with a semi-infinite reaction layer as a substrate. The same number of unknown parameters is present, which allows a solution of the system of nonlinear equations to be found using numerical methods. It was simultaneously solved using Mathematica (V5.0). Given a starting point with layer thicknesses of 1 nm and equal mass fractions that sum up to 1 for each layer, the program searches for a numerical solution using the Newton method. An example is given in the Appendix. The accuracy goal is 8 digits, and if it was not reached within 100 iterations, the procedure was applied again with the most recent approximation as a starting point.

### Model Compounds

Metallic iron was taken as the model compound for the steel 100Cr6 with metallic iron as the main component (see Table 2.7). Traces of carbides were detected in samples tribostressed with oscillating load at 30°C, but this mathematical model does not allow the composition of the substrate to be determined. Magnetite (Fe\(_3\)O\(_4\)) was chosen as the model compound for the oxide layer because it contains both Fe(II) and Fe(III), as found in the samples.

Depending on the film composition found in the reaction layer, different model compounds were used for modelling it. For non-contact films formed in ZnDTP solution, zinc phosphate tetrahydrate was used for the reaction layers for the tribofilms of the oscillating-load test, zinc pyrophosphate was used at 30, 80 and 150°C.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Model compound</th>
<th>Formula</th>
<th>Temperature range</th>
<th>Density ([\text{kg/m}^3])</th>
<th>Band gap ([\text{eV}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic</td>
<td>Aliphatic carbon</td>
<td>(\text{CH}_3[\text{CH}_2]_n\text{CH}_3)</td>
<td>25-180°C</td>
<td>1000</td>
<td>5</td>
</tr>
<tr>
<td>Organic</td>
<td>Zinc phosphate</td>
<td>(\text{Zn}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O})</td>
<td>25-110°C(^1)</td>
<td>3040</td>
<td>3.4 [124]</td>
</tr>
<tr>
<td>Organic</td>
<td>Zinc pyrophosphate</td>
<td>(\text{Zn}_2\text{P}_2\text{O}_7)</td>
<td>130-150°C(^1)</td>
<td>3750</td>
<td>3.4 [124]</td>
</tr>
<tr>
<td>Organic</td>
<td>Iron phosphate</td>
<td>(\text{Zn}(\text{PO}_3)_2)</td>
<td>180°C</td>
<td>3040</td>
<td>3.68 [124]</td>
</tr>
<tr>
<td>Organic</td>
<td>Iron phosphate</td>
<td>(\text{FePO}_4)</td>
<td>25-180°C</td>
<td>2870</td>
<td>3.4</td>
</tr>
<tr>
<td>Oxide</td>
<td>Magnetite</td>
<td>(\text{Fe}_3\text{O}_4)</td>
<td>25-180°C</td>
<td>5170</td>
<td>3.0 [126]</td>
</tr>
<tr>
<td>Substrate</td>
<td>Iron (metallic)</td>
<td>(\text{Fe})</td>
<td>25-180°C</td>
<td>7870</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^1\) for the tribofilms of the oscillating-load test, zinc pyrophosphate was used at 30, 80 and 150°C.
formed at temperatures up to 110°C, zinc pyrophosphate between 130 and 150°C and zinc metaphosphate at 180°C. For the tribological films formed during the combinatorial step test, the same compounds were used while for the tribofilms formed during the combinatorial oscillating-load test, zinc pyrophosphate was used as a model compound at all temperatures, as suggested by the oxygen-to-phosphorus ratio lower than 4:1. For samples stressed in solutions blended with phosphorothionates, iron phosphate was the model compound.

For the carbon layer, aliphatic carbon was used as a model compound for all samples.

**Sensitivity Factor**

According to the section “Multilayer Model” above, the sensitivity factor in this work is defined as

<table>
<thead>
<tr>
<th>Layer</th>
<th>Model compound</th>
<th>Element</th>
<th>PHI 5700</th>
<th>PHI Quantera</th>
<th>Theta Probe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>27°</td>
<td>34°</td>
<td>42°</td>
</tr>
<tr>
<td>Organic</td>
<td>Aliph. carbon</td>
<td>C1s</td>
<td>0.197</td>
<td>0.159</td>
<td>0.16</td>
</tr>
<tr>
<td>Reaction</td>
<td>Zinc phosphate</td>
<td>O1s</td>
<td>0.875</td>
<td>0.701</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P2p3/2</td>
<td>0.158</td>
<td>0.147</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S2p3/2</td>
<td>0.211</td>
<td>0.195</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe2p3/2</td>
<td>0.796</td>
<td>0.689</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn3s</td>
<td>0.098</td>
<td>0.079</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn2p3/2</td>
<td>0.836</td>
<td>0.697</td>
<td>0.73</td>
</tr>
<tr>
<td>Zinc pyrophosphate</td>
<td>O1s</td>
<td>1.008</td>
<td>0.808</td>
<td>0.81</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P2p3/2</td>
<td>0.181</td>
<td>0.169</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S2p3/2</td>
<td>0.243</td>
<td>0.224</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
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<td>Fe2p3/2</td>
<td>0.916</td>
<td>0.794</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn3s</td>
<td>0.113</td>
<td>0.091</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn2p3/2</td>
<td>0.967</td>
<td>0.806</td>
<td>0.85</td>
</tr>
<tr>
<td>Zinc metaphosphate</td>
<td>O1s</td>
<td>0.800</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td>P2p3/2</td>
<td>0.144</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>S2p3/2</td>
<td>0.193</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe2p3/2</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td>Zn3s</td>
<td>0.090</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn2p3/2</td>
<td>0.762</td>
<td></td>
<td></td>
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<tr>
<td>Iron phosphate</td>
<td>O1s</td>
<td>0.802</td>
<td>0.643</td>
<td>0.64</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P2p3/2</td>
<td>0.145</td>
<td>0.135</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S2p3/2</td>
<td>0.194</td>
<td>0.179</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe2p3/2</td>
<td>0.729</td>
<td>0.632</td>
<td>0.64</td>
</tr>
<tr>
<td>Oxide</td>
<td>Magnetite</td>
<td>O1s</td>
<td>1.214</td>
<td>0.973</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe2p3/2(II)</td>
<td>1.107</td>
<td>0.959</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe2p3/2(III)</td>
<td>1.106</td>
<td>0.958</td>
<td>0.90</td>
</tr>
<tr>
<td>Substrate</td>
<td>Iron (metallic)</td>
<td>Fe2p3/2</td>
<td>1.377</td>
<td>1.193</td>
<td>1.20</td>
</tr>
</tbody>
</table>
\[ S_{i,M} = \sigma_A(h\nu) \cdot L_A(\gamma) \cdot G(E_i) \cdot \lambda_{i,M} \cdot \cos \theta \cdot \frac{\rho_M}{A_i}, \]  

Equation 2.17

whereas \( \sigma_A(h\nu) \) is the photoionization cross-section, \( L_A(\gamma) \) the angular asymmetry factor, \( G(E_i) \) the étendue, \( \lambda_{i,M}(E_A) \) the inelastic mean free path (IMFP) of the electrons in the matrix \( M \), \( \theta \) the emission angle, \( \rho_M \) the density and \( A_i \) the atomic mass of the element \( i \). The sensitivity factors calculated for different elements in different compounds are given in Table 2.8 for the XPS instruments used. Details about the parameters used for calculating the sensitivity factors are described in the following sections.

**Photoionization Cross-section**

The photoionization cross-section \( \sigma_A(h\nu) \) is the "probability that an incident photon traversing a material will produce a photoelectron from a given subshell, expressed as an area unit per event" [127]. Values calculated by Scofield in 1976 [111] were used for this work, where \( \sigma \) is given in units of the C1s cross-section of 13600 barns and depends on the energy of the X-ray source \( h\nu \) and on the subshell of the element \( A \).

**Angular Asymmetry Function**

The intensity of photoelectrons from non-spherical atomic orbitals differs with the angle \( \gamma \) between the source and analyser (see Figure 2.12). This effect is corrected by the angular asymmetry function \( L_A(\gamma) \) [112, 113]:

\[ L_A(\gamma) = 1 + \frac{1}{2} \beta \cdot \left( \frac{3}{2} \sin^2 \gamma - 1 \right) \]  

Equation 2.18

The values for the asymmetry factor \( \beta \) were calculated by Reilman et al. [112] based on quantum mechanics and reported for the different energies of the X-ray source and for the various subshells. \( \beta \) is 2 for the s-orbitals, 1.09 for P2p, 1.14 for S2p, 1.45 for Fe2p and 1.40 for Zn2p using AlK\( \alpha \) irradiation. For the PHI 5700 \( \gamma \) is 54° which is the "magic angle" at which the last term becomes zero and \( L_A(\gamma) = 1 \). For the PHI Quantera \( \gamma \) is 45° and \( L_A(\gamma) \) ranges from 0.75 and 0.86, depending on the element and its orbital. In the Theta Probe, \( \gamma \) (and thus \( L_A(\gamma) \)) depends on the emission angle (EM):

\[ \gamma = \cos^{-1} \left[ \cos \theta_i \cdot \cos EM + \sin \theta_i \cdot \sin EM \cdot \cos \varepsilon \right] \]  

Equation 2.19

where \( \theta_i \) is the angle between the source and the surface normal (30°) and \( \varepsilon \) is the angle at the surface normal of the spherical triangle (source – surface normal – analyser, see Figure 2.12) and is 110° (given \( \gamma = 67.38° \) for EM = 53°
by the manufacturer and assuming that the emission angles and the surface normal are on one plane).

Étendue

In the constant-energy mode, photoelectrons with a kinetic energy $E_i$ pass a lens system, which focuses and retards the electrons to the applied pass energy $E_p$ of the hemispherical analyser. The number of transmitted electrons strongly depends on the kinetic energy of the electrons and is a function of the applied settings as lens modes (magnification/aperture slit dimensions), analyser type/operation (energy resolution) and the X-ray illumination (large area flood or monochromatic focused spot). Measuring a range of kinetic energies at once, and for the Theta Probe even dependent on the emission angle, the pass energy varies slightly and the detector efficiency might be different for the different conditions. Therefore, the étendue $G(E_i)$ was used as it is defined for Auger electron spectroscopy where $G(E_i)$ is equal to the product of the analysed area times the transmission function times the detector efficiency (see Equation 2.8). To obtain quantitative results, the measured intensities have to be corrected for the étendue determined for the applied settings.

For the PHI 5700 the following function for the étendue was used:

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

Equation 2.20

$RR$ is the retard ratio ($RR=E_i/E_p$) and $a$ and $b$ are fitted parameters. These were determined by measuring the Cu2p, CuLMM and Cu3p peaks of sputter-cleaned copper at different pass energies. The peak areas corrected for the pass energy and normalized according the formula for Cu2p peaks:

$$\frac{I_{\text{corr., normalized}}}{I_{\text{Cu2p}}} = \frac{I_{\text{Cu2p}}}{E_{p,i}} \max_i \left(\frac{I_{\text{Cu2p}}}{E_{p,i}}\right)$$

Equation 2.21

This gives a data set for all three peaks, which were plotted against the retard ratio in a log-log plot, which is then fitted with the parameters $a$ and $b$. Measuring on an area with a diameter of 120 μm, $a$ was 1.87 and $b$ was 0.015 [7]. Measuring with a pass energy of 46.95 eV, this results in similar values for the étendue ranging from 0.92 for electrons from P2p with the highest kinetic energy up to 0.95 for electrons from Zn2p with the lowest kinetic energy.

For the PHI Quantera a parabolic étendue (Equation 2.22) had to be applied to obtain a good fit of the log-log plot.

$$\frac{I}{E_p} = \ln\left[a \cdot \ln(\text{RR})^2 + b \cdot \ln(\text{RR}) + c\right]$$

Equation 2.22
**Table 2.9:** Values of the parameters $a$ and $b$ for the étendue of the Theta Probe for angle-resolved measurements using a beam size of 30 μm.

<table>
<thead>
<tr>
<th>EM [°]</th>
<th>26.75</th>
<th>34.25</th>
<th>41.75</th>
<th>49.25</th>
<th>56.75</th>
<th>64.25</th>
<th>71.75</th>
<th>79.25</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>14.71</td>
<td>10.96</td>
<td>11.77</td>
<td>16.55</td>
<td>22.90</td>
<td>25.77</td>
<td>23.52</td>
<td>22.78</td>
</tr>
<tr>
<td>$b$</td>
<td>0.3304</td>
<td>0.2915</td>
<td>0.3504</td>
<td>0.4182</td>
<td>0.4233</td>
<td>0.4939</td>
<td>0.4702</td>
<td>0.4713</td>
</tr>
</tbody>
</table>

Using a 20 μm X-ray beam size, $a$ was -0.13, $b$ was 0.71 and $c$ was 1.72. Using a pass energy of 69 eV, the resulting values ranged from 1.00 for P2p to 0.96 for Zn2p.

Using the Theta Probe, the function given in Equation 2.20 was used for the étendue. The values of $a$ and $b$ for the different emission angles using a beam size of 30 μm are given in Table 2.9. Applying a pass energy of 200 eV, the values for the étendue were between 0.90 (P2p at 42° EM) and 0.99 (Zn2p at small EM).

**Inelastic Mean Free Path**

The inelastic mean free path $\lambda_{M}(E_a)$ (IMFP) is defined as "the average of distances, measured along the trajectories, that particles with a given energy travel between inelastic collisions in a substance" [127]. The values were calculated using the model compounds described above and the formulae given by Tanuma et al. [115, 116] (see Table 2.10).

**Table 2.10:** Inelastic mean free paths of electrons from different chemical states in different compounds. (X-ray source: AlKα)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxide</td>
<td>285.0</td>
<td>1.88</td>
<td>2.32</td>
<td>2.85</td>
<td>2.66</td>
<td>2.84</td>
<td>2.77</td>
<td>3.62</td>
</tr>
<tr>
<td>NBO</td>
<td>530.2</td>
<td>1.58</td>
<td>1.95</td>
<td>2.39</td>
<td>2.23</td>
<td>2.38</td>
<td>2.32</td>
<td>3.02</td>
</tr>
<tr>
<td>BO</td>
<td>533.4</td>
<td>1.58</td>
<td>1.94</td>
<td>2.38</td>
<td>2.23</td>
<td>2.37</td>
<td>2.32</td>
<td>3.01</td>
</tr>
<tr>
<td>Phosphate</td>
<td>133.7</td>
<td>2.06</td>
<td>2.54</td>
<td>3.12</td>
<td>2.91</td>
<td>3.11</td>
<td>3.04</td>
<td>3.98</td>
</tr>
<tr>
<td>Sulphide</td>
<td>162.3</td>
<td>2.03</td>
<td>2.50</td>
<td>3.07</td>
<td>2.87</td>
<td>3.06</td>
<td>2.99</td>
<td>3.92</td>
</tr>
<tr>
<td>Sulphate</td>
<td>168.9</td>
<td>2.02</td>
<td>2.49</td>
<td>3.06</td>
<td>2.86</td>
<td>3.05</td>
<td>2.98</td>
<td>3.90</td>
</tr>
<tr>
<td>Metallic</td>
<td>706.9</td>
<td>1.36</td>
<td>1.67</td>
<td>2.05</td>
<td>1.92</td>
<td>2.04</td>
<td>1.99</td>
<td>2.58</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>709.6</td>
<td>1.36</td>
<td>1.67</td>
<td>2.04</td>
<td>1.91</td>
<td>2.03</td>
<td>1.98</td>
<td>2.57</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>710.9</td>
<td>1.36</td>
<td>1.67</td>
<td>2.04</td>
<td>1.91</td>
<td>2.03</td>
<td>1.98</td>
<td>2.57</td>
</tr>
<tr>
<td>FeOOH</td>
<td>711.8</td>
<td>1.36</td>
<td>1.67</td>
<td>2.04</td>
<td>1.91</td>
<td>2.03</td>
<td>1.98</td>
<td>2.56</td>
</tr>
<tr>
<td>FePO₄</td>
<td>713.5</td>
<td>1.36</td>
<td>1.66</td>
<td>2.04</td>
<td>1.90</td>
<td>2.02</td>
<td>1.98</td>
<td>2.56</td>
</tr>
<tr>
<td>Zinc</td>
<td>140.4</td>
<td>2.05</td>
<td>2.53</td>
<td>3.11</td>
<td>2.90</td>
<td>3.10</td>
<td>3.03</td>
<td>3.97</td>
</tr>
<tr>
<td>Zn3s</td>
<td>1022.6</td>
<td>0.95</td>
<td>1.16</td>
<td>1.41</td>
<td>1.33</td>
<td>1.40</td>
<td>1.37</td>
<td>1.74</td>
</tr>
<tr>
<td>Zn2p₃/₂</td>
<td>1022.6</td>
<td>0.95</td>
<td>1.16</td>
<td>1.41</td>
<td>1.33</td>
<td>1.40</td>
<td>1.37</td>
<td>1.74</td>
</tr>
</tbody>
</table>
2.5 Laser Profilometry

The topography of the discs was measured with laser profilometry (UBM, type UBC 14, UBM Messtechnik GmbH, Ettlingen, Germany) to determine the wear. A Kr⁺⁺-laser beam (spot size 1 µm, wavelength 407 and 413 nm) was dynamically focused onto the sample and the z-value measured (accuracy ±10 nm if measuring in the ±50 µm range) [93]. The sample table can be laterally moved and an area of 13·13 mm² was measured with a resolution of 120 points/mm. The data were stored in a z-value matrix. The machine settings for performing the measurement are given in the Appendix.

2.5.1 Data Processing

The resulting profilometer file is converted into an ascii file using the macro “asciicon.mac” provided with the measuring software. Using Matlab software, a colour plot of the height vs. the lateral position was created (see Figure 3.44 and Figure 3.78) to get an overview of the measurement. The roughness of the sample can be obtained applying another program by choosing several regions on the image. The roughness was then calculated taking 100 points/region into account.

To determine the wear rate, radial profiles were read out of the z-value matrix, flattened by subtracting a parabolic fit and averaged over sectors of 5° (50 lines) to increase the signal-to-noise ratio. Applying a linear background, the areas above and below the background were summed up and converted into deposition and wear rates. The program code for creating surface plots and for determining the wear and deposition rate is given in the Appendix. For the wear test, the load was cycled four times per turn. Therefore the same tribological conditions were present on the sample four times, and the wear- and deposition rates of these four sets were averaged to reduce the noise of the results.
2.6 Optical Microscopy

Optical microscopy images of the step-test samples were taken using a Reichert-Jung Polyvar microscope (Leica Microsystems Nussloch GmbH, Wetzlar, Germany) with objectives from 5x to 100x and equipped with a CCD camera (Leica Microsystems GmbH, Wetzlar, Germany). For images of the oscillating load samples, an AX10 Imager M1m (Carl Zeiss, Oberkochen, Germany) with objectives from 5x to 100x and equipped with a CCD camera was used.
Chapter 3

Results

In the first part of this chapter, the results obtained with the combinatorial step test are presented. With this test, the temperature dependence of the film formation of the two anti-wear additives ZnDTP and an ashless phosphorothionate was investigated for different applied loads.

The second part shows the results of the combinatorial oscillating-load test, where the load was cycled during one turn of the disc in order to investigate the load dependence of the film formation on one single tribotrack. Here the effect of different additives such as ZnDTP and phosphorothionates with different chain lengths was investigated at different temperatures.

In the last part, the influence of sliding speed and load on friction and wear was tested within one experiment. In addition, different sliding partners, the effect of anti-wear additives are compared at low and high temperature.
3.1 Combinatorial Step Test

In a step test, the radius of the tribotrack was decreased by 25 μm every five turns in order to produce a large tribostressed area for the following XPS analysis performed with the PHI 5700 with an analysed diameter of 120 μm. Areas with different applied loads were produced on each disc to compare the effect of load. Two types of additives (metal containing ZnDTP and the ashless metal free phosphorothionate b-TPPT) were tested at different temperatures to improve the understanding of the mechanism of anti-wear film formation.

3.1.1 ZnDTP

Tribological Tests

The colour plot of the friction coefficient μ for a step test (11 overlapping tracks with 5 turns) with 5 N load performed at 130°C is shown in Figure 3.1. The friction force jumped to higher values every 5 turns due to the stepwise change of the tribotrack to a new one.

The mean friction coefficient μ for several loads at different temperatures is shown in Figure 3.2. Starting from a low value of 0.14±0.02 at room temperature for all loads, it increased with increasing temperatures to a high-friction regime for temperatures above 90°C; here the friction coefficient was 0.20±0.02, i.e. 45% higher than that at room temperature. No significant load dependence of the friction coefficient was observed. The uncertainty at low loads is found to

Figure 3.1: Colour plot of the friction coefficient μ as a function of the angular position on the sample and the number of turns. The sample was tribostressed in a step test in ZnDTP solution with 5 N load at 130°C.
Results: Combinatorial Step Test

Figure 3.2: Friction coefficient $\mu$ for 5, 1 and 0.2 N load in dependence of the temperature of the ZnDTP oil bath.

be equal to ±0.025, which is very high. This value was calculated applying the error propagation after Gauss and assuming a measuring uncertainty of the load cell of 5 mN.

Optical microscopy of samples tribostressed in a step test clearly showed the 11 wear tracks close to each other (see the 5 N tracks in Figure 3.3). There was almost no visual difference between tribostressed samples from 25°C to 150°C—only tribostressed samples at 180°C showed a brownish layer covering the non-contact area. At lower loads, less pronounced traces of the tribotracks were found. In the case of the 180°C samples, the brownish layer was not completely removed with lower loads.

Figure 3.3: Optical microscopy images of samples tribostressed in a step test with 11 steps and 5 N load in ZnDTP solution performed at 25, 130 and 180°C.

XPS Results

Survey and high-resolution (detailed) spectra were recorded on the areas tribostressed with different loads and on the non-contact areas. In the survey spectra, only signals from phosphorus, sulphur, carbon, oxygen, iron and zinc
were detected. Subsequently, detailed spectra of phosphorus 2p together with zinc 3s, sulphur 2p, carbon 1s, oxygen 1s, iron 2p, zinc 2p and zinc LMM were measured. As an example, the spectra from the non-contact area and the tribostressed region recorded at 130°C with 5 N load are shown in Figure 3.4; similar spectra were measured at lower loads.

The survey spectra showed the very prominent peaks of Zn2p3/2 and Zn2p1/2 at binding energies of 1023 and 1046 eV respectively, the O1s peak at 532 eV and the ZnLMM Auger signal at a kinetic energy of 987 eV (at 499 eV on the binding energy scale). Smaller peaks of Fe2p, C1s, S2p and S2s (not labelled, at 287 eV), P2p and P2s (not labelled, at 192 eV), Zn3s (not labelled, 141 eV) were detected. Below 100 eV numerous peaks of Fe (3s, 3p and 3d), Zn (3p and 3d), O (2s and 2p), P (3s and 3p), S (3s and 3p) and C2p were revealed, but those at lower binding energy values were overlapping in the so-called valence band region.

The signals of phosphorus, sulphur, iron and zinc of the 2p orbital exhibit two peaks 2p3/2 and 2p1/2. This splitting arises from the coupling of the spin and orbital angular momentum. The area of the 2p3/2 peak is always twice that of the 2p1/2 peak and the binding energy of the 2p1/2 peak is the higher of the two peaks. In the phosphorus and sulphur signals these two peaks are close to each other, resulting in an asymmetric signal. The model curves used for fitting the experimental peaks were linked to each other: the ratio of 2p1/2/2p3/2 contributions was fixed at 0.5 and the difference in energy was maintained equal to 1.25 eV for sulphur and 0.85 eV for phosphorus [4].

In addition to the phosphorus signals at 133.7±0.1 eV, a peak originating from zinc 3s was detected at 140.5±0.1 eV. For quantification, this signal was used instead of the most intense zinc photoelectron line, Zn2p3/2, since the Zn3s is in the same binding energy range as phosphorus, sulphur and oxygen and therefore exhibits with an IMFP of 2.9 nm in a pyrophosphate a similar IMFP as the other elements present in the film. Using the zinc 2p signal with its much smaller IMFP of 1.3 nm would cause inaccurateness because of its different sampling depth (proportional to IMFP) compared to the other elements present in the films.

In the case of sulphur, two different peaks, each composed of S2p3/2 and S2p1/2, were detected: one at 162.3±0.1 eV of the oxidation state -2, found in sulphides [128, 129] and thiols [130, 131] or if sulphur substitutes oxygen in a phosphate [53] and one at 168.9±0.1 eV assigned to sulphate groups [128, 129].
Figure 3.4: XPS survey and detailed spectra of P2p with Zn3s, S2p, C1s, O1s and Fe2p of a non-contact area and an area tribostressed with 5 N load at 130°C in ZnDTP solution. (Data acquired with the PHI 5700.) In the O1s contributions of NBO at 531.8 eV there are other contributions from sulphate, hydroxide or carbonate and in the BO there is, at low temperature, the contribution from water.
The most intense component in the carbon signal was from aliphatic carbon (C-C, C-H), found at 284.9±0.1 eV. Minor contributions were found at 286.9±0.1 and 289.2±0.2 eV.

The oxygen signal consisted of three peaks at 530.2±0.1 eV, 531.8±0.1 eV and 533.4±0.1 eV. The low-binding-energy peak at 530.2 eV is assigned to iron and zinc oxide [4, 132, 133]. The main peak at 531.8 eV originates from non-bridging oxygen (NBO) in (poly)phosphates and from other oxygen-containing groups such as sulphate [129], carbonate or hydroxides [4, 66, 70]. The peak at 533.4 eV is assigned to bridging oxygen (BO), which links phosphate groups together to form phosphate chains [66, 69, 70].

The iron spectra showed two main peaks with maxima of Fe2p3/2 at 711 eV and of Fe2p1/2 at 724 eV (spin-orbit splitting). Curve synthesis was performed only on the Fe2p3/2 signal. The main components were the peaks from iron oxide, Fe(II) and Fe(III), at 709.6 and 710.9 eV, respectively, as well as the Fe(II)-satellite at 715.1 eV with 7% intensity of the main peak [4, 133]. On the higher-binding-energy side there was another peak at 713.5 eV, which was assigned to iron phosphate [69].

Spectra at different Loads

XPS-spectra taken at areas tribostressed by applying a 1 N load were very similar to those collected of the tribofilm formed after applying 5 N (see Figure 3.5). A further decrease of the load to 0.2 N did not change the peak positions, whereas the components at lower BE of both S2p at 162.3 eV and O1s at 530.2 eV showed a change in the relative peak intensity: the S2p decreases and the O1s increases with the applied load.

130°C in ZnDTP

Figure 3.5: XPS detailed spectra of P2p with Zn3s, S2p and O1s measured on areas tribostressed with different loads and on the non-contact area produced at 130°C in ZnDTP solution. (Data acquired with the PHI 5700.)
Spectra at different Temperatures

The shape of the spectra changed with temperature, and four regimes could be separated: 25°C, 60-110°C, 130-150°C and 180°C. Spectra of phosphorus 2p with zinc 3s, sulphur 2p and oxygen O1s in these temperature regions are shown in Figure 3.6 for the non-contact and for the tribostressed regions.

In the non-contact areas produced at room temperature, only trace amounts of phosphorus, sulphur and zinc were detected. As shown in Figure 3.7, the binding energy of phosphorus was lower compared to films produced at higher temperatures. The main contribution to the oxygen signal came from iron oxide, together with a small contribution from zinc oxide. The iron spectra (not shown) exhibited peaks due to metallic iron (706.9 eV [129, 132]), iron oxide and iron hydroxide (711.8 eV [4, 133]).

**Figure 3.6:** XPS detailed spectra of P2p with Zn3s, S2p and O1s measured on non-contact areas (above) and with 5 N tribostressed areas (below) produced at different temperatures in ZnDTP solution. (Data acquired with the PHI 5700.)
The spectra of the non-contact region in the 60-110°C temperature range exhibited more prominent peaks of phosphorus, sulphur and zinc than at room temperature. In the oxygen spectra (Figure 3.6 above, 100°C) a higher contribution at 531.8 eV was detected, while the oxide peak was still significant.

Above 130°C, the signals of the non-contact area showed more intense peaks of phosphorus, sulphur and zinc but less intense peaks of iron and O(oxide) compared to those taken at lower temperatures.

At 180°C the signals for the non-contact region were broader and consisted of additional components: a peak at 135.2±0.2 eV in the case of phosphorus (see Figure 3.6 and Figure 3.7, fwhm 1.7 ± 0.1 eV), one at 534.8±0.3 eV in the case of oxygen and one at 1023.6±0.2 eV for zinc 2p$_{3/2}$. Sulphur was detected only in traces and the low-binding-energy peak of sulphur at 162.1 eV was shifted up to a higher binding energy of 163.7±0.4 eV. No iron was detected anymore.

Different spectra of the elements described above were recorded in the contact regions (Figure 3.6, below). While the peak positions and shapes were similar to those from the non-contact region, major deviations in the peak areas were found: The tribostress at 25°C led to higher intensities of phosphorus, sulphur and zinc compared to the non-contact film. The spectra of the contact regions in the range of 60-110°C had similar shapes as those at 130-150°C but with smaller signals of phosphorus and sulphur, and more intense signals of Fe (also with metallic iron being detected) and of the O(oxide)-peak. At 180°C there were also small signals of iron oxide detected, which means that after the tribostress a thinner film was present than in the non-contact region.

![Figure 3.7: Binding energy of phosphorus 2p$_{3/2}$ vs. temperature for areas tribostressed in ZnDTP solution with 5 N load and the non-contact areas. Note that (only) at 180°C there were 2 peaks at 133.7±0.1 and 135.2±0.2 eV (fwhm of all peaks: 1.7±0.1 eV). (Data acquired with the PHI 5700.) R. Pinna [70] measured the reference compounds.]
3D-Colourplots of Oxygen

Imaging-angle-resolved XPS was performed to obtain three-dimensional information about the tribofilm and the surrounding non-contact area. While imaging XPS provides lateral information, simultaneous angle-resolved measurements provide information on the in-depth distribution. A higher emission angle (angle between the analyser and the surface normal) corresponds to a higher surface sensitivity.

The 3D colour plots of the oxygen signal shown in Figure 3.8 are from a sample that was tribostressed at 150°C. At these temperatures, a thick tribofilm was formed, which provides a reasonable signal-to-noise ratio of the oxygen peak for all 4624 spectra collected within an overnight measurement. The number of steps in the tribological experiment was decreased from 11 to 3 because the XPS-instrument allowed measurements with 30 µm spot size. While the lateral information shows possible lateral inhomogeneities over the tribofilm, the

![Figure 3.8: 3D colour plots of the three oxygen peaks: oxide, non-bridging oxygen (NBO) and bridging oxygen (BO), measured on the tribostressed area and the surrounding non-contact area. The colour indicates the peak's percentage of the sum of the O1s peaks in dependence on the lateral position (plan view) and the emission angle (z-axis). The tribostressed area was produced with three tribotacks close to each other with 5 N load in ZnDTP solution at 150°C. (Data acquired with the Theta Probe.)](image-url)
Results: Combinatorial Step Test

depth information completes the spatial image of the oxygen distribution within the films. The peaks were fitted by constraining the binding energy of the oxide peak to lie between 530.2 and 530.3 eV, the NBO being fixed to be 1.6 eV above the oxide peak, and the BO 3.1 eV above the oxide. The percentages of given oxygen peaks with respect to the sum of all the oxygen peaks are shown in the 3D-plots (Figure 3.8). The colour indicates the three percentages of the oxygen 1s peaks: the lighter the colour, the higher the contribution of this peak to the oxygen signal.

High intensity of the oxide was found in the tribostressed region with especially high intensity in the centre of the region, where the contact pressure was higher than at the edge of the contact region. Higher intensity was measured at lower emission angles, implying that the oxide lies mainly at the bottom of the analysed volume. NBO was the highest contribution to the oxygen peaks and itself highest at the edge of the tribostressed region. In the tribostressed region its percentage was higher in the outer part of the film while in the non-contact region it was lower in the outer part. The percentage of BO was much higher in the thermal film than in the tribofilm. In both cases it was more prominent at higher emission angles, and thus in the outer part of the film.

Bridging Oxygen / Non-bridging Oxygen

The BO-to-NBO ratio was plotted against both temperature and emission angle (Figure 3.9) to show the film composition, with a focus on the polyphosphates. To determine this ratio, the contribution of oxygen in sulphate groups (4 times the corrected intensity of sulphur 2p at 168.8 eV) was subtracted from the NBO peak. At temperatures below 90°C for tribostressed regions and below 130°C for non-contact regions the ratio is not plotted, because adsorbed water and hydroxides contributed to the oxygen signal assigned to BO and NBO. At

![Figure 3.9: Ratio of bridging oxygen to non-bridging oxygen plotted for areas tribostressed with 5 N load and non-contact regions as a function of the temperature of the ZnDTP oil bath (left; PHI 5700) and emission angle (right, temperature: 150°C; Data acquired with the Theta Probe).](image)
90°C and above, a mixture of ortho- and pyrophosphates (P$_2$O$_7^{4-}$, short chain length) is formed in the contact region. With higher temperature, the chain length increased (150°C: ~3 phosphate groups linked together on average) up to a cross-linked polyphosphate at 180°C (see figure 10, left). In this cross-linked polyphosphate, bridging oxygen atoms link the chains together; the corresponding phosphorus groups contain then 3 bridging oxygen atoms and 1 non-bridging oxygen. With lower loads applied, the BO/NBO ratios were similar to the 5 N load regions, no significant change in chain length was observed. The non-contact areas show slightly higher BO/NBO ratios at all temperatures above 130°C than in the contact regions, meaning that the chains are longer in the non-contacted region.

The depth distribution of the polyphosphates can be deduced from the angle-resolved XPS measurements (Figure 3.9, right), where higher ratios were found at higher emission angles for both the non-contact as well as for the triboostressed region. This means that the shorter chains were in the inner part of the film whereas the longer polyphosphates were to be found near the outside.

**Thickness and Composition**

In the previous sections it was demonstrated that a multilayered system with depth-dependent composition is present. For this reason the thickness and composition of the adsorbed films have been calculated using the multi-layer model (see page 53). The model is based on the simplifying assumption that the individual layers (metallic iron with overlaying oxide layer covered by the reaction layer and with an organic layer on top) are homogenous laterally and in depth. The application of this model is discussed in chapter 4.

For calculating the thickness of the oxide layer, metallic iron has to be detected in a certain amount. According to Seah [109], the intensity of the substrate has to be at least 5% of the total intensity to determine the thickness of the overlayer. This was the case for the room temperature samples and the non-contact area treated at 60°C; an oxide layer thickness of 2.6±0.1 nm was calculated.

The thicknesses of the reaction layers as a function of the load and the temperature is shown in Figure 3.10. The thickness of the non-contact reaction layer increased from 0.4 nm at room temperature up to greater than 6 nm above 150°C. The exact thickness of the reaction layer above 150°C could not be calculated because the percentage of the intensity of the elements present in the oxide layer to the intensities from above was smaller than 5% [89]. At
180°C, no iron oxide was detected anymore and therefore the thickness of the overlaying reaction layer must be thicker than at 150°C.

In the contact region, thicker films than in the non-contact region were formed at temperatures below 110°C: Applying a load of 5 N, there was an increase from 0.5 nm at room temperature up to 2.3 nm at 110°C. Slightly thinner reaction layers were formed with lower loads. Above 110°C, the reaction layers were thinner than in the non-contact regions. For 5 N load the thickness remained rather constant up to 150°C and increased at 180°C to a value of 4.8 nm. Thicker films were formed where lower loads were applied. The thickness of the organic layer after ultrasonic cleaning was between 0.5 and 2.0 nm for both the contact and the non-contact areas.

The ratios of the elements present in the substrate and in the reaction layer were calculated under the assumption of homogenous layers. Below 110°C, the substrate in the non-contact regions was a mixture of iron hydroxide and iron oxide with a ratio of $O:Fe = 2.6\pm0.2:1$. The same composition was found for the tribostressed region at room temperature. In the contact regions tribostressed with 5 N at 60-110°C, there was still a mixture of iron hydroxide and iron oxide with a ratio of $O:Fe = 1.9\pm0.2:1$, which means that less iron hydroxide but more iron oxide was present. With lower loads applied, the ratio was $2.3\pm0.1:1$ for 1 N load and $2.4\pm0.3:1$ for 0.2 N, which was between the values for the high load and for the non-contact area. Between 130°C and 180°C, a ratio of $1.3\pm0.2:1$ was found for both the non-contact and the tribostressed regions, which was close to the stoichiometry of $Fe_3O_4$ with $O:Fe = 1.33:1$.

---

**Figure 3.10:** Reaction layer thicknesses of samples tribostressed in ZnDTP solution at different temperatures, calculated for different loads and for the non-contact areas. On the basis of the experience on repeated experiments the accuracy of the results is estimated to be better than 10%.
The elemental ratios in the ZnDTP molecule and the reaction layer for both the non-contact regions and the tribostressed samples are presented in Table 3.1. In the non-contact area treated at room temperature the ratio of O:P:Zn of 13:1:4.8 indicates that mainly zinc oxide is present. Going up to 100°C, the sulphur concentration and the zinc-to-phosphorus ratio increased while the iron concentration decreased. The non-contact films at high temperatures (130-150°C) contained much less oxygen and iron. Furthermore, the content of sulphur is lower than in the ZnDTP molecule, while the zinc concentration is still higher than in ZnDTP. At 180°C no iron was detected, and sulphur was also present at a very low concentration.

The tribostress led to a depletion of sulphur in the tribofilm compared to the original ZnDTP stoichiometry, while the zinc concentration was higher than in ZnDTP, but not as pronounced as in the non-contact areas. With decreasing load, the composition changed slightly towards the composition of the non-contact areas.

Table 3.1: Elemental ratios of the elements present in the reaction layer normalised by phosphorus. In the case of oxygen, the oxide peak was not taken into account. For iron, only the peak assigned to iron phosphate was attributed to the reaction layer.

<table>
<thead>
<tr>
<th>ZnDTP</th>
<th>Temperature [°C]</th>
</tr>
</thead>
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<td></td>
<td>25</td>
</tr>
<tr>
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<td>O</td>
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<tr>
<td></td>
<td>P</td>
</tr>
<tr>
<td></td>
<td>S(II):</td>
</tr>
<tr>
<td></td>
<td>S(VI):</td>
</tr>
<tr>
<td></td>
<td>Zn :</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
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<td>5.8:</td>
</tr>
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<td>P</td>
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<td>S(II):</td>
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<td></td>
<td>S(VI):</td>
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<td>Zn :</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>1 N O</td>
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</tr>
<tr>
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<td>P</td>
</tr>
<tr>
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<td>S(II):</td>
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<td>Zn :</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>0.2 N O</td>
<td>8.7:</td>
</tr>
<tr>
<td></td>
<td>P</td>
</tr>
<tr>
<td></td>
<td>S(II):</td>
</tr>
<tr>
<td></td>
<td>S(VI):</td>
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<tr>
<td></td>
<td>Zn :</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
</tr>
</tbody>
</table>
contact area. But the film composition at 0.2 N was still closer to the tribofilm produced with 5 N than to the non-contact film.
3.1.2 Phosphorothionate b-TPPT

Tribological Tests

Figure 3.11 shows the friction coefficient $\mu$ for samples tribostressed in butylated TPPT solution as a function of the applied load and temperature. The coefficients are equally distributed around 0.17, no clear effect of temperature or load was observed.

![Friction Coefficient $\mu$ for different loads in dependence on the temperature of the b-TPPT solution.](image)

**Figure 3.11:** Friction coefficient $\mu$ for different loads in dependence on the temperature of the b-TPPT solution.

XPS Results

Spectra at different Temperatures

Detailed spectra of phosphorus, sulphur and oxygen measured on samples treated at different temperatures are shown in Figure 3.12. In the non-contact areas, the binding energy of phosphorus was 133.5±0.2 eV, which was 0.7 eV lower compared to the pure b-TPPT (see Appendix). The thermal films produced at room temperature and 100°C contained almost no phosphorus, small amounts were detected at 125°C and prominent signals were detected at 150 and 180°C. In contrast to the films produced in ZnDTP solution, no second peak was detected at 180°C, the fwhm of the films produced in b-TPPT solutions was always 1.7±0.1 eV.
At room temperature, there were traces of two sulphur peaks: a low-binding-energy peak at 161.9±0.3 eV and a high-binding-energy peak at 168.8±0.1 eV, assigned to sulphate [128, 129]. At higher temperatures, there were only sulphate peaks detected: in traces between 25 and 125°C and prominent peaks above 150°C. On the low binding energy side of the sulphate peaks there were small shoulders, which were likely due to degradation effects (for details see chapter “X-Ray Degradation” on page 84).

Three peaks were found in the oxygen spectra of samples treated between 25 and 125°C: two main peaks at 530.2 and 531.8 eV assigned to oxides and non-bridging oxygen (NBO) and a minor peak or at 533.4 eV due to adsorbed water, at 125°C likely due to water adsorbed during washing with ethanol after the experiment or from air exposure before XPS analysis. Besides the terminat-

Non-contact Area in b-TPPT

<table>
<thead>
<tr>
<th>Phosphorus 2p</th>
<th>Sulphur 2p</th>
<th>Oxygen 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>180°C</td>
<td>S(VI)</td>
<td>BO II</td>
</tr>
<tr>
<td>150°C</td>
<td>S2p</td>
<td>BO</td>
</tr>
<tr>
<td>125°C</td>
<td>S2p</td>
<td>NBO</td>
</tr>
<tr>
<td>100°C</td>
<td>S(II)</td>
<td>Oxide</td>
</tr>
<tr>
<td>25°C</td>
<td></td>
<td>180°C</td>
</tr>
</tbody>
</table>

5 N Load in b-TPPT

<table>
<thead>
<tr>
<th>Phosphorus 2p</th>
<th>Sulphur 2p</th>
<th>Oxygen 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>180°C</td>
<td>S(VI)</td>
<td>BO II</td>
</tr>
<tr>
<td>150°C</td>
<td>S2p</td>
<td>BO</td>
</tr>
<tr>
<td>125°C</td>
<td>S2p</td>
<td>NBO</td>
</tr>
<tr>
<td>100°C</td>
<td>S(II)</td>
<td>Oxide</td>
</tr>
<tr>
<td>25°C</td>
<td></td>
<td>180°C</td>
</tr>
</tbody>
</table>

Figure 3.12: XPS detailed spectra of P2p, S2p and O1s measured on non-contact areas (above) and with 5 Ntribostressed areas (below) produced at different temperatures in b-TPPT solution. (Data acquired with the PHI 5700.)
ing oxygen of the phosphate groups, there are several contributions to the NBO peak: oxygen from the hydroxide, oxygen bound in the sulphate groups and oxygen present in the organic layer. At higher temperatures (150 and 180°C), the oxide peak was less intense while the high-binding-energy peak now assigned to bridging oxygen (BO) was more prominent. As already observed in the ZnDTP spectra acquired at 180°C, there was a peak found at 535.2±0.2 eV (BO II), which might be due to oxygen linking phosphate chains together. In the high-temperature regime, no hydroxides and water were present in the films because they evaporate at these temperatures.

On the carbon spectra measured on samples produced below 100°C, an additional peak at 283.3±0.2 eV assigned to carbides was detected. At higher temperatures, spectra similar to the carbon on the ZnDTP samples were acquired. The signals of iron spectra were intense up to 125°C with contributions due to metallic iron, iron (II), iron (III), iron hydroxide (up to 100°C) and iron phosphate (starting from 125°C). At 150 and 180°C, the signals of iron were less intense and metallic iron was no longer detected.

Similar spectra as described above were recorded in the tribostressed regions (Figure 3.12, below). Both the peak position and the shapes remained constant, only small deviations in the peak areas were found: The tribostress between room temperature and 125°C led to more intense phosphorus and sulphur (II) peaks while no change in the sulphate peaks were found. In the oxygen signal, more intense oxide peaks were found with the tribostress while the intensities of both NBO and BO were slightly smaller. At 150°C, the tribostress led to more pronounced phosphorus and sulphate peaks together with increased signals of NBO and BO. At 180°C, slightly less phosphorus, sulphate and NBO was detected. No significant differences between the tribostressed and the non-contact regions were found on the carbon and iron signals.

**Spectra at different Loads**

XPS-spectra taken at areas tribostressed with 10 N and 1 N load were similar to the 5 N spectra (see Figure 3.13). The spectra of samples tribostressed with the highest load were slightly broader than the ones tribostressed with lower loads. The major difference was observed between the non-contact area and the tribostressed areas; the non-contact area showed smaller intensities of phosphorus, sulphur and NBO.
**Figure 3.13:** XPS detailed spectra of P2p, S2p and O1s measured on areas tribostressed with different loads and on the non-contact area produced at 150°C in b-TPPT solution. (Data acquired with the PHI 5700.)

**Angle-resolved XPS**

Angle-resolved XPS was performed to obtain information about the depth distribution of the elements (see Figure 3.14). The apparent atomic concentration was calculated assuming a homogenous compound consisting of iron phosphate. Plotting the concentration vs. the emission angle (EA) allows the depth distribution of the elements to be determined. If the concentration of an element increases with higher EA (more surface sensitive), it is present in the outer part of the investigated volume (e.g. carbon) while if the concentration drops with higher EA, the element is present in the inner part of the investigated volume.

**Figure 3.14:** Apparent atomic concentration vs. emission angle of a non-contact area and an area tribostressed with 5 N load at 150°C in b-TPPT solution. (Data acquired with the Theta Probe.)
In the non-contact area and on the tribofilms (5 N load shown here), the concentrations of carbon and BO increase with higher EA while the concentrations of NBO, phosphorus, sulphate and iron(phosphate) are decreasing. The concentrations of oxygen(oxide) and iron(oxide) dropped, which indicates that these are at the very bottom. No metallic iron was detected.

These results suggest the presence of a multilayered structure with metallic iron on the bottom (was not detected), covered with iron oxide (steep negative slope). On this a reaction layer consisting of NBO, BO, P, S and Fe(phosphate) was formed, which was covered with an organic layer. The positive slope of BO together with a negative slope of NBO suggests, that longer chains (with a higher content of BO) were present in the outer part of the reaction layer, while the shorter chains (with more NBO) were in the inner part of the layer.

**Thickness and Composition**

On the basis of the angle-resolved XPS a layer structure of the film has to be taken into account for the calculation of the thickness and the composition of each layer. At 25°C a three-layer model with metallic iron as a substrate, iron oxide in between and the reaction products incorporated in an organic layer on top was applied because not enough iron phosphates and sulphates were detected to be treated as a homogenous film covering the complete surface.

Above 100°C not enough metallic iron was detected and thus iron oxide taken as semi-infinite was the substrate. Above 125°C, higher amounts of iron phosphates and sulphates were detected allowing the assumption of a laterally ho-
volume (e.g. O(NBO)).

In the non-contact area and on the tribofilms (5 N load shown here), the concentrations of carbon and BO increase with higher EA while the concentrations of NBO, phosphorus, sulphate and iron(phosphate) are decreasing. The concentrations of oxygen(oxide) and iron(oxide) dropped, which indicates that these are at the very bottom. No metallic iron was detected.

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**Figure 3.15:** Reaction layer thicknesses of samples tribostressed at different temperatures in b-TPPT solution, calculated for the tribostressed regions and for the non-contact areas. The accuracy of the results is estimated to be better than 10%.
mogenous reaction layer and thus to be treated as separate layer. Iron phosphate was taken as a model compound for calculating the inelastic mean free path in the reaction layer for the electrons emitted from layers underneath and from the reaction layer itself.

For the experiment performed at 25°C the oxide layer was found to be 2.1±0.2 nm thick independent on the applied load. At the other temperatures the oxide layer was assumed to be semi-infinite.

The thicknesses of the reaction layers are presented in Figure 3.15. At 25 and 100°C only fractions of a monolayer were present and thus the thickness could not be calculated. At 125°C there were thin reaction layers formed with thicknesses of 0.3-0.4 nm. There was no significant temperature or load dependence. Thicker layers were formed at 150°C with 2.8±0.3 nm and at 180°C with 3.1±0.2 nm. With decreasing load the films were thicker.

The thickness of the organic layer increased with higher temperature, from around 2.1±0.3 nm below 125°C to 2.8±0.4 nm at 150°C and 3.5±0.3 nm at 180°C. No load dependence was found.

Below 125°C, the iron oxide layer contained large amounts of iron hydroxide, a ratio of O:Fe = 2.2±0.2:1 was obtained, which corresponds to a mixture of iron oxide and iron hydroxide. At 150 and 180°C, the Fe:O ratio was 1.3±0.3:1, which is close to the stoichiometry of Fe₃O₄ with O:Fe = 1.33:1.

The elemental ratios in the b-TPPT molecule and the reaction layer for both

Table 3.2: Ratios of the elements present in the reaction layer normalised by phosphorus. In the case of oxygen, the oxide peak was not taken into account. For iron, only the peaks assigned to iron phosphate and iron sulphide were attributed to the reaction layer.

<table>
<thead>
<tr>
<th>Composition</th>
<th>O : P : S(II) : S(VI) : Fe</th>
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</thead>
<tbody>
<tr>
<td>b-TPPT</td>
<td>3 : 1.0 : 1.0</td>
</tr>
<tr>
<td>100°C</td>
<td>10 N 11 : 1.0 : 0.2 : 1.9 : 4</td>
</tr>
<tr>
<td></td>
<td>5 N 11 : 1.0 : 0.4 : 1.8 : 4</td>
</tr>
<tr>
<td></td>
<td>1 N 10 : 1.0 : 0.2 : 1.6 : 3</td>
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<tr>
<td></td>
<td>nc 10 : 1.0 : 0.4 : 1.6 : 3</td>
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<tr>
<td>125°C</td>
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<td>1 N 9 : 1.0 : 0.0 : 1.6 : 0.6</td>
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<tr>
<td></td>
<td>nc 9 : 1.0 : 0.0 : 1.5 : 0.6</td>
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</table>
the non-contact areas and the tribostressed samples are presented in Table 3.2 except for the room temperature samples. There, phosphorus was not detected or only in traces and therefore the ratios could not be determined. In the non-contact area treated at room temperature, some sulphides and sulphates were found. At 100°C, there were traces of iron (II) sulphate together with phosphate detected. Increasing the temperature to 125°C, high amounts of high-binding-energy iron was detected together with the same amount of sulphate groups as phosphate groups, as given by the P:S ratio of 1:1. At 150 and 180°C, the reaction layer was a mixture of iron phosphate with iron sulphate, whereas 50% more sulphate groups were found.

The reaction layer formed under tribostress at room temperature consisted of sulphides and sulphates, on one sample together with phosphates. The films formed under tribostress at 100°C were similar to the non-contact area, while at 125°C, more sulphides were found in the tribofilm. At 150 and 180°C, a similar film composition with iron phosphates and iron sulphates was found on the tribotrails as in the non-contact areas, sulphides were not detected.

**Thermal Film Formation on Tribofilms**

On a sample tribostressed on all 3 regions with a load of 5 N, the effect of thermal film formation on top of the tribofilm was investigated. While the first and the second region showed comparable film thicknesses (see Table 3.3), the third (and last) region showed thinner reaction and organic layers. The non-contact area of this series exhibited the thickest layers.

The composition of the reaction layer was the same for the second and third region while the composition of the first region was between the freshly formed tribofilm and the non-contact area.

**Table 3.3:** Effect of thermal film formation on top of the tribofilm on the thickness and composition of the films. The sample was tribostressed with 5 N load on three regions (labelled according the order of experiment 1st, 2nd and 3rd) at 150°C in b-TPPT solution.

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>nc</td>
<td>3.3</td>
<td>2.6</td>
<td>11 : 1.0 : 1.1 : 0.4</td>
</tr>
<tr>
<td>1st</td>
<td>3.0</td>
<td>2.6</td>
<td>13 : 1.0 : 1.5 : 0.6</td>
</tr>
<tr>
<td>2nd</td>
<td>2.9</td>
<td>2.5</td>
<td>15 : 1.0 : 2.0 : 0.7</td>
</tr>
<tr>
<td>3rd</td>
<td>2.4</td>
<td>2.0</td>
<td>15 : 1.0 : 2.0 : 0.7</td>
</tr>
</tbody>
</table>
X-Ray Degradation

The films of this series were investigated after 1 and 19 hours of X-ray irradiation (see Figure 3.16). With increasing irradiation time, the sulphate peak at 168.8 eV exhibited a low-binding-energy peak at 167.7±0.1 eV with increased intensity. With longer irradiation, less intense high-binding-energy peaks of oxygen and carbon were measured while the iron peaks became more prominent, likely due to an evaporation of volatile compounds.

150°C in b-TPPT

**Figure 3.16:** Detailed spectra of P2p, S2p and O1s measured on a region tribostressed with 10 N and on a non-contact area (nc) in dependence on X-ray irradiation time. The peaks labelled with “_1” were measured after 1 hour of irradiation during 6 hours while the peaks labelled with “_2” were measured after 19 h of irradiation during 3 h. The sample was tribostressed at 150°C in b-TPPT solution. (Data acquired with the PHI 5700.)
X-Ray Degradation

The films of this series were investigated after 1 and 19 hours of X-ray irradiation (see Figure 3.16). With increasing irradiation time, the sulphate peak at 168.8 eV exhibited a low-binding-energy peak at 167.7±0.1 eV with increased intensity. With longer irradiation, less intense high-binding-energy peaks of oxygen and carbon were measured while the iron peaks became more prominent, likely due to an evaporation of volatile compounds.

150°C in b-TPPT

**Figure 3.16:** Detailed spectra of P2p, S2p and O1s measured on a region tribostressed with 10 N and on a non-contact area (nc) in dependence on X-ray irradiation time. The peaks labelled with "_1" were measured after 1 hour of irradiation during 6 hours while the peaks labelled with "_2" were measured after 19 h of irradiation during 3 h. The sample was tribostressed at 150°C in b-TPPT solution. (Data acquired with the PHI 5700.)
3.2 Combinatorial Oscillating-Load Test

This test was performed in pure oil and in oils blended with ZnDTP and metal-free phosphorothionates. Friction, wear and the chemical composition of the surface were measured on these samples for comparing the additives and understanding the tribochemical mechanism of film formation.

3.2.1 Pure Oil

Tribological Tests

A colour plot of the friction coefficient $\mu$ of a typical tribological test performed at 80°C is shown in Figure 3.17. The load was cycled according to the curves on the left side of the colour plot. Therefore the same angular position of the rotating disc always experienced the same load. The colour indicates the friction coefficient. It changed during the first 200 turns and then remained stable until the end of the experiment. There was a pronounced load dependence with higher friction coefficients at places with lower applied loads (angular position around 0° (and 360° respectively) and 180°).

The friction coefficient of the samples stressed in pure oil at 30°C was $0.18 \pm 0.01$ at 10 N load (see Figure 3.18). With decreasing load higher friction coefficients were measured. At 80°C, the friction was higher than at room tem-
Figure 3.18: Friction coefficient $\mu$ vs. load for different temperatures in pure oil.

Figure 3.19: Surface plot with the colour representing the surface height (left) and extracted profiles of different loads at radii of ~5 mm and the running-in at ~6 mm (right). The sample was tribostressed with oscillating load at 80°C in pure oil.
track but a rougher surface compared to the non-contact area was produced.

As demonstrated with the selected profiles, the wear rate increased with higher load (see Figure 3.20). The dimensional wear coefficient $k$ ($k=V/L\cdot l$), which is the wear volume $V$ divided by the applied load $L$ and the sliding distance $l$, was much higher for low loads at 30°C and decreased with higher loads (see Figure 3.21). At 150°C, the wear coefficient of $0.8\pm0.2\cdot10^{-6}$ mm$^3$/Nm at 150°C was much lower than at 30 and 80°C. A repeated of this experiment showed the same result.

**Figure 3.20:** Wear rate of a sample tribostressed in pure oil (PAO) at 80°C in an oscillating-load test. The load dependence in function of the angular position of the disc is shown in the scheme below.

**Figure 3.21:** Dimensional wear coefficient $k$ on the disc in dependence on the applied load for different temperatures of the pure Oil.
XPS Results

The XPS spectra of a sample tribostressed with 10 N load at 80°C are shown in Figure 3.22. The survey spectrum showed peaks of carbon (1s), oxygen (1s and KLL) and iron (LMM, 2s, 2p; 3s and 3p below 100 eV) only.

The spectrum of carbon consisted of four contributions. The main peak was aliphatic carbon at 285.0 eV [134]. Minor contributions were found at 286.8 eV due to carbon bound to oxygen [121, 134], at 289.0±0.2 eV because of carbonate [129, 135] or carboxylic groups [121, 134] and a very small peak, which is not resolved in the spectrum shown in Figure 3.22, was found at 283.1±0.2 eV assigned to carbides [136, 137].

The oxygen signal was composed of three peaks. The main peak at 530.2±0.1 eV was assigned to iron oxide [132, 133], the peak at 531.8±0.1 eV to carbonates and hydroxides [134, 135] and the peak found at 533.0±0.1 eV to adsorbed water [133].

The iron signal was intense and showed two main peaks 2p_{3/2} and 2p_{1/2} due to the spin-orbit splitting. For the quantitative analysis, only the Fe2p_{3/2} peak was used. The main components were from iron oxide, where the Fe(III) peak at 710.9 eV was more intense than the Fe(II) peak at 709.6 eV [129, 132, 133] (with its satellite at 715.1 eV with an intensity of 7% of the main peak [132, 133]). At 706.9 eV, there was a small peak due to metallic iron [129, 132].

10 N load at 80°C in pure Oil

![Graphs of survey, carbon 1s, oxygen 1s, and iron 2p spectra](image)

Figure 3.22: XPS survey and detailed spectra of C1s, O1s and Fe2p of a spot tribostressed with 10 N load at 80°C in pure oil (PAO). (Data acquired with the PHI Quantera.)
XPS Results

The XPS spectra of a sample tribostressed with 10 N load at 80°C are shown in Figure 3.22. The survey spectrum showed peaks of carbon (1s), oxygen (1s and KLL) and iron (LMM, 2s, 2p; 3s and 3p below 100 eV) only.

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10 N load at 80°C in pure Oil

![Survey](https://via.placeholder.com/150)
![Carbon 1s](https://via.placeholder.com/150)
![Oxygen 1s](https://via.placeholder.com/150)
![Iron 2p](https://via.placeholder.com/150)

Figure 3.22: XPS survey and detailed spectra of C1s, O1s and Fe2p of a spot tribostressed with 10 N load at 80°C in pure oil (PAO). (Data acquired with the PHI Quantera.)
Spectra at different Loads

With the oscillating-load test, different loads were applied on different spots. In Figure 3.23, the detailed spectra acquired on spots tribostressed with different loads are compared with the non-contact area on the disc and the tribostressed region on the ball for a tribotest performed at 80°C.

The carbon signals of the tribotrack (labelled according to the applied load with 10 N, 5 N and 0.5 N) were similar. The carbon signal of the non-contact areas showed more intense high-binding-energy peaks and the signal of the ball showed a very prominent peak of aliphatic carbon due to a thick layer of residual oil because of a more careful washing. The oxygen signals at different loads were similar, whereas the oxide peak in the 0.5 N was more intense. The oxide peak of the non-contact area was smaller compared to the tribotacks, and the oxygen signal on the ball was weaker due to the thicker oil film covering the sample. The iron signal of the non-contact area contained higher amounts of metallic iron than the tribostressed regions. The overall iron intensity on the ball was lower again, but besides the iron oxide signals there was still metallic iron detected.

80°C in pure Oil

Figure 3.23: XPS detailed spectra of C1s, O1s and Fe2p measured on the tribotrack stressed with different loads, on the non-contact area and on the centre of the tribostressed part of the ball. The test was performed at 80°C in pure oil (PAO). (Data acquired with the PHI Quantera.)

Spectra at different Temperatures

In Figure 3.24, spectra of the 10 N spot acquired on samples tribostressed at different temperatures are compared. The carbon 1s signals were similar at all temperatures. Small changes were only observed for the signal at lower binding
energy (283.1 eV): The peak of the sample tribostressed at 30°C showed the carbide contribution, which was absent at 150°C. The oxygen spectra of the different samples were almost identical: differences in the relative intensities are revealed. At 30°C there were peaks of metallic iron and Fe(II), which was very prominent. With increasing temperature, these peaks became weaker and at 150°C only Fe(III) was present.

**Angle-resolved XPS**

Using angle-resolved XPS, the distribution of the elements in dependence on the depth of the sample was determined. The apparent atomic concentration was calculated assuming a homogenous compound of iron oxide throughout the whole depth (see Figure 3.25). On a spot tribostressed with 8 N load at 80°C, the concentration of metallic iron and carbides dropped to zero with higher emission angles (EA), which implies that these elements were present at the very bottom of the analysed volume. Steep negative slopes were registered for the oxide peaks of oxygen and iron, which suggests that these elements were in the inner part of the analysed volume, but on top of the metallic substrate. The slopes of all carbon peaks were positive while the curves of the oxygen peaks assigned to water and C-O binding were approximately horizontal. This implies that these elements were present on top of the oxide layer. Within the organic layer containing water and oxygen bound to carbon there were gradients; the carbon was preferentially at the outer part of this layer while water and the oxygen bound to the carbon chains were rather in the inner part of the organic layer.
**80°C in pure Oil**

![Graph showing apparent atomic concentration vs. emission angle](image)

**Non-contact Area**

![Graph showing apparent atomic concentration vs. emission angle](image)

**Figure 3.25:** Apparent atomic concentration vs. emission angle of a spot tribostressed with 8 N load and of a non-contact area. The sample was tribostressed at 80°C in pure oil (PAO). (Data acquired with the Theta Probe.)

In the non-contact area, different concentrations from the tribotrack were found. The assignment of the elements in their various chemical environments to the different layers was the same. From the substrate, the intensity of metallic iron was much higher at low EA, but it dropped to zero at higher EA. The concentrations of both oxide peaks were decreasing with higher EA while the concentration of the elements assigned to the organic layer increased.

**Thickness and Composition**

On the basis of the results above, the thickness and composition was calculated assuming a three-layer model with metallic iron as a substrate, iron oxide as an intermediate layer and with an organic layer on top. The thickness of the oxide layer could only be determined for the non-contact areas of the 30°C samples, where the thickness was 2.9±0.1 nm. For the other samples, the intensity of metallic iron was less than 5% of the overlayer intensities and a two-layer structure with iron oxide as a semi-infinite substrate covered with an organic layer was used for calculating the thicknesses and compositions.

The thicknesses of the organic layers are shown in Figure 3.27. On the disc, thicker layers were obtained at higher temperatures. In the non-contact areas, slightly thicker layers were formed. The cleaning of the ball from residual oil was more difficult because with the ultrasonic bath sometimes the ball turned and then the tribostressed area could not be found anymore. Due to the more careful washing, in many cases the thickness could not be determined because not enough intensity from the iron oxide was obtained.
The concentrations in the organic layer are summarized in Table 3.1. The main component at all temperatures was aliphatic carbon found at 285 eV. The concentration of carbon bound to oxygen (286.7±0.1 eV) ranged from 6 to 10 at.%, whereas only at 150°C a load dependence towards lower concentration at higher load was found. The concentration of the carbonate or carboxylic groups decreased with higher load. The concentration of oxygen was slightly lower than expected from the carbon contributions at high binding energies assuming the presence of carbonates. The content of oxygen should therefore be equal to C(C-O)+3C(carbonate). At 30°C, the ratio of the measured concentra-
tion to the expected concentration was 0.8±0.1:1, at 80°C 0.7±0.1:1 and at 150°C 0.5±0.1:1. The concentration of water was between 5 and 9%, whereas lower concentrations were found at higher loads.

Table 3.4: Composition of the organic layer for different experimental temperatures and loads. The signals from aliphatic carbon at 285 eV, carbon bound to oxygen (286.7 eV), carbonate or carboxylic groups (288.8 eV), oxygen bound to carbon (531.9 eV) and oxygen assigned to water (533.1 eV) were taken into account for the organic layer.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>BE [eV]</th>
<th>Carbon [at.%]</th>
<th>Oxygen [at.%]</th>
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</thead>
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<td></td>
<td>285.0</td>
<td>286.7</td>
<td>288.8</td>
</tr>
<tr>
<td>30°C Disc</td>
<td>10 N</td>
<td>57 ±0</td>
<td>7 ±0</td>
</tr>
<tr>
<td></td>
<td>5 N</td>
<td>60 ±1</td>
<td>6 ±0</td>
</tr>
<tr>
<td></td>
<td>0.5 N</td>
<td>44 ±0</td>
<td>8 ±0</td>
</tr>
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<td>nc</td>
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<td>7 ±0</td>
</tr>
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<td>30°C Ball</td>
<td>centre</td>
<td>90 ±0</td>
<td>3 ±0</td>
</tr>
<tr>
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<td>nc</td>
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<td>4 ±0</td>
</tr>
<tr>
<td>80°C Disc</td>
<td>10 N</td>
<td>54 ±0</td>
<td>9 ±0</td>
</tr>
<tr>
<td></td>
<td>5 N</td>
<td>55 ±0</td>
<td>9 ±0</td>
</tr>
<tr>
<td></td>
<td>0.5 N</td>
<td>52 ±1</td>
<td>9 ±1</td>
</tr>
<tr>
<td></td>
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<td>34 ±1</td>
<td>9 ±1</td>
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<td>3 ±0</td>
</tr>
<tr>
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<td>nc</td>
<td>83 ±1</td>
<td>4 ±0</td>
</tr>
<tr>
<td>150°C Disc</td>
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<td>65 ±10</td>
<td>7 ±1</td>
</tr>
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<td>7 ±1</td>
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<td>7 ±1</td>
</tr>
<tr>
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<td>nc</td>
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<td>7 ±3</td>
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</table>
3.2.2 ZnDTP

Tribological Tests

A colour plot of the friction coefficient $\mu$ of a typical tribological test performed at 80°C is shown in Figure 3.28. The load was cycled according to the plot on the left side of the colour plot in such a way that the same angular position always experienced the same load. The friction coefficient changed only slightly during the first 500 turns and remained constant during the last 500 turns. Regions with lighter colour and therefore higher friction coefficient are to be found in the track at 0° (and 360°) and 180°, which correspond to the areas where the

![Figure 3.28: Colour plot of the friction coefficient $\mu$ of a sample tribostressed at 80°C in ZnDTP solution. On the left side the applied load is plotted vs. the angular position of the rotating disc.](image)

![Figure 3.29: Friction coefficient $\mu$ vs. load for experiments performed at different temperatures in ZnDTP solution.](image)
lowest load of 0.5±0.1 N was applied. Slightly higher friction coefficients at lower loads were observed at all temperatures, as shown in Figure 3.29. The friction coefficient increased with increasing temperature; for 10 N load it rose from 0.13±0.01 at 30°C to 0.15±0.01 at 80°C up to 0.20±0.01 at 150°C.

**Wear**

The wear rate increased in a quasi-linear fashion with applied load (Figure 3.30). High scatter of the wear rate due to the increased surface roughness

![Graph of wear rate vs. load](image1)

**Figure 3.30:** Wear rate of a sample tribostressed in an oscillating-load test at 80°C in ZnDTP solution. The load dependence in function of the angular position of the disc is shown in the scheme below.

![Graph of wear rate vs. angular position](image2)

**Figure 3.31:** Dimensional wear coefficient k on the disc in dependence on the applied load for different temperatures of the ZnDTP solution.
caused by the wear was observed at high loads. The dimensional wear coefficients $k$ (wear rates divided by the applied load, Figure 3.31) showed lower average wear coefficients at higher loads. With increasing temperature, higher wear coefficients were obtained; for 10 N load, the wear coefficient increased from $1.1 \pm 0.6 \times 10^{-6}$ mm$^3$/Nm at 30°C to $1.6 \pm 0.3 \times 10^{-6}$ mm$^3$/Nm at 80°C to $1.8 \pm 0.7 \times 10^{-6}$ mm$^3$/Nm at 150°C.

**XPS Results**

Survey and detailed high-resolution spectra were measured on both the disc and on the ball. Survey spectra were used for peak identification and to check the presence of contaminants. Detailed spectra of phosphorus 2p together with zinc 3s, sulphur 2p, carbon 1s, oxygen 1s, iron 2p, zinc 2p$_{3/2}$ and zinc LMM were recorded to identify the different chemical states of the species and to perform the quantitative analysis.

Spectra of a spot tribostressed with 10 N load at 80°C are shown in Figure 3.32. The survey spectrum shows intense peaks of zinc: Zn2p$_{3/2}$ and Zn2p$_{1/2}$ at binding energies of 1023 and 1046 eV, Zn3s at 141 eV, Zn3p at 91 eV and several ZnLMM Auger peaks at kinetic energies $E_{\text{kin}}$ between 826 and 1009 eV (660-477 eV on the binding energy scale). Strong oxygen peaks were found from O1s at 532 eV and from the O$_{\text{KLL}}$ Auger peak at 987 eV $E_{\text{kin}}$. Minor peaks originated from iron (Fe2p at 711 eV, Fe2s at 850 eV, Fe3s at 91 eV, Fe3p at 56 eV and Fe$_{\text{LMM}}$ at 584 and 702 eV $E_{\text{kin}}$), carbon (C1s at 285 eV), sulphur (S2s at 227 eV and S2p at 162 eV) and phosphorus (P2s at 192 eV and P2p at 134 eV). Between 12 and 0 eV there is the valence band.

On the spots tribostressed with 10 N load at 80°C (see Figure 3.32), phosphorus 2p$_{3/2}$ was at 133.7±0.1 eV. In the same spectrum at 140.5±0.1 eV, there was the zinc 3s peak. This peak was used for the quantitative analysis instead of the more intense zinc 2p$_{3/2}$ peak because the kinetic energy of the Zn3s electrons is closer to that of P2p and S2p and therefore the IMFPs and therefore the sampling depths are similar.

The sulphur 2p$_{3/2}$ peak was found at 162.2±0.1 eV, and can be assigned to a sulphur having a formal oxidation state of -2, as found in sulphides [128, 129], thiolates [130, 131] or when sulphur is substituting oxygen atoms in poly(thio)-phosphates.

In the carbon 1s spectrum, the most intense peak was at 285.0 eV due to aliphatic carbon [87, 134]. Minor contributions were found at 286.8 eV due to carbon bound to oxygen and sulphur [121, 134, 138] and at 289.0±0.2 eV indicating carbonate [129, 135] and/or carboxylic groups [121, 134].
The oxygen 1s signal was composed of 3 peaks: the first at 530.3±0.1 eV being assigned to oxygen in iron and zinc oxides [4, 132, 133], the main peak at 531.7±0.1 eV to non-bridging oxygen (NBO) in polyphosphates and to oxygen bound to carbon [4, 66, 70] and the high-binding-energy peak at 533.4 eV to bridging oxygen (BO) in polyphosphates [66, 67].

The iron Fe 2p signal was split into two main peaks at 711 and 724 eV, labelled as Fe$^{2+}$ and Fe$^{3+}$ caused by the interaction of the unpaired electron created by photoemission with other unpaired electrons in the atom [87]; only the iron 2p$_{3/2}$ signal was used for quantification. On this sample, very low intensity iron signals were detected. Peaks of two oxidation states Fe(II) and Fe(III) in iron oxides at 709.6±0.1 and 711.0±0.1 eV [129, 132, 133] were detected, while no signal attributable to metallic iron (707 eV) was revealed. Both oxides exhibit high-binding-energy satellites but only the satellite of iron (II) at 715.1±0.1 eV was within the fitted region: it was fixed at an area of 7% of the main peak [132, 133]. A small, high-binding-energy peak at 713.5 eV assigned to iron phosphate [69] was detected.

**10 N Load at 80°C in ZnDTP**

![Graphs showing XPS survey and detailed spectra of P2p with Zn3s, S2p, C1s, O1s and Fe2p measured on the tribotrack stressed with 10 N load at 80°C in ZnDTP solution.](image)

*Figure 3.32: XPS survey and detailed spectra of P2p with Zn3s, S2p, C1s, O1s and Fe2p measured on the tribotrack stressed with 10 N load at 80°C in ZnDTP solution. (Data acquired with the PHI Quantera.) In the O1s contributions of NBO at 531.8 eV there are other contributions from sulphates, hydroxides or oxygen bound to carbon.*
Spectra at different Loads

Detailed spectra of P2p, Zn3s, S2p and O1s taken from small areas tribostressed with different loads, as well as from the non-contact area and of the centre of the ball are presented in Figure 3.33. The spectra of areas tribostressed with 5 N were almost identical to those stressed with 10 N. A further decrease of the load to 0.5 N did not change the binding energy values of the photoelectron signals (uncertainty ±0.1 eV). The intensity of phosphorus, zinc and sulphur signals decreased with decreasing load, while the peak in the oxygen O1s spectrum assigned to the oxide became more pronounced.

In the non-contact regions, only low-intensity signals of phosphorus and zinc were detected at slightly lower binding energies of 133.4±0.2 and 140.3±0.1 eV. The sulphur peak at 162.1±0.1 eV was much smaller compared to that measured in the 10 N area, but there was an additional noisy peak at 168.4±0.3 eV assigned to sulphate [128, 129]. The non-contact region also revealed a more pronounced oxide peak at 530.0±0.1 eV in the oxygen spectrum, while in the carbon spectrum, the high-binding-energy peak (carbonates and/or carboxylic groups) at 288.8±0.1 eV was more intense. The contributions to the O1s signals, labelled as NBO, also included those due to oxygen present in iron hydroxides and sulphate groups. In addition, adsorbed water has to be considered together with the BO-peak [133]. The iron peak in the non-contact region was very pronounced and metallic iron was detected at 706.7 eV. On some samples, small peaks at 711.8 eV assigned to iron hydroxide were found [4, 133].

The peaks measured in the centre of the tribostressed region on the ball were similar to those collected on the disc after tribotesting with 5 and 10 N.
load, but slightly higher intensity of the phosphorus and sulphur (II) peaks were observed.

**Spectra at different Temperatures**

Spectra of the 10 N area produced at 30°C, 80°C and 150°C are presented in Figure 3.34. At 30°C, the binding energy of phosphorus 2p₃/₂ (133.6±0.2 eV) was slightly lower than at 80°C. A small sulphate peak was detected on the tribotrack and in the oxygen spectrum the peak of BO was less intense than that detected at 80°C. The spectra from samples tribostressed at 150°C were almost identical to the 10 N area produced at 80°C. The binding energies of P2p, Zn3s and the low-binding-energy peaks of S2p were shifted of 0.2 eV each, while the intensities of the peaks were similar. At this high temperature, minor contributions from sulphates were found on the tribotacks at 169.2±0.1 eV. Almost no oxide peak in the oxygen signal and only weak iron signals were revealed. The spectra of the areas tribostressed with 0.5 N load were in between the ones of the high loads and the non-contact area.

The spectra of the non-contact areas at 30°C were almost identical to the non-contact region of the 80°C samples and those recorded at 150°C were similar to the tribostressed ones, with slightly less intense phosphorus peaks but higher contribution of the sulphate peaks. Only traces of iron were detected.

On the tribostressed regions on the balls at all temperatures, similar spectra were observed as on the tribotacks on the discs stressed with high loads.

**Figure 3.34:** XPS spectra of P2p with Zn3s, S2p and O1s measured on the tribotrack stressed with 10 N load at 30, 80 and 150°C in ZnDTP solution. (Data acquired with the PHI Quantera.) In the O1s contributions of NBO at 531.8 eV there are other contributions from sulphates, hydroxides or oxygen bound to carbon.
Imaging XPS

Imaging-XPS pictures and line scans were taken to determine the position of the analysed area and to check for lateral inhomogeneities of the tribotrack and of the non-contact area. The total peak area is colour coded and plotted as a function of the lateral position. In the case of oxygen, the spectra collected for the maps were additionally fitted with three peaks at 530.3, 531.9 and 533.4 eV and the maps reconstructed with a linear least square fit routine (see bottom row of Figure 3.35 and Figure 3.36).

An example of the images collected on a tribotrack produced with 10 N at 80°C and on the ball is shown in Figure 3.35 and Figure 3.36 to compare the films formed on both sliding partners. The tribotrack on the disc was clearly visible in the phosphorus 2p image, where the tribotrack showed higher intensity than the non-contact area. The same distribution was found with the sulphur (II) peak at 162 eV binding energy. There was less contrast in the case of the sulphate peak at 168 eV, where slightly higher intensity was found in the non-contact area (not shown). To create the colour plots, the more intense zinc 2p$_{3/2}$ peak was used instead of the Zn3s peak because of the better signal-to-noise ratio. Again the tribotrack shows a higher signal, and there was a region along

10 N Load at 80°C in ZnDTP

![Figure 3.35: Imaging-XPS of the tribotrack on the disc tribostressed with 10 N load at 80°C in ZnDTP solution. (Images acquired with the PHI Quantera.)](image-url)
Ball at 80°C in ZnDTP

The tribotrack with even higher intensity. The carbon image of the disc shows that there was slightly less carbon in the tribotrack than in the surrounding area, whereas the total oxygen map showed higher levels in the tribostressed region. The three different oxygen peaks showed that the oxide, which is more intense in the non-contact area, was covered with a film containing both non-bridging (NBO) and bridging oxygen (BO). The iron signal in the contact area appears lower than in the non-contact area due to the formation of a thicker reaction layer.

In the tribostressed region on the ball (round area in Figure 3.36), the maps show higher intensities of the phosphorus, sulphur, zinc and NBO and BO signals; in this region, lower intensities of carbon, iron and O(oxide) signals were detected. In the area behind the contact area during the tribotest (left side of the contact area in the map), there was a tail with an enhanced intensity of both sulphur (II) and zinc.
3D-Colourplots of Oxygen

To obtain 3-dimensional information of the tribotrack and the surrounding area, imaging-angle-resolved XPS was performed (see Figure 3.37). Imaging XPS gives the lateral information while angle-resolved XPS provides depth information. With increasing emission angle (EA, angle between the surface normal and the analyser), the information depth decreases and therefore the surface sensitivity increases. The O1s spectra obtained from these measurements were fitted with the three peaks originating from oxide (fixed between 530.2 and 530.3 eV), NBO (1.6 eV above the oxide peak) and BO (3.1 eV above the oxide peak). The percentage of the given oxygen peak of the sum of all three peaks was plotted colour coded in dependence of the lateral position (plane view) and the emission angle (upright projection). A brighter colour herewith corresponds to a higher contribution of the peak to the oxygen signal.

The presented spot was the same as in Figure 3.35 and was tribostressed with 10 N load at 80°C. High intensity of the oxide peak was found in the non-contact region and at lower emission angles, which means that the tribotrack

![Figure 3.37: 3D colour plots of the three oxygen peaks: oxide, non-bridging oxygen (NBO) and bridging oxygen (BO), measured on the tribotrack where 10 N load was applied and the surrounding non-contact area. The sample was tribostressed at 80°C in ZnDTP solution. The colour indicates the peak’s percentage of the sum of the O1s peaks in dependence on the lateral position (plan view) and the emission angle (z-axis). (Data acquired with the Theta Probe.)](image-url)
was coated with an overlayer and that the oxide was mainly at the bottom of the analysed volume. NBO was the highest contribution to the oxygen peaks and itself highest in the tribostressed region. It was more pronounced on the left part of the tribotrack where with iXPS a reduced amount of zinc was found (see Figure 3.35). In both the tribostressed and the non-contact region its percentage was higher in the outer part of the film. The percentage of BO was much higher in the tribostressed film, especially at the right part of it where an increased amount of zinc was found. In both the tribofilm and the non-contact area it was more prominent at higher emission angles, and thus in the outer part of the film. While in the tribotrack the bridging oxygen is causing the high-binding-energy peak, the main component to the high-binding-energy peak in the non-contact area is due to adsorbed water.

**Angle-resolved XPS**

To determine in a non-destructive way the elemental distributions as a function of the depth, angle-resolved spectra of the tribotacks stressed with different loads and of the non-contact areas were taken. Figure 3.38 shows the angle-resolved spectra acquired on a spot tribostressed with 10 N load at 80°C. With higher emission angle (higher surface sensitivity), the peak areas of phosphorus 2p3/2 at 133.8 eV decreased. The area at 64° EA was 64% of the intensity found at 27° EA. On the same spectrum at 140.5 eV, there was the zinc 3s peak. The peak area of Zn3s decreased to 71% at 64° EA while the Zn2p3/2 dropped to 38%. The peak areas of sulphur in the oxidation state -2 at 162.4 eV decreased in a similar way as observed for phosphorus and zinc 3s while the areas of the different carbon peaks increased. With higher EA, the areas of the oxide and NBO peaks decreased while the areas of the BO peaks stayed almost constant. The peak of metallic iron and iron sulphides disappeared with higher EA while the areas of the oxide peaks Fe(II) and Fe(III) decreased, whereas Fe(II) dropped more than the Fe(III). The iron phosphate peak was more pronounced at higher EA.

To compare the in-depth distribution of the elements, the apparent atomic concentration was plotted as a function of the EA (see Figure 3.39). The apparent atomic concentration was calculated under the assumption of a homogenous compound within depth. The peak areas were corrected only for the angular asymmetry factor \( L_A(\gamma) \), the étendue \( G(E) \), the photoionization cross-section \( \sigma_I \) and the IMFP \( \lambda(E) \). Of course, the assumption of a homogenous compound as a function of depth is wrong but plotting the apparent atomic concentration vs. the emission angle makes it possible to specify if an element is present in
the bulk or on the surface of the analysed volume. If the concentration of an element rises with increasing emission angle (e.g. carbon), then the element is present in the outer part of the analysed volume. If the concentration decreases with higher angle, then it is in the inner part of the volume (e.g. O(NBO)).

An example of a spot tribostressed with 10 N load and the corresponding non-contact area at 80°C is shown in Figure 3.39. For the 10 N area, the highest slope was found for the carbon concentration (sum of aliphatic carbon and the two high-binding-energy peaks), which indicates that there was an organic layer on top of the sample. From the oxygen peaks, the NBO exhibited the highest concentration. It decreased with increasing EA and therefore it was placed rather in the inner part of the analysed volume. The peaks of oxide and BO were found at similar concentration, but while the oxide peak decreased

**Figure 3.38:** XPS detailed spectra of P2p with Zn3s, S2p, C1s, O1s, Fe2p and Zn2p$_{3/2}$ measured on the tribofilm formed applying 10N load at 80°C in ZnDTP solution. (Data acquired with the Theta Probe.) In the O1s contributions of NBO at 531.8 eV there are other contributions from sulphates, hydroxides or oxygen bound to carbon.
with higher EA, the concentration of BO increased. The concentrations of phosphorus, sulphur, zinc and iron(phosphate) were almost constant which implies that they were present in the middle of the volume. The peaks of Fe(II) and Fe(III) were taken together to Fe(ox) whose concentration dropped with increasing EA, therefore iron oxide was present in the inner part. Metallic iron was detected only at small EAs and therefore is placed on the bottom of the volume.

This indicates that a multilayered structure was present on the tribotrack with metallic iron on the bottom, covered by iron oxide (Fe(II), Fe(III) and O(ox)). On top of that a reaction layer with phosphorus, sulphur, zinc, iron phosphate and the two oxygen species NBO and BO was formed. On top of the reaction layer there was an organic layer. Angle resolved measurements on regions stressed with different loads and on the non-contact areas showed different concentrations but the same layer structure, independent on the applied temperature. If iron hydroxide was present, its concentration decreased somewhat with increasing EA and therefore it was assigned to the oxide layer. The carbide concentration dropped with higher EA and was assigned to belong to the metallic substrate. This is in agreement with the nominal composition of the disc as well as with the analysis of sputter cleaned discs.

This 4-layer structure was used to calculate the thicknesses and compositions of the individual layers. The apparent concentrations of BO and NBO suggest the presence of gradients between layers and thus the assumption that each layer is homogeneous in thickness and composition seems to be not fulfilled. Nevertheless the application of this model still produces more accurate

80°C in ZnDTP

![Graphs showing apparent atomic concentration vs. emission angle for 10 N Load and Non-contact Area at 80°C.](image)

**Figure 3.39:** Apparent atomic concentration vs. emission angle of a weartrack tribostressed with 10 N load and of the non-contact area at 80°C. (Data acquired with the Theta Probe.)
data compared to calculations assuming a homogenous compound on the steel substrate.

**Thickness and Composition**

Applying the multi-layer model, the thicknesses and compositions of the individual layers were calculated simultaneously as described in section 2.4.52.4.5. The thickness of the oxide layer could be calculated only if metallic iron was present with an intensity of at least 5% of the overlayer intensity [89]. This was the case for some samples tribostressed at 30°C with a load of 0.5 N and for the non-contact areas of the 30 and 80°C samples. The thickness of the oxide layers was 2.4±0.2 nm at the 30°C samples and 2.9±0.2 nm on the non-contact areas treated at 80°C. The thicknesses of the organic layers after ultrasonically cleaning were between 0.4 and 2 nm.

The thicknesses of the reaction layers are shown in Figure 3.40 for different loads and temperatures. At both 30 and 80°C films of about 4 nm were formed at 5 N and 10 N loads, while in the non-contact areas of both disc and ball only very thin films of less than 1 nm were found. In the tribostressed region in the centre of the ball, similar thicknesses were measured as on the disc stressed at high loads. At 80°C, the deposited material behind the contact region of the ball (compare with Figure 3.36) led to an increased film thickness of 3.7±0.4 nm compared to the non-contact areas of the same samples (1.4±0.7 nm).

At 150°C, tribofilms of 6 nm or thicker were formed on the disc. When the layers had a thickness higher than 6 nm then no signal from the iron oxide layer

![Figure 3.40: Thickness of the reaction layer on the discs and balls in dependence of the applied load and temperature. Please note that “nc” stands for the non-contact area and “centre” means the middle of the tribostressed region of the ball. Thicknesses higher than 6 nm could not be calculated, therefore on the y-axis >6 nm is reported.](image-url)
was detected and the reaction layer has to be assumed to be semi-infinite and the thickness of the film is reported higher than 6 nm. Thinner films of 4±1 nm were observed with 0.5 N load. In the non-contact areas, thick thermal films of more than 6 nm were produced. On the ball, thick reaction layers were found all over the ball.

To describe the *composition of the iron oxide layer*, the oxygen-to-iron ratio was calculated. At 30°C, the ratio on the 0.5 N tribotracks was 1.3±0.3:1, which was close to the ratio of Fe₃O₄ with O:Fe = 1.33:1. The ratio of 2.2±0.2:1 in the non-contact region was much higher; a mixture of iron hydroxide with iron oxide was likely to be present. At 150°C there was not enough iron oxide detected to give accurate ratios.

The *composition* of the reaction layer changed with the applied load and temperature (see Table 3.5). While on the tribotracks and the thermal films at 150°C the amount of oxygen was about 3 times that of phosphorus, far more oxygen was present in the non-contact areas at 30 and 80°C. Compared to the ZnDTP molecule, where a S:P ratio of 2:1 is present, a depletion of sulphur was found in the tribotracks and non-contact areas, while on the ball the deposited material behind the tribological contact at 80°C was enriched in sulphur. Small amounts of sulphates were found in the non-contact areas only and in trace quantities in the tribotracks produced at 150°C. In comparison to ZnDTP (Zn:P

| Table 3.5: Elemental ratio of the reaction layer normalised to phosphorus. In the case of oxygen, only the NBO and BO peaks were taken into account. For iron, only the peak assigned to iron phosphate was attributed to the reaction layer. |
|---|---|---|---|---|---|---|
|   | O   | P   | S(II) | S(VI) | Zn   | Fe   |
| 30°C Disc 10 N | 2.9±0.1 | 1.0 | 0.5±0.1 | 0.0±0.0 | 0.7±0.1 | 0.1±0.1 |
| 5 N | 2.8±0.3 | 1.0 | 0.5±0.1 | 0.0±0.0 | 0.7±0.1 | 0.1±0.0 |
| 0.5 N | 2.9±0.5 | 1.0 | 0.5±0.1 | 0.0±0.0 | 0.8±0.1 | 0.0±0.0 |
| nc | 8±3 | 1.0 | 0.7±0.7 | 0.4±0.8 | 4.4±1.8 | 0.0±0.0 |
| Ball centre | 2.8±0.2 | 1.0 | 0.5±0.1 | 0.0±0.0 | 0.6±0.1 | 0.1±0.0 |
| nc | 6±2 | 1.0 | 0.3±0.1 | 1.0±0.7 | 1.2±0.5 | 0.0±0.0 |
| 80°C Disc 10 N | 2.5±0.3 | 1.0 | 0.5±0.1 | 0.0±0.0 | 0.9±0.1 | 0.0±0.0 |
| 5 N | 2.6±0.2 | 1.0 | 0.5±0.1 | 0.0±0.0 | 0.9±0.1 | 0.0±0.0 |
| 0.5 N | 3.0±0.4 | 1.0 | 0.7±0.1 | 0.0±0.0 | 1.1±0.1 | 0.0±0.0 |
| nc | 10±3 | 1.0 | 1.9±0.5 | 1.0±0.6 | 7±2 | 0.0±0.0 |
| Ball centre | 2.8±0.2 | 1.0 | 0.4±0.0 | 0.0±0.0 | 0.7±0.1 | 0.0±0.0 |
| nc | 6±3 | 1.0 | 1.4±1.0 | 0.7±0.8 | 2±2 | 0.1±0.1 |
| depo | 4±2 | 1.0 | 6±1 | 0.6±0.6 | 5±2 | 0.0±0.0 |
| 150°C Disc 10 N | 3.0±0.2 | 1.0 | 0.3±0.0 | 0.1±0.1 | 0.9±0.1 | 0.0±0.0 |
| 5 N | 2.9±0.2 | 1.0 | 0.3±0.1 | 0.0±0.0 | 0.9±0.1 | 0.0±0.0 |
| 0.5 N | 3.3±0.5 | 1.0 | 0.4±0.1 | 0.1±0.1 | 0.9±0.1 | 0.1±0.1 |
| nc | 3.8±0.2 | 1.0 | 0.9±0.3 | 0.3±0.1 | 1.5±0.1 | 0.0±0.0 |
| Ball centre | 2.9±0.0 | 1.0 | 0.3±0.0 | 0.0±0.0 | 0.8±0.0 | 0.0±0.0 |
| nc | 4.3±0.0 | 1.0 | 1.3±0.1 | 0.4±0.0 | 1.8±0.1 | 0.0±0.0 |
| depo | 3.4±0.0 | 1.0 | 1.2±0.0 | 0.3±0.0 | 1.6±0.0 | 0.0±0.0 |
= 0.5:1), the reaction layers were enriched in zinc. Usually only small amounts of iron in the form of iron phosphate were to be found.

For the tribofilms at 30°C, the oxygen-to-phosphorus ratio of 2.9±0.1:1 is lower than expected for a short-chain polyphosphate. This might suggest that some sulphur (II) has most likely substituted oxygen in the phosphate chain. The tribofilm thus mainly consisted of a short chain zinc poly(thio)phosphate, together with traces of zinc sulphide. At 30°C, almost no changes in the film composition were observed with decreasing load. In the non-contact areas, there were small amounts of zinc oxide with traces of phosphate compounds and sulphides.

The 10 N tribofilm produced at 80°C mainly contained short-chain zinc poly(thio)phosphate, with some sulphides. Applying a 5 N load led to the same film composition, and with 0.5 N there was slightly more sulphur present. The non-contact film was similar to that at 30°C, but with higher amounts of zinc sulphide and zinc sulphate.

At 150°C, the 10 N tribofilm was made of short-chain zinc poly(thio)phosphate, together with small amounts of zinc sulphate and sulphides. Again the same film composition was found at 5 N load. At the lowest load of 0.5 N, the main compound was still zinc poly(thio)phosphate, but the film contained more zinc sulphide and sulphate. Some iron substituting for zinc was detected as well. In the non-contact area there was a long-chain zinc poly(thio)phosphate with higher amounts of zinc sulphate and zinc sulphide.

The composition of the tribofilm on the ball was very similar to the tribofilms produced at high loads; no significant differences were detected. The non-contact areas on the ball half a millimetre in front and behind the contact were equivalent, within the usual uncertainty, and similar to the non-contact areas on the disc. The material deposited at 80°C about 250 μm behind the sliding contact mainly consisted of zinc sulphide. At 150°C, the composition of the deposited material was similar to that of the non-contact areas.

**Chain Length**

The binding energy of phosphorus 2p$_{3/2}$ can be used to identify the kind of phosphate formed on the surface: i.e. between orthophosphates (single phosphate groups), or short- or long-chain polyphosphates [4, 66, 68-70]. The chain length of these polyphosphates can be calculated using the BO-to-NBO ratio (see Figure 3.41). The ratios were corrected by subtracting the contributions to the NBO signal of oxygen in sulphate groups and oxygen bound to carbon in the organic layer.
At both 30°C and 80°C, shorter chain lengths were observed corresponding to higher contact pressures. In the non-contact areas of 30 and 80°C, the binding energy of phosphorus P2p3/2 of 133.3±0.2 eV indicates that orthophosphates were present [70]. The BO-to-NBO ratio of the non-contact areas is not plotted for these temperatures, because adsorbed water was contributing to the BO peak of these samples.

At 150°C, chains of ~4 phosphate groups were found at high contact pressures while shorter chains of 3 units were found at low pressures. This was confirmed by the binding energy of phosphorus being at 134.0±0.2 eV at high pressures and 0.2 eV lower at low pressure. In the non-contact areas, the thermal film consisted of a long-chain polyphosphate, as indicated by the BO-to-NBO ratio of almost 0.5.

The chain-length of the tribostressed region on the ball remained unchanged with the applied temperature and ranged between 3 and 6 phosphate units. In the non-contact areas and in the near contact area (deposited material) at 150°C, long chains were calculated.

![Figure 3.41: Bridging to non-bridging oxygen ratio vs. the applied load and temperature. The ratio is corrected for the contributions to NBO originating from sulphate groups and carbon bound to oxygen](image-url)
3.2.3 Phosphorothionate TPPT

Tribological Tests

A colour plot of the friction coefficient is shown in Figure 3.42. The sample was tribostressed at 80°C in a solution containing the non-alkylated phosphorothionate TPPT. The load was cycled from 0.5 to 10 N according to the plot on the left side of the colour plot. Applying low loads (0° and 180° angular position), darker areas in the colour plot were visible: the friction coefficient decreased slightly with lower load. The coefficient of friction did not vary with in-

![Figure 3.42: Colour plot of the friction coefficient $\mu$ of a sample tribostressed at 80°C in TPPT solution. The friction coefficient is plotted colour coded as a function of the number of turns and the angular position of the rotating disc. On the left side of the colour plot, the applied load is plotted vs. the angular position.](image1)

![Figure 3.43: Friction coefficient $\mu$ vs. load for different temperatures in TPPT solution.](image2)
Results: Combinatorial Oscillating-Load Test

Increasing number of turns.

Applying 10 N load at 30°C, a very low μ of 0.07±0.01 was obtained (see Figure 3.43). With increasing load, the coefficient increased as well, reaching 0.19±0.06 at 0.5 N load. At 80 and 150°C, much higher μ's were measured at all loads (0.19±0.01 at 10 N load). At lower loads, the μ's tended to decrease, reaching the value of 0.18±0.05 at 0.5 N load.

Wear

The profiles of a disc and the corresponding ball tribostressed at 80°C are shown in Figure 3.44. On the disc, the two weartracks of the oscillating-load test

![Figure 3.44: Surface plot with the colour representing the surface height of a tribostressed disc (left) and the corresponding ball (right). The sample was tribostressed with oscillating load at 80°C in TPPT solution.](image)

![Figure 3.45: Wear rate of a sample tribostressed in an oscillating-load test at 80°C in TPPT solution. The load dependence in function of the angular position of the disc is shown in the scheme below.](image)
Figure 3.45: Wear coefficient $k$ for different loads and temperatures in TPPT solution.

(inner track) and the running-in (outer track) are visible as darker circles. On the ball, an area of a diameter of 230 µm was tribostressed. It was flattened during the running-in and the oscillating-load test, the average roughness $R_a$ was 0.69±0.09 µm. The roughness of the disc in the non-contact area was less than 0.01 µm.

From the profile, the wear rate and wear coefficient was determined for the different loads (see Figure 3.45 and Figure 3.46). The wear coefficient was very low at 30°C, much higher at 80°C with 4.6±0.3·10^{-6} mm³/Nm at 10 N load and at 150°C, the wear rate decreased with higher loads down to 2.5±0.3·10^{-6} mm³/Nm at 10 N load.

XPS Results

Survey and detailed high-resolution spectra were measured on the balls and discs to analyse the composition at the surface. Survey spectra were used for peak identification and to check the presence of contaminants such as sodium. For quantitative analysis and to identify the different chemical states of the elements, detailed spectra of phosphorus 2p, sulphur 2p, carbon 1s, oxygen 1s and iron 2p were recorded.

Figure 3.47 shows the spectra collected on a sample, which was tribostressed with 10 N load at 150°C in TPPT solution. The survey spectrum showed peaks of oxygen (KLL and 1s), iron (LMM, 2s, 2p, 3s and 3p), carbon 1s and traces of sulphur and phosphorus.

The phosphorus 2p$_{3/2}$ signal was found at 133.6±0.1 eV, a value typical for phosphate compounds [4, 66, 68]. The sulphur spectrum exhibited only a high-binding-energy signal at 169.0±0.1 eV assigned to sulphates [128, 129]. The
carbon 1s signal showed a main peak at 285.0 eV due to aliphatic carbon [87, 134] and two high-binding-energy peaks at 286.8±0.1 and 288.9±0.1 eV. The oxygen spectrum consisted of three peaks: the oxide peak at 530.3±0.1 eV [132, 133], the non-bridging oxygen (NBO) peak at 531.9±0.1 eV and the bridging oxygen (BO) at 533.4±0.1 eV [66, 67]. The NBO includes terminating oxygen in phosphate groups [66, 67] and contributions from oxygen bound to carbon [134, 135], sulphates [129] and iron hydroxides [133]. The main component of the iron 2p\textsubscript{3/2} signal was from Fe(III) at 710.9±0.1 eV [129, 132] and minor peaks were from Fe(II) at 709.6±0.1 eV [132, 133] and from iron (II) and iron (III) phosphate at 711.9±0.1 and 713.5 eV [4, 69].

Spectra at different Loads

Figure 3.59 shows the detailed spectra of P2p, S2p and O1s acquired on spots tribostressed with different loads, of the non-contact area and of the centre of the tribostressed region on the ball of an experiment performed at 150°C in TPPT solution. The phosphorus and sulphur spectra of areas tribostressed with 5 N and 0.5 N were similar to the 10 N areas. The binding energy of phosphorus was 133.5±0.1 eV at 5 N and 133.4±0.1 eV at 0.5 N load and the binding energy of the sulphate peaks stayed at the same energy. The oxide peaks (in both oxygen and iron spectra) were prominent at 10 N and 0.5 N load while
they were less intense at 0.5 N load. In the non-contact area, more intense peaks of phosphorus and sulphur were found at the same binding energies as at 10 N load while weak signals of the iron oxide were measured.

On the tribostressed region in the centre of the ball, only traces of phosphorus and sulphur were detected, but, in contrast to the scars on the disc, a low-binding-energy peak of sulphur was detected at 161.9 eV. This peak was due to sulphur in the oxidation state -2 found in sulphides [128, 129], thiolates [130, 131] or if sulphur is substituting oxygen in a (poly)thiophosphate. High intensities of iron oxide were measured together with intense signals from metallic iron [129, 132] or iron sulphide [128, 129] at 706.8 eV (see low-binding-energy peak in Figure 3.49 right) and carbides at 283.3 eV [136, 137] (see Figure 3.49 left).
Spectra at different Temperatures

Spectra measured on tribofilms formed with 10 N load at different temperatures are presented in Figure 3.50. At 30°C, an intense phosphorus peak was found at 133.4±0.2 eV. Weak signals of sulphur in the oxidation states -2 and +6 were found at 162.5±0.1 and 168.5±0.3 eV and only a small high-binding-energy peak of oxygen was observed. At 30°C and 80°C, adsorbed water might contribute to that peak. In contrast to the 150°C sample, where the iron signal was mainly composed of Fe(III), there were high intensities of metallic iron and Fe(II) at 30°C. In the carbon 1s signal, there was a weak peak revealed due to carbides at 283.2±0.2 eV. At lower loads, the spectra were similar to the 10 N spectra, but at 0.5 N load with smaller intensities of phosphorus and sulphur. In the non-contact areas, the phosphorus and sulphur signals were below the detection limit. In the centre of the tribostressed area on the ball, there was an intense low-binding-energy peak of sulphur.

At 80°C, only weak signals of phosphorus and sulphur were detected at the same binding energy as at 30°C while the peaks of iron oxide were very intense. A mixture of Fe(II) and Fe(III) was detected together with an intense peak of metallic iron. With lower loads, the intensity of phosphorus decreased while a strong sulphate peak was found at 0.5 N load. In the non-contact area, only traces of sulphur at 168.7±0.1 eV were found. On the tribostressed region of the ball, a very pronounced phosphorus peak was detected, together with an intense low-binding-energy peak of sulphur. On some spots, contributions from iron-hydroxides to the iron spectrum were detected.

Figure 3.50: XPS spectra of P2p, S2p and O1s measured on the tribotrack stressed with 10 N load at 30, 80 and 150°C in TPPT solution. (Data acquired with the PHI Quantera.)
Imaging XPS

With imaging XPS, the wear track produced with 10 N load at 150°C in TPPT solution and its environment was investigated (see Figure 3.51). No significant difference in the phosphorus intensity was found between the wear track (from bottom left to right top of the images) and the non-contact area. The low-binding-energy peak of sulphur (labelled S2p(II)) was very weak. Higher intensities of the sulphate peak and of carbon were found in the proximity of the wear track while on the wear track higher intensities of oxygen and iron were found.

10 N Load at 150°C in TPPT

![Graphical representation of XPS data for 10 N load at 150°C in TPPT](image)

Ball at 150°C in TPPT

![Graphical representation of XPS data for Ball at 150°C in TPPT](image)

Figure 3.51: Imaging-XPS of the tribotrack on the disc stressed with 10 N load at 150°C in TPPT solution and the corresponding ball. Complete spectra were acquired on each point of the map and the areas under the peaks were taken for the colour plot. (Images acquired with the PHI Quantera.)
On the ball, higher intensities of phosphorus and sulphur (II) were observed on the tribostressed region while sulphate seemed equally distributed. As observed on the wear track, more carbon was present in the non-contact area while higher intensities of oxygen and iron were measured on the tribostressed region.

3D-Colourplots of Oxygen

In Figure 3.52, the angle-resolved imaging XPS results are presented for a tribotrack produced with 10 N load at 150°C in TPPT solution. On the tribotrack, there were very intense oxide peaks and the percentage of oxide of the total oxygen peak area was high. Therefore the tribotrack is bright on the O1s(Oxide)-image. With increasing emission angle (z-axis, higher surface sensitivity), the percentage of the oxide peak decreased and appears darker in the image. On the non-contact area, only traces of the oxide were detected. On the tribotrack, the percentage of both the non-bridging oxygen (NBO) and the bridging oxygen (BO) increased with higher emission angles, which indicates that the reaction layer with NBO and BO was on top of the oxide layer. In the non-contact area, where the oxide peak was almost absent, the stronger NBO was

![Figure 3.52: 3D colour plots of the three oxygen peaks: oxide, non-bridging oxygen (NBO) and bridging oxygen (BO), measured on the tribotrack where 10 N load was applied and the surrounding non-contact area. The sample was produced at 150°C in TPPT solution. The colour indicates the peak's percentage of the sum of the O1s peaks in dependence on the lateral position (plan view) and the emission angle (z-axis). (Data acquired with the Theta Probe.)](image-url)
rather on the bottom of the analysed volume while the BO was present on the outer part. This suggests that in the inner part of the reaction layer short chain (poly-)phosphate were formed while in the outer part longer polyphosphate chains were formed.

**Angle-resolved XPS**

The elemental distribution of the elements with depth was determined with angle-resolved XPS. On the spot tribostressed with 10 N at 150°C, the apparent concentration of the total carbon (sum of aliphatic carbon and high-binding-energy peaks) increased with increasing EA, and so did each component of the sum. On the other hand, the concentrations of the oxide peaks of oxygen and iron decreased with increasing EA. The concentrations of NBO, phosphorus and sulphate were rather constant while the concentrations of BO and the high-binding-energy peak of iron were increasing incrementally. Different concentrations but similar slopes were obtained at lower applied loads.

In the non-contact area produced at 150°C, a higher concentration of carbon was found, increasing from 53 % at 27° EA to 71 % at 64° EA. Due to the dominating carbon, the concentration of the other elements decreased with increasing EA or, in the case of BO, remained on the same level. The concentration of the oxides was much lower compared to the tribotrack, also due to the thick organic layer on top of the sample. Nevertheless, the concentration of the oxides dropped towards zero while the concentrations of NBO, BO, phosphorus and sulphur remained on a relatively high level also at high EA.

**150°C in TPPT**

![Figure 3.53: Apparent atomic concentration vs. emission angle of a spot tribostressed with 10 N load and of the non-contact area produced at 150°C in TPPT solution. (Data acquired with the Theta Probe.)](image)
These results suggest that a multilayered system was present using the phosphorothionate TPPT. The substrate was metallic iron (not detected on this sample) with an oxide layer on top. On that a reaction layer containing NBO, BO, phosphorus, sulphur and iron phosphate was formed. On top, there was an organic layer with aliphatic carbon and the high-binding-energy peaks together with oxygen bound to carbon and below 80°C adsorbed water.

### Thickness and Composition

Based on the 4-layer structure of the surface films described above, the thickness and composition of each layer was calculated (see page 53). In the case of the non-contact areas at 30 and 80°C there were not enough reaction products for a laterally homogenous reaction layer and thus the reaction products were modelled to be a part of the organic layer on top. The thickness of the oxide layer was calculated to be 2.9±0.3 nm at 30°C and 3.4±0.2 nm at 80°C. At 150°C, no or not enough metallic iron was detected to calculate the thickness accurately; the three-layer model assuming a semi-infinite oxide layer to be the substrate was applied instead.

The thickness of the reaction layer is plotted in Figure 3.55. At 30°C, it was the thickest at high loads and in the contact region of the ball and decreased with decreasing load. In the non-contact areas no complete reaction layer was found. At 80°C thinner layers were obtained on the tribotrack. At 150°C a different trend was observed with thinner layers on the tribotrack stressed with high loads and with thicker layers of 3.4±0.2 nm on the non-contact area. On the ball, thinner reaction layers were formed than in the corresponding spots on the

![Figure 3.54: Thickness of the reaction layer on the discs and balls in dependence of the applied load and temperature formed in TPPT solution. Please note that “nc” stands for the non-contact area and “centre” means the middle of the tribostressed region of the ball.](image-url)
The oxide layer consisted of a mixture of iron oxide and iron hydroxide for all temperatures and loads except for the non-contact area treated at 150°C, where a depletion of oxygen was observed.

At 30°C, the reaction layer of the tribostressed areas consisted mainly of iron phosphate with traces of sulphides and sulphates, as indicated by the O:P:S ratio of 4:1:0.2 (Table 3.6). No significant load dependence of the composition was found. In the non-contact area, the main component was iron sulphate and only traces of phosphates were detected. Therefore the ratios could not be calculated accurately and are not presented in Table 3.6. On the ball, large amounts of iron sulphides were formed during the tribostress, together with small amounts of phosphates and sulphates.

At 80°C, iron phosphate was still the main component of the tribotacks, but with decreasing load the contribution of sulphates increased. In the non-contact areas mainly sulphates were detected with traces of phosphates. On the ball, the tribostressed region was composed of a mixture of sulphides and phosphates. On the non-contact areas of the ball, higher amounts of phosphates were found compared to the disc.

At 150°C, both the tribofilms and the thermal films were a mixture of iron phosphate and sulphate with approximately equal amounts of phosphorus and sulphur. On the ball, again large amounts of sulphides were detected, being the main component of the films formed. In the non-contact areas, similar films as on the disc were found.

**Table 3.6:** Elemental ratios of the elements present in the reaction layer normalised by phosphorus. In the case of oxygen, the oxide peak was not taken into account. For iron, only the peaks assigned iron phosphate and iron sulphide were attributed to the reaction layer.

<table>
<thead>
<tr>
<th></th>
<th>O</th>
<th>P</th>
<th>S(II)</th>
<th>S(VI)</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Disc</td>
<td>3.8±0.8</td>
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<td>0.1±0.1</td>
<td>0.1±0.1</td>
<td>0.3±0.1</td>
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<tr>
<td>5 N</td>
<td>3.9±0.7</td>
<td>1.0</td>
<td>0.1±0.0</td>
<td>0.1±0.0</td>
<td>0.2±0.1</td>
</tr>
<tr>
<td>0.5 N</td>
<td>4.4±0.3</td>
<td>1.0</td>
<td>0.1±0.1</td>
<td>0.1±0.1</td>
<td>0.3±0.1</td>
</tr>
<tr>
<td>Ball centre</td>
<td>5.4±1.3</td>
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<td>2.3±1.5</td>
<td>0.4±0.2</td>
<td>2.7±1.8</td>
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<td>80°C</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Disc</td>
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<td>1.0</td>
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<td>0.0±0.0</td>
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</tr>
<tr>
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<td>1.7±0.3</td>
<td>1.8±0.9</td>
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<tr>
<td>Ball centre</td>
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<td>0.9±0.0</td>
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<td>1.0±0.0</td>
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<td>0.6±0.0</td>
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<td>150°C</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Disc</td>
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<td>1.0</td>
<td>0.9±0.0</td>
<td>0.1±0.1</td>
<td></td>
</tr>
<tr>
<td>5 N</td>
<td>9±1</td>
<td>1.0</td>
<td>0.8±0.0</td>
<td>0.0±0.0</td>
<td></td>
</tr>
<tr>
<td>0.5 N</td>
<td>14±1</td>
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<td>1.2±0.0</td>
<td>0.2±0.0</td>
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</tr>
<tr>
<td>nc</td>
<td>11±1</td>
<td>1.0</td>
<td>0.9±0.0</td>
<td>0.2±0.1</td>
<td></td>
</tr>
<tr>
<td>Ball centre</td>
<td>14±1</td>
<td>1.0</td>
<td>2.1±0.0</td>
<td>1.3±0.0</td>
<td>2.1±0.0</td>
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<td>1.0</td>
<td></td>
<td>1.3±0.2</td>
<td>0.1±0.0</td>
</tr>
</tbody>
</table>
The main component of the *organic layers* was carbon containing some oxygen. At 30° and 80°C, adsorbed water was also detected.
3.2.4 Phosphorothionate b-TPPT

Tribological Tests

A colour plot the friction coefficient $\mu$ measured on a sample tribostressed in oil blended with 1 wt.% of the butylated triphenyl phosphorothionate b-TPPT at 80°C is shown in Figure 3.55. The friction coefficient $\mu$ was slightly lower during the first 200 turns and then remained stable during the last 800 turns. At lower loads (around angular positions of 0°, 180° and 360°), $\mu$ was lower as can be seen from the darker colours in these regions.

The friction coefficients for all experiments performed in b-TPPT solution are reported in Figure 3.56. At high loads, $\mu$ was lower at 30°C (0.17±0.01) than at

![Figure 3.55](image)

Figure 3.55: Colour plot of the friction coefficient $\mu$ of a sample tribostressed at 80°C in b-TPPT solution.

![Figure 3.56](image)

Figure 3.56: Friction coefficient $\mu$ vs. load for different temperatures in b-TPPT solution.
Results: Combinatorial Oscillating-Load Test

80 and 150°C (0.19±0.01). Due to the uncertainty associated with these measurements not clear trend can be stated at lower loads.

Wear

In b-TPPT solutions, the dimensional wear coefficient $k$ was higher at lower loads, but the error bars and thus the uncertainty were larger (see Figure 3.59). The wear coefficient appears to be independent on the applied temperature and on the applied load when 5N and 10N loads where applied (2.6±0.6·10^{-6} mm^3/Nm). At low loads the scatter of the data is very high.

![Figure 3.57: Dimensional wear coefficient $k$ on the disc for different loads and temperatures in b-TPPT solution.](image)

XPS Results

Spectra collected on an area on the disc tribostressed with 10 N load at 150°C in b-TPPT solution are shown in Figure 3.58. The survey spectrum exhibited peaks of Oxygen (1s and KLL), iron (LMM, 2s, 2p, 3s and 3p), carbon 1s and traces of sulphur and phosphorus. To identify the chemical state of the elements and for quantitative analysis, the detailed spectra of P2p, S2p, C1s, O1s and Fe2p were acquired.

The phosphorus 2p_{3/2} peak was at a binding energy of 133.5±0.2 eV, which was 0.7 eV lower than found in frozen b-TPPT (see Appendix) or in tributyl thiophosphate [53], a molecule with the same neighbour-atoms of phosphorus. Sulphur 2p_{3/2} was at 168.9±0.1 eV, which corresponds to the oxidation state +6, found in sulphates [128, 129]. In the carbon 1s spectrum, the most intense signal was at 285.0 eV due to aliphatic carbon [87, 134]. Minor contributions were
Results: Combinatorial Oscillating-Load Test

10 N Load at 150°C in b-TPPT

Figure 3.58: XPS survey and detailed spectra of P2p, S2p, C1s, O1s and Fe2p measured on the tribotrack stressed with 10 N load in b-TPPT at 150°C. (Data acquired with the PHI Quantera.)

found at 286.7±0.1 eV due to carbon bound to oxygen [121, 134] and at 288.9±0.1 eV because of carbonates [129, 135] and/or carboxylic groups [121, 134]. The oxygen 1s signal consisted of 3 peaks, the first at 530.3±0.1 eV assigned to oxygen in iron oxides [132, 133], the main peak at 532.0±0.1 eV assigned to non-bridging oxygen (NBO) in (poly-)phosphates [66, 67], sulphates [129] and to oxygen bound to carbon [134] and the high-binding-energy peak at 533.4 eV assigned to bridging oxygen (BO) in polyphosphates [66, 67]. The iron 2p3/2 signal was at 709.6±0.2 eV assigned to iron in the oxidation state +3 [129, 132]. This peak exhibits a satellite at 720 eV [132], but it was not included into the fitted region.

Spectra at different Loads

Detailed spectra of P2p, S2p and O1s of small areas tribostressed at 150°C in b-TPPT solution with different loads, of the non-contact area and of the centre of the tribostressed region of the ball are presented in Figure 3.59. The intensities of phosphorus, sulphur (sulphate), oxygen and iron (not shown) from the tribofilm formed on the analysed spots on the disc did not change with the applied load. The binding energy values remained constant within the experimental uncertainty. In the non-contact region, the sulphate signal was more


150°C in b-TPPT

Figure 3.59: XPS spectra of P2p, S2p and O1s measured on the tribotrack stressed with varying load, on the non-contact area of the disc and on the centre of the tribostressed region on the ball. The experiment was performed at 150°C in b-TPPT solution. (Data acquired with the PHI Quantera.)

tense while the intensities of iron and oxygen from iron oxide were found to be much lower.

In the tribostressed region of the ball, a small low-binding-energy peak was detected at 162.0±0.2 eV assigned to sulphur (II) found in sulphides [128, 129], thiolates [130, 131] or in sulphur is substituting oxygen in a (poly)thiophosphate; the sulphate peak was also very small. The phosphorus signal was less intense compared to the ones collected in the tribotracks. The oxide peak in the oxygen spectrum exhibited a similar intensity as that measured in the tribofilms on the disc while the iron signal was very pronounced with a prominent peak at 706.9±0.1 eV, assigned to metallic iron [129, 132] and/or iron sulphide [128, 129]. In the carbon spectrum (not shown), a small carbide peak was detected at 283.2±0.2 eV [136, 137].

Spectra at different Temperatures

The temperature dependence of the collected spectra is shown for 10 N load in Figure 3.60. At 30°C, the spectra of the tribostressed regions generally showed less intense peaks of phosphorus 2p3/2 at 133.4±0.1 eV and only weak signals of sulphur (II) at 161.8±0.2 eV and sulphur (VI) at 168.0±0.1 eV (sulphate) were detected, while the signals of metallic iron and of iron oxide were more intense. Carbides were detected at all loads (283.2±0.1 eV). Adsorbed water might contribute to the high-binding-energy peak of oxygen [133]. In the non-contact areas, only traces of phosphorus at 133.2±0.1 eV were detected, but more water and hydroxides were present than on the tribotracks. On the tri-
bostressed region of the ball, similar spectra as on the 10 N spot on the disc were recorded.

The spectra of the tribotacks stressed at 80°C with 10 N load were similar to those tribostressed at 150°C. Intense peaks of phosphorus were found at 133.4±0.1 eV. Small amounts of sulphur (II) at 162.5±0.2 eV and sulphur (VI) at 168.6±0.3 eV were detected and the iron signal showed more intense peaks of metallic iron and Fe(II). On some samples, traces of iron at 711.9±0.1 eV assigned to iron hydroxide or iron(II)phosphate were found [4, 69, 133]. In the non-contact area, only traces of sulphates were detected. In the centre of the ball there was phosphorus and sulphur in both oxidation states found at the same binding energies as on the tribotrack.

Imaging XPS

On the tribotrack (from bottom left to right top of the images) of a sample tribostressed with 10 N load at 150°C (see Figure 3.61), higher intensities of phosphorus and the high-binding-energy peak of sulphur was found while only traces of the low-binding-energy peak were detected. Carbon was more intense outside of the tribotrack. The biggest contrast was found looking at oxygen and iron, both elements were more pronounced on the tribotrack than in the non-contact area.
10 N Load at 150°C in b-TPPT

Figure 3.61: Imaging-XPS of the tribotrack on the disc tribostressed with 10 N load at 150°C in b-TPPT solution. (Images acquired with the PHI Quantera.)

Figure 3.62: 3-D colour plots of the three oxygen peaks: oxide, non-bridging oxygen (NBO) and bridging oxygen (BO), measured on the tribotrack and the surrounding non-contact area. The spot was tribostressed with 10 N load at 150°C in b-TPPT solution. The colour indicates the peak’s percentage of the sum of the O1s peaks in dependence on the lateral position (plan view) and the emission angle (z-axis). (Data acquired with the Theta Probe.)
3D-Colourplots of Oxygen

Figure 3.62 shows the 3-dimensional distribution of oxygen on the 10 N tribotrack and the surrounding non-contact area of a sample tribostressed at 150°C in b-TPPT solution. The tribotrack exhibited a much higher percentage of the oxide peak and therefore appears in a lighter colour in the O1s(oxide) plot, especially at low emission angles. With increasing emission angle (more surface sensitive) the percentage in both the contact and the non-contact area decreased. This indicates that the oxide was present on the bottom of the analysed volume. The non-bridging oxygen (NBO) showed much less contrast between the tribotrack and the non-contact area. On the tribotrack, its percentage raised with increasing emission angle, while in the non-contact area the concentration stayed constant. The percentage of the high-binding-energy peak assigned to bridging oxygen (BO) was higher in the non-contact area, especially at high emission angles, and lower on the tribotrack. This indicates that the thermal film contained longer chains than the tribofilm, and that the linking was even higher in the outer part of the film.

Angle-resolved XPS

The elemental distribution in function of the depth was determined with angle-resolved XPS. For the plots presented in Figure 3.63, the apparent atomic concentration (intensities corrected only for the angular asymmetry factor $L_A(\gamma)$, the étendue $G(E_i)$, the photoionization cross-section $\sigma$, and the IMFP $\lambda(E_i)$) was

10 N Load in b-TPPT

Figure 3.63: Apparent atomic concentration vs. emission angle of spots tribostressed with 10 N load at different temperatures in b-TPPT. (Data acquired with the Theta Probe.)
plotted vs. the emission angle for tribotacks stressed with 10 N load at different
temperatures. At 30°C, the concentration of carbon (sum of aliphatic carbon
and high-binding-energy peaks) rose with higher EA suggesting that the organic
layer was present on top of the sample. The concentrations of the oxide peaks
in oxygen and iron decreased while the concentration of NBO was constant and
increased in the case of the BO. The concentration of metallic iron and carbides
dropped with higher EA, which suggests that these elements were located on
the very bottom of the analysed volume. Phosphorus and sulphur were de-
tected only in traces and therefore the slope of these curves could not be de-
termined accurately.

At higher temperatures, different concentrations were found, but the slopes
were similar to those described before. Higher concentrations of phosphorus
and sulphur were obtained; they stayed on the same level for all emission an-
gles and therefore were located in the middle of the analysed volume or were
evenly distributed. Spots tribostressed with lower loads showed the same depth
distribution of the elements. In the non-contact areas at 30°C and 80°C almost
no phosphorus and sulphur were found while at 150°C high concentrations of
these elements were present with small slopes only.

These results suggest that a multilayered system was present. The substrate
was metallic iron with some carbides covered with an iron oxide film, on which a
reaction layer with phosphorus, sulphur and oxygen (NBO) was formed. On top
there was an organic layer, which contained aliphatic carbon, carbon with
higher binding energy and an oxygen contribution from functional groups con-
taining oxygen, found at the same energy as in the NBO. At 30 and 80°C, ad-
sorbed water was the main component of the high-binding-energy peak of oxy-
gen, present in the organic layer. At 150°C, bridging oxygen was the main com-
ponent of the high-binding-energy peak, which was part of the reaction layer.

**Thickness and Composition**

The 4-layer model (section 2.4.5) was used to calculate the thickness and
composition of each layer of the tribofilm. The thickness of the oxide layer was
3.1±0.3 nm at 30°C and 3.5±0.1 nm at 80°C. At 150°C it could only be deter-
mined on the tribostressed region of the ball, there it was 3.1±0.3 nm.

The thickness of the reaction layer could not be determined for some areas
tested at 30°C and 80°C because there only fractions of a monolayer were ob-
tained. In these cases the reaction products were modelled as being incorpo-
rated in the organic layer. There is a complex dependence on the applied load
and temperature (see Figure 3.64). On the 10 N spot at 30°C, the thickness is
Results: Combinatorial Oscillating-Load Test

Figure 3.64: Thickness of the reaction layer on the discs and balls in dependence of the applied load and temperature formed in b-TPPT solution. Please note that “nc” means the non-contact area and “centre” the middle of the tribo-stressed region of the ball.

0.4 nm and with 0.5 N load 0.3 nm what corresponds to a monolayer of adsorbed species. At 5 N load and in the non-contact areas no continuous film was formed. At 80°C the reaction layers were around 0.5 nm thick regardless of the load, while no continuous film was formed in the non-contact area. At 150°C the thickest reaction layers were formed, in the non-contact areas thicknesses of 2.9±0.6 nm were found while the tribofilms were below 1 nm, whereas thinner layers were obtained with higher loads. The thickness of the organic layer was between 1.5 and 4.5 nm.

The oxide layer consisted of a mixture of iron oxide with iron hydroxide, the oxygen-to-iron ratio was 2.0±0.2:1 for all conditions except the non-contact areas of the 150°C samples, where a ratio of 1.3±0.5:1 was found. This corresponds to an iron oxide with a stoichiometry close to that of Fe₃O₄ with O:Fe=1.33:1.

The tribofilms at 30°C were composed of iron phosphate together with minor amounts of sulphides and sulphates, no load dependence of the composition was observed (see ratios in Table 3.7). In the non-contact area only traces of phosphates were detected. The tribostressed region on the ball was composed of a mixture of iron phosphate, sulphate and sulphides. In the non-contact area of the ball, only traces of phosphates were detected and the elemental ratios not be calculated accurately.

At 80°C, the tribofilms were made of phosphates, with traces of sulphides and sulphates. Again, no load dependence of the composition was found. In the non-contact area only sulphates were present. On the tribostressed region of the ball, a mixture of phosphates and sulphides was found while in the non-
contact area, iron sulphate was the main compound, with traces from iron phosphate and iron sulphide.

Increasing the temperature to 150°C, higher amounts of sulphates were present in the tribofilms, with increasing concentrations with lower loads. In the non-contact area, about the double amount of sulphate than phosphates was detected. On the tribostressed region on the ball, there was a similar composition as at 80°C found with almost equal amounts of phosphates and sulphides. In the non-contact areas of the ball, there were similar films as on the disc.

**Table 3.7:** Elemental atomic concentration ratios of the elements present in the reaction layer normalised by phosphorus. In the case of oxygen, the oxide peak was not taken into account. For iron, only the peaks assigned to iron phosphate and iron sulphide were attributed to the reaction layer.

<table>
<thead>
<tr>
<th></th>
<th>O</th>
<th>P</th>
<th>S(II)</th>
<th>S(VI)</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>30°C</strong> Disc 10 N</td>
<td>4.6±0.6</td>
<td>1.0</td>
<td>0.4±0.0</td>
<td>0.1±0.1</td>
<td>1.1±0.1</td>
</tr>
<tr>
<td>5 N</td>
<td>4.0±0.0</td>
<td>1.0</td>
<td>0.2±0.2</td>
<td></td>
<td>1.3±0.0</td>
</tr>
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<td>0.5 N</td>
<td>5.2±1.2</td>
<td>1.0</td>
<td>0.3±0.3</td>
<td>0.3±0.3</td>
<td>1.7±0.0</td>
</tr>
<tr>
<td>nc</td>
<td>4.0±0.0</td>
<td>1.0</td>
<td></td>
<td></td>
<td>2.3±0.7</td>
</tr>
<tr>
<td>Ball centre</td>
<td>5.0±1.0</td>
<td>1.0</td>
<td>0.3±0.3</td>
<td>0.3±0.3</td>
<td>3.4±1.3</td>
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<tr>
<td><strong>80°C</strong> Disc 10 N</td>
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<td></td>
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<tr>
<td>5 N</td>
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<td>0.8±0.1</td>
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3.2.5 Phosphorothionate n-TPPT

Tribological Tests

The friction coefficient $\mu$ of an oscillating-load test performed at 80°C in nonylated triphenyl phosphorothionate n-TPPT solution is shown in Figure 3.65. The friction coefficient did not change significantly upon time. It was higher with higher applied load, as shown with the brighter colour at around 120 and 300°, which was short after the highest load was applied (see also Figure 3.66).

At 30°C, $\mu$ was 0.17±0.01 at 10 N load and increased with lower loads where also a higher uncertainty is evident. At 80° and 150°C, higher $\mu$’s of about 0.20 were obtained for all loads.

![Figure 3.65: Colour plot of the friction coefficient $\mu$ of a sample tribostressed at 80°C in n-TPPT solution.](image)

![Figure 3.66: Friction coefficient $\mu$ vs. load for different temperatures in n-TPPT solution.](image)
Wear

In n-TPPT solution, the dimensional wear coefficient $k$ decreased with increasing load at 30 and 150°C while it increased at 80°C (see Figure 3.67). For 10 N load, it was $1.8 \pm 0.1 \cdot 10^{-6} \text{mm}^3/\text{Nm}$ at 30°C, increased at 80°C to $5.0 \pm 0.7 \cdot 10^{-6} \text{mm}^3/\text{Nm}$ and was again $1.8 \pm 0.1 \cdot 10^{-6} \text{mm}^3/\text{Nm}$ at 150°C.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{wear_coefficient}
\caption{Wear coefficient $k$ for different loads and temperatures in n-TPPT solution.}
\end{figure}

XPS Results

The spectra of a sample tribostressed with 10 N load at 150°C in n-TPPT solution are shown in Figure 3.68. The survey spectrum showed peaks of oxygen, iron, carbon and traces of sulphur and phosphorus.

The detailed spectrum of phosphorus showed a small P2p3/2 peak at 133.7±0.1 eV. In the signal of sulphur, there was a pronounced sulphate peak with a binding energy of S2p3/2 at 169.0±0.1 eV [128, 129]. The carbon 1s spectrum exhibited a main peak at 285.0 eV due to aliphatic carbon [87, 134]. Smaller peaks were found at higher binding energies (286.7±0.1 and 288.6±0.1 eV). The oxygen 1s spectrum contained three peaks: an oxide peak at 530.2±0.1 eV [132, 133], a NBO peak at 531.9±0.1 eV [66, 67] and a BO peak at 533.4 eV [66, 67]. There were additional contributions from sulphate groups and oxygen bound to carbon to the NBO peak [134, 135]. The iron spectrum contained peaks of the oxidations states +2 and +3 at 709.6 and 710.9 eV [129, 132, 133]. On other spots there were also contributions from iron phosphate at 711.9±0.1 and 713.5 eV [4, 69].
Results: Combinatorial Oscillating-Load Test

10 N Load at 150°C in n-TPPT

Survey

- Carbon 1s
- Oxygen 1s
- Phosphorus 2p
- Sulphur 2p
- Iron 2p

Figure 3.68: XPS survey and detailed spectra of P2, S2p, C1s, O1s and Fe2p measured on the tribotrack stressed with 10 N load at 150°C in n-TPPT solution. (Data acquired with the PHI Quantera.)

Spectra at different Loads

A comparison of spectra acquired on areas tribostressed with different loads, of the non-contact area and of the tribostressed centre of the ball is shown in Figure 3.69. Applying 5 N load, the spectra were similar to the 10 N spectra, only the binding energy of P2p₃/₂ was shifted by 0.2 eV to lower binding energy.

150°C in n-TPPT

Phosphorus 2p

- S(VI)

Sulphur 2p

- BO
- Oxide

Oxygen 1s

- NBO
- Oxide

Figure 3.69: XPS spectra of P2p, S2p and O1s measured on the tribotrack stressed with varying load, on the non-contact area of the disc and on the centre of the tribostressed region on the ball. The experiment was performed at 150°C in n-TPPT solution. (Data acquired with the PHI Quantera.)
With 0.5 N load, the binding energies of phosphorus and sulphur stayed constant as found with 5 N load, but the phosphorus and the oxide peaks were less intense. In the non-contact areas, phosphorus was found at 133.5 eV and the sulphate peak at 169.0 eV was more pronounced than on the tribostressed samples. Only small oxide peaks and iron signals were detected.

On the tribostressed region of the ball, only traces of phosphorus were detected at 133.6 eV. As observed with the other phosphorothionates, again a low-binding-energy peak of sulphur was present on the ball at 162.2 eV. There was an intense oxide peak combined with a strong iron peak. From the substrate, both metallic iron and a carbide peak at 283.3 eV were revealed.

**Spectra at different Temperatures**

At 30°C, small peaks of phosphorus (133.6±0.1 eV) and sulphur (161.9±0.1 and 168.0±0.1 eV) were detected only with 10 N load (see Figure 3.70). At lower loads and in the non-contact area, both phosphorus and sulphur were below the detection limit. On the tribostressed region of the ball, phosphorus (133.3 eV) and sulphur were more intense, whereas the area of the low-binding-energy peak at 162.0 eV was about the double of the high-binding-energy peak at 168.0 eV. On all spots, peaks of carbides and metallic iron were detected.

On areas tribostressed with high loads at 80°C, small signals of phosphorus at 133.4±0.2 eV and the two oxidation states -2 (at 162.0±0.2 eV) and +6 (at 168.4±0.1 eV) of sulphur were present, as shown in Figure 3.70. With 0.5 N load and in the non-contact area, only sulphate peaks at 168.5±0.1 eV were de-
Results: Combinatorial Oscillating-Load Test

tected. On the tribostressed region of the ball, the low-binding-energy peak of sulphur was very pronounced (at 161.6 eV), the sulphate peak was weak while no phosphorus was detected. As at 30°C, all spectra of the 80°C sample exhibited signals of metallic iron and carbides.

Imaging XPS

The lateral distribution of the elements on the tribotrack and the ball was checked with imaging XPS (see Figure 3.71). On the tribotrack (from bottom left

10 N Load at 150°C in n-TPPT

![Image of imaging XPS for tribotrack and ball at 150°C in n-TPPT]

Ball at 150°C in n-TPPT

![Image of imaging XPS for ball at 150°C in n-TPPT]

Figure 3.71: Imaging-XPS of the tribotrack on the disc stressed with 10 N load at 150°C in n-TPPT solution and the corresponding ball. Complete spectra were acquired on each point of the map and the area under the peak taken for the colour plot. (Images acquired with the PHI Quantera.)
to right top of the images) stressed with 10 N load at 150°C, higher intensity of phosphorus and sulphur was found compared to the non-contact areas, whereas only weak signals of the low-binding-energy peak of sulphur were obtained. Oxygen and iron was also more prominent on the tribotrack while higher intensity of carbon was found in the non-contact area.

On the ball, the tribostressed region is the circular area in the centre of the image. It shows lower intensities of phosphorus and sulphate than on the tribotrack, while the intensity of the low-binding-energy peak of sulphur was much more pronounced. As on the disc, higher intensity of carbon was found in the non-contact area and higher oxygen and iron intensities in the tribostressed region.

3D-Colourplots of Oxygen

To check the 3-dimensional distribution of oxygen on the tribotrack and the surrounding non-contact area, angle-resolved imaging XPS was performed; a sample tribostressed with 10 N at 150°C is shown in Figure 3.72. The percentage of the oxide peak to the total oxygen signal was much higher on the tribotrack (see bright area from bottom right to top left). With increasing emission

Figure 3.72: 3D colour plots of the three oxygen peaks: oxide, non-bridging oxygen (NBO) and bridging oxygen (BO), measured on the tribotrack where 10 N load was applied and the surrounding non-contact area. The sample was produced at 150°C. The colour indicates the peak’s percentage of the sum of the O1s peaks in dependence on the lateral position (plan view) and the emission angle (z-axis). (Data acquired with the Theta Probe.)
angle (higher surface sensitivity), the percentage of oxide decreased, indicating that it was present on the bottom of the analysed volume. In case of the non-contact area it was covered with thick films so that almost no intensity from the oxide layer was detected.

The non-bridging oxygen (NBO) was laterally equally distributed, only the edge of the tribotrack showed a higher percentage of NBO. The bridging oxygen (BO) was much more pronounced in the non-contact area. On the tribotrack, both the NBO and the BO concentrations increased with higher emission angles while on the non-contact area the BO increased and the NBO decreased with higher emission angles. This suggests that the tribofilm consisted of shorter chains than the thermal films, whereas longer chains were present in the outer part of the film.

**Angle-resolved XPS**

The elemental distribution of the elements with depth was determined with angle-resolved XPS. For the 10 N area, the apparent atomic concentration of carbon (sum of aliphatic carbon and high-binding-energy peaks) raised with increasing emission angle while the concentrations of the oxide peaks of oxygen and iron dropped (see Figure 3.72 left). Small positive slopes were obtained for the BO, Sulphate and the high-binding-energy peak of iron (FePO₄) and small negative slopes for phosphorus and NBO.

In the non-contact area (see Figure 3.72 right), the carbon concentration was higher and increased with higher EA. Because of its high concentration, the

**150°C in n-TPPT**

![Figure 3.73: Apparent atomic concentration vs. emission angle of a 10 N tribotrack and of a non-contact area produced at 150°C in n-TPPT solution. (Data acquired with the Theta Probe.)](image)
concentrations of the other elements all decreased with the exception of BO, where the concentration was stable.

These results suggest that the same multilayer structure as observed for the other phosphorothionates TPPT and b-TPPT was present.

**Thickness and Composition**

Applying the multi-layer model (see page 53), the thickness of the oxide layer was determined to be 3.0±0.3 nm for 30 and 80°C. With 10 N load at 30°C, the thickness of the reaction layer was 0.3 nm what corresponds to a monolayer of reaction products. At lower loads and in the non-contact region not complete layers were formed on the surface and thus the thickness could not be determined. On the areas tribostressed with high loads at 80°C the reaction layer thickness was 0.4 nm (see Figure 3.74). Prominent layers were formed only at 150°C with 1.2 nm at high loads, incrementally thicker at 0.5 N load and with 3.3±0.1 nm much thicker in the non-contact area. On the ball at 150°C, films with about half of the thickness obtained on the disc were formed. The thickness of the organic layer was between 2 and 3 nm, thicker films with 4.5 nm were obtained on the non-contact areas on the balls treated at 150°C.

The oxide layer at 30 and 80°C was composed of a mixture of iron oxide and iron hydroxide, a ratio of O:Fe of 2.0±0.3:1 was found. The reaction layer formed under 10 N tribostress at 30°C was a mixture of iron phosphates, sulphides and sulphates as indicated by the ratios presented in Table 3.8. At lower loads and in the non-contact areas no reaction layers were formed. On the tribostressed region of the ball, iron sulphide was the main component, together

![Figure 3.74: Thickness of the reaction layer on the discs and balls in dependence of the applied load and temperature formed in n-TPPT solution. Please note that "nc" stands for the non-contact area and "centre" means the middle of the tribostressed region of the ball.](image-url)
with some phosphates and sulphates. On the non-contact areas of the ball iron sulphate was found.

At 80°C, increased amounts of sulphides were detected compared to 30°C. At low loads, higher amounts of sulphates were observed while only traces of phosphates were detected. The non-contact area was composed of iron sulphate embedded in the organic layer. On the tribostressed region of the ball, large amounts of sulphides were found together with some sulphates and in the non-contact area, iron sulphate was the main component.

At 150°C, mainly iron sulphate with small amounts of phosphates were observed on the tribotacks at different loads and on the non-contact areas of both the disc and the ball. On the tribostressed region of the ball, large amounts of iron sulphide were found, almost as many as sulphates.

Table 3.8: Elemental ratios of the elements present in the reaction layer normalised by phosphorus. In the case of oxygen, the oxide peak was not taken into account. For iron, only the peaks assigned to iron phosphate and iron sulphide were attributed to the reaction layer.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Location</th>
<th>Load</th>
<th>O</th>
<th>P</th>
<th>S(II)</th>
<th>S(VI)</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°C</td>
<td>Disc</td>
<td>10 N</td>
<td>9±2</td>
<td>1.0</td>
<td>1.1±0.4</td>
<td>1.3±0.6</td>
<td>3.7±0.9</td>
</tr>
<tr>
<td></td>
<td>Ball</td>
<td>centre</td>
<td>9±0</td>
<td>1.0</td>
<td>2.9±0.0</td>
<td>1.4±0.0</td>
<td>3.3±0.0</td>
</tr>
<tr>
<td>80°C</td>
<td>Disc</td>
<td>10 N</td>
<td>9±1</td>
<td>1.0</td>
<td>1.4±0.4</td>
<td>1.3±0.2</td>
<td>3.3±0.8</td>
</tr>
<tr>
<td></td>
<td>Ball</td>
<td>centre</td>
<td>8±2</td>
<td>1.0</td>
<td>1.3±0.5</td>
<td>1.1±0.4</td>
<td>2.9±1.1</td>
</tr>
<tr>
<td></td>
<td>Disc</td>
<td>5 N</td>
<td>8±2</td>
<td>1.0</td>
<td>2.5±1.5</td>
<td>0.3±0.2</td>
<td>0.5±0.0</td>
</tr>
<tr>
<td></td>
<td>Ball</td>
<td>centre</td>
<td>45±2</td>
<td>1.0</td>
<td>6.9±0.4</td>
<td>0.6±0.1</td>
<td>0.5±0.1</td>
</tr>
<tr>
<td>150°C</td>
<td>Disc</td>
<td>10 N</td>
<td>18±1</td>
<td>1.0</td>
<td>3.8±0.5</td>
<td>3.2±0.5</td>
<td>3.4±0.4</td>
</tr>
<tr>
<td></td>
<td>Ball</td>
<td>centre</td>
<td>24±5</td>
<td>1.0</td>
<td>2.6±0.6</td>
<td>3.9±0.5</td>
<td>1.8±0.4</td>
</tr>
</tbody>
</table>
3.3 Wear Test

Different loads and sliding speeds were tested in a single combinatorial wear experiment on each disc. Applying this test, different additives (pure oil, ZnDTP and b-TPPT), tribopairs (non-hardened steel-steel (100 HV10) and ceramic-steel contacts) at different temperatures (25°C and 150°C) were compared in respect to their friction and wear behaviour.

3.3.1 Tribological Results

Colour plots of the friction coefficient for the wear tests performed with a sliding speed of 25 mm/min at 150°C are shown in Figure 3.75. The load was cycled four times per turn from 1 to 10 to 1 N as is shown in the scheme below each colour plot. The generally brighter colour of the steel-steel contact shows that these samples exhibit higher friction coefficients than those tribostressed with a ceramic ball. In addition, higher friction coefficients were obtained at lower loads. Stick-slip was observed in the steel-steel contacts at high load as

![Figure 3.75: Colour plots of the friction coefficient, measured during oscillating-load tests as a function of the angular position on the disc and the number of turns, for different additives and tribopairs. The load was varied from 1 to 10 N, as shown in the schemes below the colour plots. The tests were performed with 25 mm/min sliding speed at 150°C.](image-url)
can be seen by the fluctuating values at high loads, which result in a tiger-like pattern.

No significant differences were detected within the four load cycles, all four quadrants showed the same frictional properties. During the first turns, running-in effects are distinguished by the different pattern observed, in comparison to the last 50 turns, where the frictional conditions were almost constant.

On each disc, different sliding speeds ranging from 10 to 1000 mm/min were tested at different radii (see Figure 3.76 and Figure 3.77). For calculating the average friction coefficients in dependence of the applied load, the first 20% of the data points were not taken into account because of the running-in effects. If stick-slip occurred, only the maximum friction force of each stick-slip event was taken (see section 2.3.4).

At 25°C (see Figure 3.76), the friction coefficients of the steel-steel contacts were between 0.2-0.6, lower μ values were observed at higher sliding speeds and higher loads. No significant dependence of the friction coefficient on the additives was found for these experiments. For the ceramic-steel contact, μ was between 0.1 and 0.2. The same tendencies with lower μ at higher speed and load were observed, but less pronounced than for the steel-steel contact. Again,

Steel-Steel Contact at 25°C

![Figure 3.76: Friction coefficients in dependence on load and sliding speed at 25°C for steel-steel (non-hardened) and ceramic-steel contacts in pure oil, ZnDTP solution and b-TPPT solution.](image-url)
no significant dependence on the additives was found.

On the steel-steel contact at 150°C (see Figure 3.77), the friction coefficients were higher compared to the room-temperature samples. At this temperature, the presence of the anti-wear additives resulted in lower friction, especially at low speeds and high loads. In the case of the ceramic-steel contact, similar results as at room temperature were obtained.

Stick-slip phenomena occurred in the steel-steel contacts at low sliding speeds and high loads. Applying a load of 10 N, stick-slip was observed up to a sliding speed of 158 mm/min. No stick-slip occurred above 398 mm/min or in the case of ceramic-steel contacts.

3.3.2 Wear

The height-profile of a disc tribostressed in ZnDTP solution at 150°C with oscillating load, is given as example in Figure 3.78. Sliding speeds ranging from 10 to 1000 mm/min were applied on different tracks, which can be seen as full circles with darker and lighter regions, depending on the applied load. The outer track, which is partially cut, was produced during the running-in of the ball. Dur-
Results: Wear Test

Figure 3.78: Surface plot with the colour representing the surface height (left) and an extracted profile (right). The sample was tribostressed with a steel ball with oscillating load and different velocities at 150°C in ZnDTP solution.

During the tribological test the applied load was registered as a function of the angular position, which was calibrated using reference marks for later data processing. Herewith, the applied load has not necessarily to be applied always at the same angular position for the different sliding speeds.

An example of the radial profiles is shown on the right of Figure 3.78. It can be extracted from the height profiles (see Appendix for the routines). The six wear tracks with the deposited material on the side are visible by the deep valleys with the peaks on the side in the radial profile. On the steel balls, the tribostressed area was worn while on the ceramic ball, no change with the tribostress was observed.

Wear Rate

Using radial profiles (see Figure 3.78 right), the wear rate was calculated by taking the area below a linear background (thin line in the profile) and converting it into wear rates. Taking the area above the background, the deposition rate was obtained. This was done in dependence on the angular position in order to extract load dependent wear and deposition rates for the different sliding speeds.

The wear rate for oscillating load is shown in Figure 3.79 for a sample tribostressed in ZnDTP solution at 150°C. Higher wear was noted where higher loads were applied while at low loads minimal wear was found. There were no significant differences within the 4 cycles with the same tribological conditions. For 10 N load, the dimensional wear coefficient $k (k=V/L\cdot l; \text{wear volume } V \text{ divided by the applied load } L \text{ and the sliding distance } l)$ was with 0.0008-0.0009 mm$^3$/Nm the highest at the lowest sliding speed. At higher sliding speeds, wear...
Results: Wear Test

Figure 3.79: Wear rate in dependence on the angular position of the disc. The sample was tribostressed with a steel ball with oscillating load (see scheme on the bottom of the plot) at 150°C in ZnDTP solution. The sliding speeds ranged from 10 mm/min (black) to 1000 mm/min (light grey).

Coefficients between 0.0004 and 0.0005 mm³/Nm were obtained, whereas there was a tendency towards lower wear at higher sliding speeds.

Load Dependence

For calculating the mean dimensional wear coefficient $k$ of several independent measurements (see Figure 3.80 top), the profiles of the four cycles were averaged, the wear rates of the sliding speeds of the experiments from 25 to 158 mm/min averaged and divided by the applied load. These sliding speeds were chosen because similar friction and wear was obtained at these speeds. In this way the noise observed in Figure 3.79 could be minimized and the load dependence be compared for different tribopairs and temperatures.

The highest wear was observed for steel-steel contacts at 150°C, whereas the dimensional wear coefficients were higher at low loads. Changing to room temperature, less wear was observed on a constant level for all loads. Only little wear was observed for the ceramic-steel contact at both temperatures, whereas the coefficient dropped to few $10^{-5}$ mm³/Nm at low loads. The additives helped to reduce wear in the case of the steel-steel contact at 150°C by about 50% compared to the pure oil. For the ceramic-steel contact at room temperature and 150°C and for the steel-steel contact at room temperature, no significant effect of the additives was observed.
Dimensional Wear Coefficient $k$

<table>
<thead>
<tr>
<th></th>
<th>Pure Oil</th>
<th>ZnDTP</th>
<th>b-TPPT</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>25°C</strong></td>
<td>$25 \times 10^{-4}$</td>
<td>$25 \times 10^{-4}$</td>
<td>$25 \times 10^{-4}$</td>
</tr>
<tr>
<td><strong>150°C</strong></td>
<td>$20 \times 10^{-4}$</td>
<td>$15 \times 10^{-4}$</td>
<td>$10 \times 10^{-4}$</td>
</tr>
<tr>
<td><strong>20°C</strong></td>
<td>$15 \times 10^{-4}$</td>
<td>$10 \times 10^{-4}$</td>
<td>$5 \times 10^{-4}$</td>
</tr>
<tr>
<td><strong>5°C</strong></td>
<td>$10 \times 10^{-4}$</td>
<td>$5 \times 10^{-4}$</td>
<td>$2 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

**Figure 3.80:** Dimensional wear coefficient $k$ vs. increasing load, averaged for sliding speeds ranging from 25 to 158 mm/min (top) and $k$ vs. sliding speed for 10 N load (bottom).

**Dependence on Sliding Speed**

For the steel-steel contacts, wear decreased with higher sliding speeds while no significant speed dependence was found for the ceramic-steel contact (see Figure 3.80 bottom). Higher wear coefficients were found for the steel-steel tribopairs at all speeds. The additives had a wear-reducing effect at all sliding speeds on the steel-steel contact at 150°C, while for the other conditions no significant effect of the additives was observed.

**Deposited Material**

From the wear profiles (see Figure 3.78 right) the amount of deposited material and the deposition rate was determined. The deposition rates vs. load and vs. sliding speed are shown in Figure 3.81. The deposition rate is highest for steel-steel contacts at 150°C, it decreases with the use of additives and it is lowest for ceramic-steel contacts. A general feature is that the maximum of deposition rate is found after the 10N load maximum had been reached, i.e. in the areas of the scar where the applied load was decreasing. This implies that
material is moved or carried with the ball and deposited later. This effect was very pronounced for the steel-steel contact and less marked, but still present, for the ceramic-steel contact.

There are two contributions to the deposited material found on the side of the wear tracks: material that had been plastically pressed out of the contact, and material that had been deposited on the side of the tribological contact but was not washed away during the cleaning of the disc after the experiment.

The deposition coefficients (see Figure 3.81 bottom) were 49±12% of the wear coefficients, whereas the lowest percentage was observed with the steel-steel contact at 150°C with 41±13%. No significant change in the percentage was observed with different sliding speeds or tribopairs, but there was more material deposited using the pure oil (53±10%) compared to the solutions containing the anti-wear additives (ZnDTP: 47±12%, b-TPPT: 46±12%).

**Deposition Rate**

<table>
<thead>
<tr>
<th>Pure Oil</th>
<th>ZnDTP</th>
<th>b-TPPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increasing</td>
<td>Decreasing</td>
<td>Increasing</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Load [N]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.002</td>
</tr>
<tr>
<td>0.004</td>
</tr>
<tr>
<td>0.006</td>
</tr>
<tr>
<td>0.008</td>
</tr>
</tbody>
</table>

**Deposition Coefficient for 10 N Load**

<table>
<thead>
<tr>
<th>Pure Oil</th>
<th>ZnDTP</th>
<th>b-TPPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sliding Speed [mm/min]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>6</td>
<td>8</td>
<td>10</td>
</tr>
</tbody>
</table>

| Steel-Steel | 25°C | 150°C |
| Ceramic-Steel | 25°C | 150°C |

**Figure 3.81:** Deposition rate vs. increasing and decreasing load, averaged for the sliding speeds ranging from 25 to 158 mm/min (top). Deposition coefficient vs. sliding speed (bottom).
In this chapter the tribological tests applied in this work are compared and the tribological contacts discussed. In a second part, the effects of temperature and contact pressure on the anti-wear films are analysed. Then the wear obtained under the different conditions is discussed, followed by proposals for the film-formation mechanism for both ZnDTP and the ashless phosphorothionates. In the last section, the surface analysis with XPS and the modelling are discussed.
4.1 Influence of the Type of Tribological Test

The tribological conditions in a practical situation, such as those in an engine, vary because of the influence of many parameters, such as the contact pressure, the temperature, the duration of the contact, the sliding speed and many other factors. Thus, ideally, the tribological test should be carried out in the motor/engine itself.

Numerous laboratory tests have been developed in order to separate the influence of the different parameters, with the aim of gaining an insight into the mechanism of reaction of the lubricant additives, of wear protection and of friction reduction. This has resulted in a plethora of information and scientific evidence that is sometimes difficult to compare and rationalize.

Starting from the theory of the tribological contact, parameters such as the duration of the mechanical test and the sliding speed are considered in the following. An attempt is made to compare different tribotests with respect to coefficient of friction, dimensional wear coefficient and tribofilm formation.

The Tribological Contact

At the beginning of the running-in of a ball-on-disc experiment, an unworn round ball slides on a flat disc. For this situation, the contact pressure can be calculated using the Hertzian theory where the radius $R$ of the contact area due to elastic deformation is [1]:

$$ R = \sqrt[3]{\frac{3L} {4E}} $$  

Equation 4.1

$L$ is the load, $r$ the radius of the ball and $E$ the combined elastic modulus, which is calculated as

$$ \frac{1}{E} = \frac{(1-v_1^2)}{E_1} + \frac{(1-v_2^2)}{E_2} $$  

Equation 4.2

where $E_1$ and $E_2$ are the Young's moduli of the two materials and $v_1$ and $v_2$ the corresponding Poisson's numbers. With the resulting radius $R$, the average contact pressure $p_{av}$ and the maximum pressure $p_{max} = 3/2p_{av}$ can be calculated [1]. For a ball with a radius of 2 mm and both tribopartners made of steel with a
Table 4.1: Hertzian contact radius \( R \) and the average and maximum contact pressures in dependence on the applied loads for a ball-on-flat configuration using \( r = 2 \text{ mm}, E_1 = E_2 = 210 \text{ GPa} \) and \( v_1 = v_2 = 0.3 \).

<table>
<thead>
<tr>
<th>Load [N]</th>
<th>( R ) [( \mu \text{m} )]</th>
<th>( p_{av} ) [MPa]</th>
<th>( p_{\text{max}} ) [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>51</td>
<td>1240</td>
<td>1861</td>
</tr>
<tr>
<td>5</td>
<td>40</td>
<td>984</td>
<td>1477</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>725</td>
<td>1088</td>
</tr>
<tr>
<td>1</td>
<td>24</td>
<td>576</td>
<td>864</td>
</tr>
<tr>
<td>0.5</td>
<td>19</td>
<td>457</td>
<td>685</td>
</tr>
<tr>
<td>0.2</td>
<td>14</td>
<td>337</td>
<td>505</td>
</tr>
</tbody>
</table>

Young’s modulus of 210 GPa and \( v=0.3 \), very high contact pressures in the gigapascal range are obtained (see Table 4.1).

During the running-in and the following tribotest, both the ball and the disc are worn and the contact geometry changes. On the worn ball a relatively flat area is produced, as determined with laser profilometry (e.g. Figure 3.44). With optical microscopy, the tribostressed area on the ball was measured and thus the average contact pressure could be calculated, as presented for balls tribostressed with the oscillating-load test in various solutions (see Table 4.2).

For the oscillating-load test in ZnDTP solutions, the contact pressure at the end of the experiment ranged from 500 MPa at 10 N load to 25 MPa at 0.5 N load. Compared to the Hertzian contact, this was less than half for 10 N load and almost 20 times less for 0.5 N load. For the pure oil and the phosphorothionates, the wear experienced on the ball was larger, which results in contact pressures of around 200 MPa for 10 N load and 10 MPa for 0.5 N load.

Table 4.2: The radius of the tribostressed region on the ball for combinatorial oscillating-load tests and the corresponding wear rate and average contact pressures (for 10 N and 0.5 N load).

<table>
<thead>
<tr>
<th>T [°C]</th>
<th>Radius [( \mu \text{m} )]</th>
<th>Wear Coefficient ( k ) [mm³/Nm]</th>
<th>( p_{av}(10 \text{ N}) ) [MPa]</th>
<th>( p_{av}(0.5 \text{ N}) ) [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Oil</td>
<td>30</td>
<td>78±4</td>
<td>3±1( \times )10⁻⁸</td>
<td>517±54</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>94±5</td>
<td>6±1( \times )10⁻⁸</td>
<td>361±38</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>116±6</td>
<td>14±3( \times )10⁻⁸</td>
<td>239±25</td>
</tr>
<tr>
<td>ZnDTP</td>
<td>30</td>
<td>81±9</td>
<td>3±1( \times )10⁻⁸</td>
<td>505±146</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>79±1</td>
<td>3±3( \times )10⁻⁸</td>
<td>505±16</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>76±2</td>
<td>3±0( \times )10⁻⁸</td>
<td>546±29</td>
</tr>
<tr>
<td>TPPT</td>
<td>30</td>
<td>161±12</td>
<td>52±15( \times )10⁻⁸</td>
<td>124±19</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>108±8</td>
<td>10±3( \times )10⁻⁸</td>
<td>274±41</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>157±12</td>
<td>45±12( \times )10⁻⁸</td>
<td>129±19</td>
</tr>
<tr>
<td>b-TPPT</td>
<td>30</td>
<td>109±5</td>
<td>11±2( \times )10⁻⁸</td>
<td>266±23</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>97±4</td>
<td>7±1( \times )10⁻⁸</td>
<td>338±29</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>140±6</td>
<td>29±5( \times )10⁻⁸</td>
<td>164±14</td>
</tr>
<tr>
<td>n-TPPT</td>
<td>30</td>
<td>113±1</td>
<td>12±1( \times )10⁻⁸</td>
<td>251±5</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>111±1</td>
<td>11±1( \times )10⁻⁸</td>
<td>258±5</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>176±2</td>
<td>71±3( \times )10⁻⁸</td>
<td>103±2</td>
</tr>
</tbody>
</table>
The discrepancy from the contact pressures calculated from the worn area of the ball with the Hertzian theory supports the assertion that the measure of the real contact area to calculate the contact pressure provides more reliable results in the case of worn samples.

**Duration of Tribological Test**

In this work, both the step test and the wear test with 11 x 5 turns and 80 turns respectively were very-short-time experiments in comparison to real applications with service lifetimes in engines of more than 2000 hours, and thus rather represent the processes such as the initial stages of film formation [1]. With the oscillating-load test, 1000 turns were performed during 95 minutes under severe conditions. Thus the tribological film was removed and reformed continuously [1, 10] and therefore the films observed in these experiments rather represent the ongoing film formation in the presence of a fresh lubricant with excess concentration of unreacted anti-wear additives.

**Effect of the Sliding Speed**

As was demonstrated by Matsumoto [54] or Taylor et al. [76], the sliding speed plays an important role in friction and wear, since with higher sliding speed hydrodynamic effects become more important and the conditions change from boundary lubrication to the mixed or even the hydrodynamic lubrication regime.

In the step test and the oscillating-load test the sliding speeds were 0.0005 and 0.005 m/s respectively. This was below the 0.01 m/s where Taylor et al. started to observe hydrodynamic effects. Also the high friction and wear suggest that very severe conditions were present, which can only be the case in the boundary-lubrication regime. In agreement with this, lower friction and wear was observed for non-hardened steel with the wear test above 400 mm/min (=0.0067 m/s) compared to lower sliding speeds in the same test.

**Reproducibility**

A large set of parameters determines the results of tribological experiments and thus their reproducibility. For example, two experiments performed with the oscillating-load test in ZnDTP solution at room temperature showed very severe wear that was about ten times higher than usual. Correspondingly, the friction coefficients were 50% higher than normal and surface analysis revealed only very thin tribofilms. Although the experiment was repeated six times, the scuff-
ing experienced in these two experiments could not be reproduced and it was decided that these two experiments are outliers. This example shows that in tribology small changes in conditions, which might not even be noticed, can affect the results drastically. Therefore the experiments have to be conducted very carefully and the experimental conditions should be controlled as well as possible, especially if experiments at different conditions are compared afterwards.

4.1.1 Comparison of the different Tribological Tests

In this work, tribotests were performed with the combinatorial step test, the combinatorial oscillating-load test and the wear test. The step test, introduced by Eglin et al. [3, 4, 7], allows the comparison of different conditions on one disc. Nevertheless, there was a disadvantage that only a short time of tribostress per annulus was possible because multiple annuli had to be tribostressed in order to produce a tribostressed region large enough for XPS analysis with the PHI 5700, with an area of analysis of 120 μm in diameter. After a region was tribostressed, it was exposed to the lubricant while other regions were tribostressed with different conditions. This may lead to a modification of the tribofilm by thermal reactions, as demonstrated for b-TPPT at 150°C (see Table 3.3). The new generation of XPS spectrometers is able to focus the beam down to few micrometers and thus single wear tracks can be analysed. This allowed a modification of the combinatorial test: in order to minimize thermal reactions on the tribotrack, only one annulus was tribostressed with an oscillating load.

With the wear test, oscillating loads were tested on a single annulus while different sliding speeds were tested on different annuli [104]. Similar tests were performed by Spori and Eglin with different numbers of turns on different annuli to investigate the wear dependence on sliding time and load for pure oil and an oil blended with ZnDTP [7, 104]. Tests with different conditions in different annuli are ideal for expanding the parameter library for the case where no chemical surface analysis is performed and thus thermal redeposition on tribofilms is not critical.

Friction Coefficient

The friction coefficients measured with the oscillating-load test were in excellent agreement with the step tests, where constant loads were applied at similar
temperatures (compare Figure 3.2 with Figure 3.29 for ZnDTP solutions or Figure 3.11 with Figure 3.56 for b-TPPT solutions). In the case of the wear tests using the non-hardened steels it is difficult to directly compare the friction coefficients, but similar friction coefficients up to 0.6 were obtained with the oscillating-load tests performed by Spori and Eglin (compare Figure 3.76 with [7, 104]). According to Hutchings [1], such high friction is experienced in lubricated systems only if very severe conditions are present, so that no lubricant film is present to prevent steel-steel contact.

Wear

The dimensional wear coefficients $k$ obtained with the hardened steel samples stressed with the oscillating-load test were between 1 and $4 \times 10^{-6}$ mm$^3$/Nm (see Figure 3.31), which correspond to severe wear. According to Hutchings, fluid-film effects are negligible for lubricated wear of metals in the boundary-lubrication regime and the wear coefficients $k$ are between $10^{-8}$ and $10^{-6}$ mm$^3$/Nm [1]. There are two reasons for these severe conditions in these experiments: First, the sliding speeds are very low and second, the contact areas are small, resulting in a high average contact pressure up to 500 MPa with relatively low applied loads (see Table 4.2). Applying these high pressures at low sliding speeds, the lubricant is squeezed out of the contact area and no elasto-hydrodynamic lubrication takes place, resulting in high friction and severe wear.

The wear rates obtained with the non-hardened steel discs and balls of the wear test were higher than $10^{-4}$ mm$^3$/Nm (see Figure 3.80). This is at least 2 orders of magnitude higher than using the hardened steel discs and balls (see Figure 3.21, Figure 3.31 and Figure 3.57). According to Hutchings the term scuffing is used to describe such severe conditions resulting in wear coefficients $k$ being higher than $10^{-5}$ mm$^3$/Nm [1]. Similar observations with scuffing of non-hardened steel were obtained by Sheasby et al. [139] and Akagaki and Kato [140]. Sheasby et al. observed scuffing in four-ball tribotests for bearing balls with hardness values below 450 HV at 100°C at high sliding speeds in pure oil and in ZnDTP solution. They actually obtained higher wear when all 4 balls were softened compared to the experiment where the rotating ball was hard [139]. Akagaki and Kato found severe flow wear at low contact pressures on carbon steels with hardness values of 133 HV ($k=10^{-6}$-10$^{-5}$ mm$^3$/Nm; $\mu=0.2-0.3$), adhesive wear for higher contact pressures ($k=4 \times 10^{-5}$-3$\times 10^{-4}$ mm$^3$/Nm; estimated $\mu=0.8$-1.2) while for hardened discs (730 HV), they obtained oxidative wear with low wear rates ($k \sim 10^{-9}$ mm$^3$/Nm) [140].
Severe conditions were present with the combinatorial oscillating-load test and presumably with the combinatorial step test. Even more severe conditions were found in the wear test, resulting in scuffing, which in real applications would lead to the immediate failure of the machine.

**Tribofilm Formation**

In the non-contact areas treated in ZnDTP solution, similar film thicknesses were obtained with both the oscillating-load test and the step test. In contrast, thicker tribofilms were formed with the oscillating-load tests than with the step tests (see Figure 3.10 and Figure 3.40). For example when applying a load of 5 N in ZnDTP solution at 25-30°C, 4±1 nm thick reaction layers were formed with the oscillating-load test and 0.5 nm thick films with the step test only. Also at 150°C thicker films were obtained with the oscillating-load test with 5.7±0.5 nm in contrast to 2 nm with the step test. This is likely due to the duration of the tribostress, which was 5 turns per annulus for the step test and 1000 turns for the oscillating-load test. For samples tribostressed in ZnDTP solution, short-chain poly(thio)phosphate with 2-7 phosphate units were found at all temperatures on the tribotacks (Figure 3.9 and Figure 3.41), which corresponds to results obtained with constant loads and is in agreement with the proposals made in the literature [44, 51, 82]. At 150°C, the thermal film was composed of long chain poly(thio)phosphates, in agreement with the step tests and [25].

In case of the butylated phosphorothionate experiments performed at 150°C, similar thicknesses and compositions of both the tribostressed area and the non-contact areas were obtained with the step test while with the oscillating-load test, the non-contact areas were similar to those observed in the step test, but the tribofilms were much thinner and contained more phosphates (see Figure 3.15 and Figure 3.64). These results suggest that with the tribostress of the step test the thermal film was modified, and later probably covered with a thermal film, as another area was tribostressed. This was also demonstrated in Table 3.3, where the thickness and composition changed for the sequence of three equally tribostressed areas due to thermal film formation on the tribotrack. This is not the case for the combinatorial oscillating load samples, where the thermal film was worn away and only one tribotrack is produced and investigated. Thus the sample can be taken out of the solution immediately after the tribostress has finished.

A possible drawback of the combinatorial oscillating-load test is that part of the film formed at high contact pressure might be transferred to areas at low
contact pressures [49, 50]. But no evidence for a possible transfer film was found and the results are in agreement with results obtained with the step test.

**ZnDTP tribofilms**

The films observed in these studies were 10-30 times thinner than films described by other groups [42, 44, 76] but are in agreement with short-time experiments with reduced frequency of 5 Hz of Yin et al. where they estimated a tribofilm thickness between 2 and 5 nm [51]. The reason for this is most likely the much lower sliding speed of 31 mm/min = 0.0005 m/s applied in the step test or the 0.005 m/s applied in the oscillating-load test, compared to the ~0.1 m/s of Martin et al. [71, 82] or ~0.35 m/s of Kasrai et al. [51, 141]. According to Taylor et al. under similar tribological conditions, mixed lubrication begins at 0.01 m/s [76]. The speeds in this work were chosen to place the tribological test squarely within the boundary-lubrication regime.

Another reason could be the different cleaning procedure: while the samples in this work were cleaned ultrasonically in ethanol, Martin et al. rinsed them with hexane and propanol and Taylor et al. measured thicknesses in situ. Loosely bound phosphate compounds may have been washed away from the samples during ultrasonication, while other groups were measuring this layer as well.

**Phosphorothionate Tribofilms**

In the tribofilms studied in this work, mixtures of polyphosphates with sulphates were formed, in some cases containing sulphides (see Tables 3.6-3.8). This is in agreement with Najman et al., who found short-chain iron(II)polyphosphates together with iron sulphides, iron sulphates and intermediate oxidative species in tribofilms produced in TPPT solution (called MTP in their work) [34]. With longer rubbing times, they observed an increase in the sulphate concentration, finally having “comparable amounts” of phosphorus and sulphur homogenously distributed in the layer [34].

On many samples in this work, the content of iron was lower than expected when balancing the number of anions and cations. There are several possible explanations for this fact. First, at 150°C long chains are supposed to be formed as indicated by the higher binding energy of 133.6±0.1 eV compared with lower temperatures (133.3±0.1 eV), which have less charges per phosphorus atom (see Table 1.2). Second, hydrocarbon chains might still be present on part of the oxygen atoms of the poly(thio)phosphate and thus these oxygen atoms are neutral. This is supported by the presence of the high-binding-energy peak at 286.5 eV in the carbon spectra and the binding energy of the P-O-C oxygen,
Discussion

which is at 533.5 eV (see Table 7.9) and thus contributing to the BO peak. A third possibility is the adsorption of the charged phosphate on the metal hydroxide surface under the release of water as suggested by Textor et al. for the adsorption of octadecylphosphoric acid on tantalum oxide surfaces [122].

The film thicknesses in this work (see Figure 3.54, Figure 3.64 and Figure 3.74) are about ten times smaller than those of Najman et al. determined with XANES [34]. This could be because in this work much slower sliding speeds were applied than Najman’s sliding speed of 0.35 m/s, which was probably in the elasto-hydrodynamic lubrication regime.

In comparison with ZnDTP, where zinc is present in the molecule, no cations are present in the phosphorothionates. Therefore there is a limited availability of counterions for the phosphate films formed in presence of the phosphorothionates and thus thinner films are obtained compared to films produced in presence of ZnDTP.
4.2 Influence of Temperature

The temperature of the oil bath has a significant influence on the film formation of both the non-contact (thermal) films and the tribofilms. The effect of temperature was particularly studied with the step test while with the oscillating-load test, experiments were performed at 30, 80 and 150°C and with the wear test at 25 and 150°C only. Usually both the friction and the wear coefficient increased with higher temperature (see chapter 3).

4.2.1 Thermal Films

For the samples tribostressed in pure oil, the oxygen-to-iron ratio (see Figure 3.26) increased with higher temperature due to ongoing oxidation with dissolved oxygen in the lubricant, resulting in iron oxy-hydroxides. In contrast, the oxygen-to-iron ratio decreased with higher temperature for samples stressed in oils containing anti-wear additives: At temperatures below 110°C, the oxygen-to-iron ratios higher than 2:1 suggest the presence of iron oxy-hydroxide layers. With higher temperatures the ratio decreases due to a thermally induced dehydration, resulting in a substrate covered with an iron oxide layer with a stoichiometry resembling Fe₃O₄.

ZnDTP

The thermal reaction layer formed in the non-contact areas became thicker with increasing temperature, starting from 0.4 nm at room temperature up to more than 6 nm above 150°C (see Figure 3.15 and Figure 3.40). The reaction layer at room temperature in the non-contact areas consists of adsorbed dialkyldithiophosphate and zinc oxide species on the iron oxy-hydroxide. The change in the binding energy of sulphur from 162.6 eV in the ZnDTP molecule [68] to 162.1 eV in the surface film support this mechanism. Increasing the temperature to 60°C led to reactions on the surface resulting in small amounts of zinc orthophosphates. At intermediate temperatures (80-110°C), thicker reaction layers of a mixture of zinc oxide with sulphide, sulphates and phosphates were formed. The reaction layers at high temperatures (130-150°C) consisted of a mixture of zinc polyphosphates, zinc sulphates, zinc sulphides, thiols and...
sulphur substituting oxygen in the polyphosphates. The average chain length at 130°C is 2.5, while at 150°C short chains of 3 units up to very long chains were formed (see Figure 3.9 and Figure 3.41). This is in agreement with Piras et al., who found almost no thermal film formation below 80°C and thicker thermal layers containing bridging oxygen at 150°C by means of attenuated total reflection infrared spectroscopy [46, 68, 101], and with other authors [25, 32]. The temperature of about 150°C seems to be quite critical with respect to the resulting chain length. Probably a few degrees difference (accuracy of the oil bath temperature was ±3°C) can cause a significant difference in the chain length of the polyphosphate. At 180°C, the thermal films mainly consisted of a cross-linked zinc polyphosphate as indicated both by the elemental composition and the BO/NBO ratio, which was higher than 0.5. The high-binding-energy peak at 535 eV could then be due to oxygen linking adjacent polyphosphate chains together; similar binding energies of 534.4±0.2 eV were found by Piras et al. [68] for samples heated in ZnDTP solution at 150°C for 126 hours.

**Ball**

The non-contact areas on the ball 0.5 mm in front and behind the tribostressed region were essentially similar in thickness and composition as the non-contact areas on the disc, thus indicating that the thermal film was not affected because of the tribological contact half a millimetre away.

On the ball tribostressed at 80°C, there was a tail behind the tribostressed region composed mainly of zinc sulphides (see Figure 3.35 and Table 3.5). Upon frictional heating, reactive sulphur compounds are probably produced, which then react with zinc to form zinc sulphide and deposit behind the tribological contact. These products are to be found on the ball because they are always collected on the same area during the entire experiment but are thinly distributed over the entire disc. At 30°C no deposited material was found and at 150°C, a thicker deposit behind the tribological contact than in the non-contact area was formed with the same composition as the non-contact film. Thus at 150°C, more reactive species were present in the vicinity of the tribological contact, leading to the thicker film.

**Phosphorothionates**

The size of a phosphate group is about 3 Ångstroms (P-NBO bond is 1.5 Å and P-BO bond 1.6 Å [65, 125, 142]). This is assumed to be the thickness of a monolayer of reaction products forming the so-called reaction layer. For the thermal films formed below 100°C in the presence of phosphorothionates, the
thickness of the reaction layers could usually not be determined because only fractions of a monolayer were present and thus the reaction layer could not be treated as a separate layer applying the multi-layer model. Therefore the multi-layer model was modified assuming that the reaction products were part of the organic layer and the thicknesses and compositions were calculated under this assumption.

The films below 100°C were mainly composed of carbon with minor amounts of sulphates together with traces of sulphones and phosphates. Weak interactions were also reported by Rossi et al. for adsorbed tributyl thiophosphate at 80°C with the formation of mainly sulphates, but already at 100°C the molecule was activated and reacted with the iron hydroxide substrate to form sulphates and polyphosphates [53].

At 125°C a reaction layer thickness of 3 Ångstroms was found (see Figure 3.15), which allows a full coverage of the surface by adsorbed molecules. Above 150°C the phosphorothionates were thermally decomposed, as described by Gao et al. and Gellman et al. for similar molecules [30-32], resulting in thicker reaction layers of about 3 nm. In addition, the higher temperature favours the oxidation of the sulphide, resulting in higher sulphate concentrations with $S(\text{VI}):S(\text{II}):P = 1.5:0:1$ (see Table 3.2). This is in agreement with Najman et al. who found thick thermal layers at 150°C, composed mainly of iron phosphate with iron sulphate, together with some adsorbed additive molecules [34]. At 150°C, the temperature of the solution was high enough to thermally decompose the molecule in solution, likely by a scission of the P-O bond, as described by Gao et al., for the thermal decomposition of tributyl phosphate in the presence of iron oxide [31]. The resulting phosphoryl groups link then together to form thick thermal layers with similar thicknesses for the different additives.

**Additive’s Chain Length Effect**

For all types of phosphorothionates only fractions of a monolayer were obtained at 30 and 80°C (see Figure 3.54, Figure 3.64 and Figure 3.74). At 150°C thicker films of about 3 nm were found for all TPPTs. The composition of the reaction layer depended on the chain length: with longer chains the phosphate concentration decreased while the sulphur concentration increased (see Table 3.6, Table 3.7 and Table 3.8).
4.2.2 Tribofilms

Correlation between Friction, Wear and Reaction Layer Thickness

Figure 4.1 shows the correlation between friction, wear and the reaction layer thickness for spots tribostressed at different temperatures with 10 N load. Both the friction coefficient and the wear coefficient decrease with higher reaction layer thickness, indicating that thicker anti-wear films are effective in reducing friction and wear. At 150°C high friction was observed for both ZnDTP and the phosphorothionates, in the case of the ZnDTP although thick anti-wear films were present. On the samples tribostressed at 30°C in ZnDTP, there were two outliers where high friction and wear was observed in combination with only very thin and not effective anti-wear films; the reason for these outliers is still not clear.

![Figure 4.1: Correlation between friction coefficient (left), dimensional wear coefficient $k$ (right) and reaction layer thickness for 10 N load.](image-url)

ZnDTP

Tribofilms from Combinatorial Step Tests

The effect of tribological stress depends on the temperature at which the film formation has occurred: Below 100°C the frictional heat initiates the formation of the reaction layer, the tribological films being thicker than the thermal films (see Figure 3.10). At temperatures above 130°C, the thermal decomposition of
Discussion

ZnDTP results in thick reaction layers on the surfaces. In these cases the tribological stress reduces the thickness of the tribofilms.

At room temperature, a tribofilm consisting of zinc orthophosphate $\text{Zn}_3(\text{PO}_4)_2$, zinc sulphate, zinc oxide, zinc/iron sulphide and thiols is formed. The formation of zinc orthophosphate is indicated by the binding energy of phosphorus, which corresponds to the 133.4 eV found for zinc orthophosphate [66] and is in agreement with Eglin et al. [3]. At 60°C similar films grow as at room temperature but with higher amounts of zinc orthophosphate.

At intermediate temperatures (90-110°C) thicker reaction layers of 2.0±0.3 nm were formed. They were mainly composed of zinc phosphates together with zinc oxide and sulphur in both oxidation states. The presence of ortho- ($\text{Zn}_3(\text{PO}_4)_2$) up to short-chain polyphosphates ($\text{Zn}_2\text{P}_2\text{O}_7$) was determined by the ratio of bridging to non-bridging oxygen, which was around 0.2 (see Figure 3.9 left), and the binding energy of phosphorus. The binding energy of phosphorus was between the reference compounds zinc orthophosphate (133.4 eV [66]) and zinc pyrophosphate (133.9 eV [70]) and similar to the binding energy of iron phosphate (FePO$_4$: 133.7 eV [4, 70]). This mixture of ortho-, pyro- and polyphosphates with its average chain length between 1 and 3 is in agreement with Minfray et al. [82] and Yin et al. [51], who both found a mixture of iron/zinc ortho- and pyrophosphates in the bulk of tribofilms produced at 80°C and 100°C, respectively. Longer chain lengths of 4-10 units were determined by Martin et al. at 80°C using XANES [44].

The tribofilms at high temperatures (130-150°C) consist of a mixture of short-chain zinc polyphosphates with sulphur in both oxidation states, whereas less sulphur was detected than in the non-contact area. In addition, iron with a binding energy of 713.5 eV was found, supporting the presence of iron phosphate. Piras et al. found that iron needs to be present for a phosphate film formation at 150°C in presence of ZnDTP [46, 101]. The iron promotes a depolymerisation of the long chains leading to short-chain zinc and iron polyphosphates. The chain length at 130°C was between 2 and 3, while at 150°C it is 3, with increasing chain length towards the outer part of the film (see Figure 3.9 right). Longer chains in the outer part of the films were also found by Martin’s group at 80°C [44, 82] and by Yin et al. at 100°C [51] using XPS in combination with argon sputtering and other techniques. In the tribofilms formed at 150°C, a reduced sulphide content was found while more sulphates were present. This is likely due to a temperature-induced oxidation of the tribofilm [32].

At 180°C, cross-linked zinc polyphosphates with small amounts of iron pyrophosphate were formed. This explains the two components found in the phos-
phorus signal (figure 8), where the high-binding-energy peak (135.3±0.2 eV) corresponds to cross-linked polyphosphate, while the low-binding-energy peak (133.8±0.1 eV) belongs to the iron pyrophosphate. For comparison, linear, non-crosslinked chains of metaphosphate show a binding energy of 135.0 eV [70]. Some minor contributions from sulphates, zinc oxide, thiols and sulphur substituting oxygen in the phosphate were also detected.

**Tribofilms from Combinatorial Oscillating-Load Tests**

The dimensional wear coefficients for the oscillating-load tests were in the range of 1-4·10⁻⁶ mm³/Nm (see Figure 4.2), which corresponds to severe wear [1, 10]. Under these conditions the initial thermal film is removed during the mechanical test and a tribofilm is formed and continuously removed [1, 10]. This experimental setup may allow us not only to gain an insight into the changes induced by the mechanical stress as was the case in the step test (short-time test), but also to determine the composition of the tribofilm grown under an applied pressure at a given temperature.

In the tribostressed areas, the average thickness of the reaction layer increased with higher temperatures. As seen with the thermal film formation, which was higher at higher temperatures, the external temperature supports the film formation and leads, together with the frictional heat and the shear forces of the tribological stress, to the formation of thicker films. Much thicker tribofilms (4±1 nm) were formed with the oscillating-load tests at 30°C compared to the step tests, and they consisted of short-chain poly(thio)phosphates (2-3 units) with small amounts of sulphur (II), likely due to sulphur substituting oxygen in the poly(thio)phosphate. Iron phosphate was found in the reaction layer, which is an indication that nascent iron, exposed because of wear, reacts with the phosphoryl groups and supports the tribofilm formation. Another mechanism could be that iron oxide particles from the wear process react with zinc phosphates to form zinc oxide and iron phosphate according to the HSAB theory [72, 73]. The tribofilms produced with the oscillating-load test at 80°C were similar to the tribofilms at 30°C, but the chains were longer (4-6 units) compared to 30°C and in agreement with Martin et al. [44]. At 150°C, similar films compositions were obtained to those observed at lower temperatures, but with a reduced sulphur (II) and higher sulphate content, likely due to a temperature-induced oxidation process [32]. At this temperature, the thickness and composition was similar to the films produced with the step tests.
Phosphorothionates

With the step test in the presence of b-TPPT, fractions of a monolayer were adsorbed on the tribologically stressed areas below 100°C, a full coverage being reached at 125°C with a thickness of 0.3 nm and thicker films of about 3 nm being formed only above 150°C (see Figure 3.15). At higher temperatures the concentration of phosphates increased (Table 3.2). Below 125°C the concentration of sulphides increased with temperature while the sulphate concentration decreased. Above 150°C, sulphur was oxidized, resulting in a higher sulphate concentration.

With the oscillating-load test, thicker tribofilms, ranging from fractions of a monolayer up to 1.3 nm were formed at low temperatures (see section 3.2.2), likely due to the longer time of tribostress at the lower temperature. At 150°C thinner films of about 1 nm thickness were present on the tribotrack because of the removal of the thermal film with wear instead of a modification of the thermal film, as probably occurs with the step test. The tribofilm mainly consisted of phosphates with small amounts of sulphides and sulphates at 30° and 80°C. As observed with the step test, at 150°C no sulphides but more sulphates were obtained.
4.3 Influence of Pressure

The composition of the oxide layer changed with the applied contact pressure. On a disc tribostressed at higher pressure in pure oil, more hydroxides were observed (see Figure 3.26). This correlated with the decreasing content of oxygen-containing species in the organic layer with contact pressure. While the thermal energy of the applied temperature seems to favour the reaction of oxygen with iron oxide to form iron hydroxides, this was supported with the frictional heat and mixing effects of the tribostress.

In contrast to the experiments in pure oil, the oxide films tribostressed in the presence of anti-wear additives did not change the composition with the applied contact pressure.

ZnDTP Tribofilms

Different loads were investigated with both the step test and the oscillating-load test, while a larger range of contact pressures was covered with the oscillating-load test and not only friction and the surface composition but also wear were measured. In addition, thermal redeposition on the tribofilms can be excluded for the oscillating-load test while it cannot for the step test. Therefore this section focuses on the results obtained with the oscillating-load tests.

It is difficult to compare the applied loads of different studies because often only the load is given but neither the contact pressure nor the contact area are reported. With the applied loads of 0.5 to 10 N in the oscillating-load tests in ZnDTP solution, average contact pressures in the range of 25 to 500 MPa were probed (see Table 4.2).

With higher contact pressure of the oscillating-load test, lower friction and dimensional wear coefficients were obtained while with the step tests no clear load dependence of the friction coefficient was found. Only little data were found in the literature to compare the friction coefficient in a ZnDTP solution at different loads. At 150°C and 0.1 N load, Eglin obtained a higher friction coefficient of about 0.27±0.3 while with loads of 1 and 5 N the friction coefficients were 0.19±0.1 [7]. Ji et al. observed higher friction coefficients at higher loads with sliding speeds between 0.2 and 0.6 m/s [143]. It is very likely that these measurements were performed in the elasto-hydrodynamic lubrication regime.
At higher contact pressures, shorter poly(thio)phosphate chains were formed with correspondingly less sulphur. Only at 0.5 N load (150°C) were shorter chains found than at higher contact pressures. An explanation might be that on the thick tribofilms formed under high contact pressure, only the outer part with usually longer chains [44, 51, 71, 82] was probed while at 0.5 N load the entire film, including the shorter chains at the bottom, were probed. Less sulphur with higher contact pressure was also found by both Yin et al. and Eglin et al. [4, 5, 51], while Yin found longer chain lengths with higher contact pressure at much higher sliding speed (0.35 m/s) at 100°C [51], probably because the authors were operating in a different lubrication regime at these speeds. According to nanoindentation measurements, the hardness of the tribofilm correlates with the applied contact pressure [39, 42]. Therefore a softer viscous film of longer chains might be present at lower contact pressures, which would explain the incrementally higher friction coefficient observed at lower contact pressures. High contact pressures cause more frictional heating, therefore thicker films were formed on these areas. Together with the increased hardness at higher contact pressures, thicker and tougher films [144] of shorter polyphosphates were formed, which were more robust against shear forces, resulting in lower dimensional wear coefficients (see Figure 3.30).

ZnDTP Reactivity: Ball vs. Disc

During a ball-on-disc experiment, the ball is under permanent tribostress while a single spot in the centre of the tribotrack is stressed for about 40 milliseconds every 6.3 seconds. Despite the different rubbing time at varying loads experienced by the ball and the disc, both the thickness and the compositions of the reaction layers were the same for the tribostressed region on the ball and for the tribotrack on the disc stressed with high contact pressures (see Figure 3.40 and Table 3.5): a short-chain poly(thio)phosphate of 2-6 units was always found with the same amount of sulphur (II) and zinc.

Phosphorothionates

The friction coefficient at 30°C decreased with higher load while at higher temperatures no significant dependence upon load was found (see Figure 3.43, Figure 3.56 and Figure 3.66). The dimensional wear coefficient decreased with higher contact pressures, but especially at low pressures there was a large uncertainty (see Figure 3.46, Figure 3.57 and Figure 3.67). The thickness of the reaction layer increased with higher contact pressures at 30°C and 80°C because of the higher frictional heat leading to thicker films.
(see Figure 3.53, Figure 3.64 and Figure 3.74). At 150°C, thinner films were found at higher pressures. This was because thick thermal layers were formed at this temperature, which were removed during the wear process. Consequently the film had to be permanently reformed [1, 10]. The higher pressure led to higher concentrations of phosphates and sulphides in the reaction layer, while higher sulphate concentrations were found at lower pressures and in the non-contact areas (see Table 3.6, Table 3.7 and Table 3.8). Similar effects of the contact pressure were observed for other phosphorus- and sulphur-containing additives, where iron sulphides were favoured at high contact pressures, while iron disulphide and iron sulphate were found at lower pressures or on thermal films [28, 34, 35]. At low contact pressures and especially in the non-contact area, the time available for the oxidation of the sulphides is much longer than for films produced at high pressures, which were permanently reformed. Therefore films formed at higher contact pressures represent kind of “fresh” tribofilms while films formed at lower pressures represent “older” tribofilms.

**Ball vs. Disc**

On the tribostressed region on the ball, higher concentrations of sulphides and much less sulphate were found than on the disc (see Table 3.6, Table 3.7 and Table 3.8), which suggests that oxidative processes took place on the tribotrack of the disc while it was out of contact.

**Chain Length**

With increasing chain length of the additive, thinner tribofilms were formed, with the exception of films formed at 150°C, where similar thicknesses were obtained (Figure 3.53, Figure 3.64 and Figure 3.74). Also the composition of the reaction layer depended on the chain length: with longer chains the phosphate concentration decreased while the sulphur concentration increased. Longer chains of the additives enhance the solubility of the molecules in the oil (see Table 2.1). Thus, using solutions with the same molar concentration of the phosphorothionate additives, the amount of adsorbed additives on the surface is lower because of the higher solubility. Therefore fewer additives are available in the tribological contact and thus thinner tribofilms were obtained at 30 and 80°C. At 150°C, the temperature of the solution was high enough to thermally decompose the molecule in solution, which results in high amounts of intermediate species adsorbed on the surface including the wear track. Therefore tribofilms with similar thicknesses were formed at 150°C.
4.4 Wear

The effect of the applied temperature, the contact pressure and the anti-wear additives on wear was investigated with the oscillating-load test and, in addition, the effect of sliding speed and tribopairs with the wear test.

4.4.1 Temperature Effect

Combinatorial Oscillating-Load Test

Performing the oscillating-load test with hardened steel in pure oil (PAO) at 30 and 80°C revealed higher friction with some stick-slip than the experiments performed at 150°C (see Figure 3.17, Figure 3.18). At 150°C, lower friction and wear on the disc was observed (see Figure 4.2 top), while the ball and the running-in track of the disc were worn more than at lower temperatures (see Figure 4.2 bottom). With the higher wear of the ball, the contact area increases and thus the lower contact pressure at the oscillating-load tests at 150°C (see Table 4.2) could have changed the tribological conditions from the boundary-lubrication to the hard elasto-hydrodynamic-lubrication regime. As a result, lower friction and wear (on the disc) was obtained using the pure oil at 150°C.

Performing the oscillating-load test in the presence of ZnDTP resulted in lower wear coefficients compared to the pure oil at both 30 and 80°C and higher coefficients at 150°C, whereas with higher temperature higher wear was obtained. On the ball, no significant change of the wear coefficient with the different temperatures was observed and thus the contact pressures of 500 MPa for 10 N load were similar for all experiments performed in ZnDTP solution.

The wear dependence of the phosphorothionates on the temperature was complicated: At 30°C, very different wear coefficients were obtained on the disc with very low wear in the presence of TPPT. At 80°C, wear was very high with TPPT and n-TPPT but with b-TPPT it was at an intermediate level. At 150°C similar wear on an intermediate level was observed for all phosphorothionates. Examining the ball (see Figure 4.2 bottom) shows very different wear rates for the different conditions: At 30°C high wear was observed in the TPPT solution, at 80°C the wear coefficient was around $10^{-7}$ mm$^3$/Nm for all phosphorothionates and at 150°C there was higher wear on the ball, whereas the lowest for the b-TPPT. The higher wear on the ball results in higher contact areas and thus in
lower average contact pressures (see Table 4.2), which correlates in many cases with the wear obtained on the disc. For example at 30°C in TPPT solution, the average contact pressure at 10 N load was 124±19 MPa, which is about 1/4th of the contact pressures probed in presence of ZnDTP. This resulted in very low friction, wear and thick tribofilms, probably due to hydrodynamic effects. At 80°C the contact pressures were around 300 MPa for all phosphorothionates, resulting in higher wear on the disc, while at 150°C the pressures were between 100 and 150 MPa what leads to lower wear on the disc, whereas the lowest wear on the disc for the n-TPPT correlates with the lowest contact pressure.

Figure 4.2: Dimensional wear coefficient k for 10 N load on the disc (top) and the ball (bottom) in dependence of the applied temperature and the additive for the combinatorial oscillating-load tests using hardened steel.
Wear Test

In the case of the steel-steel contact (non-hardened steel) in pure oil, much higher wear was obtained at higher temperature, ranging from $3 \times 10^{-4}$ mm$^3$/Nm at room temperature to $9 \pm 1 \times 10^{-4}$ mm$^3$/Nm at 150°C. This could be due to enhanced microwelding at higher temperatures. Using the oils blended with anti-wear additives, similar wear coefficients were obtained at both temperatures. Here the higher formation rate of anti-wear films could compensate for the enhanced microwelding at higher temperature, resulting in similar wear at both 25 and 150°C.

In the ceramic-steel contact (zirconia vs. non-hardened steel), no temperature dependence of the wear coefficient was obtained, $2 \times 10^{-4}$ mm$^3$/Nm was measured for the pure oil and both additives (see Figure 3.80) at 10 N load. Using this tribopair, no microwelding takes place and therefore no temperature effect on the wear rate is expected.

4.4.2 Contact Pressure Effect

In the steel-steel contact, the friction coefficient generally decreased with higher contact pressure, as was found with the oscillating-load tests (see section 3.2) and the wear tests (Figure 3.76 and Figure 3.77). This is in agreement with work performed by Eglin et al. [3-5, 7] but in disagreement with results obtained in the hydrodynamic lubrication regime by Ji et al. [143]. The higher friction force at lower contact pressure can be due to temperature-induced adhesion, which would explain why this effect is more pronounced at 150°C than at room temperature (compare Figure 3.76 with Figure 3.77). At higher contact pressures in the wear tests, more pronounced stick-slip events with longer slipping paths were noticed than at lower contact pressures. The higher pressure leads to more energy being dissipated in the contacts, which leads to more adhesion between the asperities. During slipping, more local heat is produced, which enhances the adhesion and probably leads to microwelding.

Wear increased with higher contact pressure because of the higher shear forces. For the steel-steel contacts at 150°C, higher dimensional wear coefficients were obtained at low contact pressures in both the oscillating-load test and the wear test (see section 3.2 and Figure 3.80). This could be due to temperature-induced adhesion and microwelding in addition to the contact-pressure-induced adhesion. At lower contact pressures, thermal effects become more prominent and thus result in higher friction and dimensional wear coefficients.
The deposition rate (Figure 3.81) was much higher with decreasing pressure than with increasing pressure. Some of the debris had to be transported with the ball and deposited later. This is an indication that the deposition rate cannot be purely due to plastic deformation, i.e. material pressed out of the tribological contact by plastic flow, since that would be proportional to the applied contact pressure and would lead to a symmetric shape of the curve with the maximum at the highest load.

In the case of the ceramic-steel contact, there was no significant pressure dependence of the friction coefficient and no stick-slip phenomena occurred at any contact pressure. The dimensional wear coefficient $k$ decreased with lower contact pressure, which indicates that the conditions for the ceramic-steel contact at lower contact pressures were less severe and probably changed from extreme-pressure to anti-wear conditions. The deposition rate was slightly shifted towards decreasing pressure, but this was less pronounced than in the steel-steel case.

### 4.4.3 Sliding-Speed Effect

For the steel-steel contacts, the friction and wear coefficients decreased with higher sliding speeds for all loads, temperatures and solutions (see Figure 4.3). It followed the very left part of the Stribeck curve, where the boundary-lubrication regime changes into the hard elasto-hydrodynamic lubrication regime. In addition, above 400 mm/min, no stick-slip was observed. This was likely due to a very thin oil film being formed between the contact surfaces, which partially carried the load and helped to separate the surfaces. Therefore there was less adhesion between the asperities, resulting in lower friction and wear. On the other hand, friction and wear were still at a high level at high

![Figure 4.3: Friction coefficient of 10 N load as a function of sliding speed for steel-steel and ceramic-steel contact at 25°C or 150°C.](image)
speeds, indicating that still severe conditions are present.

For the ceramic-steel contacts, no significant sliding speed dependence was observed, neither for the friction nor for the wear.

4.4.4 Tribopair

The friction and wear coefficients for the steel-steel contacts were higher than for the ceramic-steel contacts, especially at low sliding speeds (see Figure 4.3). This is in agreement with Winn et al., who observed higher wear at the beginning of wear experiments at higher sliding speeds at 100°C in motor oils [145].

The wear mechanisms for the two tribopairs are different. The dominant effect in the steel-steel contact is adhesion with microwelding of the asperities. This leads to high friction coefficients with stick-slip and to severe wear, also denoted by the term scuffing. The zirconia used for the ceramic ball has a melting point of 2715°C, which is much higher than the melting point of steel of less than 1500°C. In addition, ceramics are chemically more stable than the reactive steel. Therefore no microwelding takes place for ceramic-steel contacts and the adhesion is smaller than for the steel-steel contact, resulting in much lower friction and wear.

On the other hand, it cannot be excluded that the lower friction and wear observed with ceramic balls is a hardness effect, as observed by Sheasby et al. They found for a hardened ball sliding on non-hardened balls that the wear rate was much smaller than when only non-hardened balls were used [139].

4.4.5 Additive

With the combinatorial oscillating-load test it is difficult to compare the different wear coefficients because the analysis of the tribostressed area of the ball showed that the dimensions varied with the conditions, resulting in different contact pressures (see Table 4.2). These ranged from 500 to 25 MPa for the different loads using ZnDTP to about 200 MPa to 10 MPa for the other solutions. Therefore the wear rates have to be treated carefully. Taking into account the wear experienced on both the ball and the disc, ZnDTP was found to perform best among the investigated additives. Among the phosphorothionates the butylated TPPT worked under various conditions and performed better than the non-alkylated and the nonylated TPPT.
The friction coefficient of the steel-steel contact of the *wear test* was lower in the solutions containing the additives, and the lowest values were obtained with ZnDTP. Besides the phosphate-film formation, this could be due to the higher sulphur content in the solution with the additives, which was 0.22 wt.% for ZnDTP and 0.08 wt.% for b-TPPT. Sulphur is supposed to have a beneficial effect at extreme pressures by forming protective layers that lower friction [10].

Concerning wear in the wear tests, the additives were effective only at 150°C in the steel-steel contact, where they reduced the wear by about 50% in comparison to the pure oil. Wang et al. observed a similar decrease in wear in steel-steel contacts with ZnDTP at higher sliding speeds, while for ceramic-steel contacts, ZnDTP was less effective [62]. Under boundary lubrication conditions, Studt showed that tribofilms on the polar alumina reduce wear, while it did not on the covalently bound silicium carbide [59]. The isoelectric point of zirconia is at pH 4, indicating that in slightly acidic medium as found in lubricants, the surface is unpolar. Therefore it is expected from Studt's results with the non-polar silicium carbide that the additives have no benefit in interaction with zirconia.

Normally under tribological conditions, the anti-wear film formed by the additives is continuously removed and reformed during the wear process. Under severe conditions, only a very thin film is formed, still allowing asperity contact [10]. On tribological and thermal films it was shown that the formation rate at 150°C was much higher than at room temperature (see sections 3.1 and 3.2). Therefore only thin reaction layers were formed in the tribotacks at room temperature, which had no effect on wear. In the case of the steel-steel contact at 150°C, the frictional heat together with the external temperature enabled the formation of thicker reaction layers on the tribotrack, which reduced the asperity adhesion and therefore reduced the experienced wear in the presence of the additives. For the ceramic-steel configuration at 150°C, similar anti-wear films as in the steel-steel configuration will have formed, but since no microwelding of the ceramic and steel asperities takes place, no beneficial effect due to the anti-wear film was obtained.

The phosphorothionate b-TPPT is activated at higher temperatures than ZnDTP, as was shown in section 3.1. At low loads, the frictional heat is less pronounced than at high loads and therefore higher dimensional wear coefficients are observed with b-TPPT at low loads at 150°C in the steel-steel contact than with ZnDTP (see Figure 3.80). At high loads, enough frictional heat is produced to activate both kinds of additives and the same anti-wear performance was obtained.
4.5 Proposed Mechanisms

4.5.1 ZnDTP

**Thermal Film Formation**

At *room temperature* in the non-contact area, a simple adsorption of the dialkyldithiophosphate took place on the native iron hydroxide surface as Zhang et al. suggested as a first step in the mechanism [141]. This was accompanied by zinc oxide, which had been formed under the tribological stress and then deposited in the non-contact area.

At *intermediate and high temperatures* in the non-contact areas, an exchange of the alkyl group from the oxygen to the sulphur atom in the dialkyldithiophosphate molecule occurs at temperatures as low as 60°C [18, 19, 25], and thermal decomposition starts catalytically at 60°C in the presence of iron powder [146]. At higher temperatures in particular, not all alkyl groups bind to the sulphur, but some chains leave the molecule and dissolve in the lubricant solution: While the sulphur in the alkylated thiophosphate remains attached to the molecule, the carbon chain bound to sulphur can leave the phosphate group as a thiol. This is in agreement with Luther et al. who found dialkylsulphides, thiols and carbon chains released from ZnDTP during thermal decomposition in the presence of iron [21]. The reaction with a neighbouring phosphoryl group starts to take place at intermediate temperatures [2, 13], supported by the presence of pyrophosphate at 90°C and above.

\[
\begin{align*}
\text{Zn}[(\text{RO})_2\text{PS}_2]_2 & \quad \text{Starting compound: ZnDTP} \\
\downarrow \text{Temperature} & \\
\text{Zn}[(\text{RO})_x\text{O}_{2-x}\text{P}((\text{RS})_y\text{S}_{2-y})_2] + R & \quad \text{Alkylation of sulphur} \\
\downarrow \text{Temperature, } \text{O}_2 & \\
\text{Zn}_{1+n/2}\text{P}_n\text{S}_x\text{O}_{3n+1-x} + \text{RS} + \text{ZnS} + \text{ZnO} + \text{ZnSO}_4 & \quad \text{Polymerisation} \\
\downarrow \text{Temperature, Tribostress, FeO}_x(\text{OH})_y & \\
\text{Fe}_y\text{Zn}_{1+n'/2+y}\text{P}_n\text{S}_x\text{O}_{3n'+1-x'} + \text{ZnO} & \quad \text{Ion exchange and depolymerisation}
\end{align*}
\]

*Figure 4.4: Suggested reaction mechanism of the film formation. n designates the phosphate chain length in the non-contact film, which gets depolymerised to a shorter chain length n' by the iron in the tribofilm.*
At higher temperatures, this process involves further phosphoryl groups and thus leads to longer polyphosphate chains, until a highly cross-linked polyphosphate is reached at 180°C. No ion exchange was observed in the non-contact areas. This is in disagreement with Zhang et al. [141], who propose the diffusion of iron from the steel into the reaction layer. Free zinc ions react with oxygen from the iron hydroxide at the interface to form zinc oxide or with sulphur to form zinc sulphide (especially at lower temperatures). Furthermore, some of the sulphur is oxidized, presumably by O₂ dissolved in the oil, to form the sulphate.

**Film Formation under Tribostress**

In the tribostressed areas, similar reactions occur. The locally higher temperatures due to the frictional heating lead to faster thermal reactions compared to those of the non-contact region. In addition, wear and local mixing effects in the tribological contact may lead to the presence of iron oxy-hydroxide particles in the reaction film and the oil (see Figure 4.5). This could result in a ligand exchange of the cation in ZnDTP and zinc phosphate and in the formation of the thermally less stable FeDTP and of iron phosphate together with zinc oxide, according to the hard and soft acids and bases principle [72, 73]; the iron oxy-hydroxide may catalyze the decomposition of the additive [46, 48]. In agreement with this mechanism, under tribological conditions there are tribofilms formed even at room temperature. At temperatures lower than 110°C, the tribofilms were thicker than the thermal films in the non-contact areas, also reflecting the frictional heat contribution to the film formation and the catalytic effect of

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**Figure 4.5:** Schematic reactions in the contact, near-contact and off-contact areas on samples tribostressed in ZnDTP solution.
iron ions. The presence of the high-binding-energy peak in the iron spectrum at 713.5 eV, which is attributed to iron phosphate formation, supports the ligand-exchange mechanism. Iron has a depolymerisation effect on the polyphosphate chain and forms short-chain iron phosphates. This result is substantiated by the fact that at high temperature, shorter-chain-length iron/zinc phosphates are found in the contact region, while longer zinc phosphate chains are formed in the non-contact area.

4.5.2 Phosphorothionates

Based on the findings above, the following mechanism is suggested (see Figure 4.6). The phosphorothionates adsorb with the sulphur atom to the surface, as described by Koyama et al. for phosphoric esters [29]. In the tribological contact, the high contact pressure, shear force and frictional heat break the S=P double bond of adsorbed molecules and sulphur reacts with iron to form iron sulphide, which is in analogy with Koyama et al. and in agreement with Rossi et al. and Najman et al. [29, 34, 53]. In addition, the phenyl rings cleave either at the C-O bond or the P-O bond, as suggested by Rossi et al. for tributyl thiophosphate (TBT) and was found for similar compounds at high temperatures [30-32, 52, 53]. While the phenyl groups are dissolved in the oil, the remaining phosphoryl groups link together and form polyphosphate chains, as occurred in ZnDTP solutions [2].

In the vicinity of the tribological contact, the frictional heat may induce additional cleavage of phenyl rings and thus phosphoryl groups are produced, which link together to form polyphosphate chains. Further, the heat supports the oxidation of the sulphides with oxygen from iron oxides, hydroxides or with oxygen dissolved in the oil to form sulphates. In addition, TPPT molecules adsorb on the surface, especially to nascent iron released in the tribological contact. Outside of the tribological contact, both the adsorption of molecules and the oxidation of sulphides take place, the latter especially at high temperatures. Part of this film was transferred to the ball during the ongoing experiment, which explains small amounts of sulphates found on the tribostressed regions on the ball.

In the non-contact areas at 30°C and 80°C, sulphates and phosphates were adsorbed onto the surface, originating from the tribologically formed species or some thermo-oxidative degradation happening already at low temperatures. Adsorbed TPPT molecules are likely removed with the washing and were not detected on the surface. At 150°C, the temperature was high enough to de-
compose the additive and to form thick thermal layers. Similar to the tribological contact, the decomposition probably starts with the sulphur of the S=P double bond, which binds to the iron oxide surface [53]. The released sulphur is oxidised to form sulphates. Then the phenyl groups cleave at either the P-O or O-C bond [30-32, 52, 53] and the remaining phosphoryl links to other phosphoryl groups to form polyphosphate chains, as found by Rossi et al. for TBT at 150°C by FTIR spectroscopy [53]. The probability that the phenyl groups cleave from the phosphorus depends on the length of the alkyl chains on the phenyl, the longer they are the more stable is the molecule. With longer chains, therefore, sulphate-rich reaction layers were formed while comparable amounts of phosphates and sulphates were present in films formed with the non-alkylated TPPT.

![Diagram](image)

**Figure 4.6**: Schematic reactions in the contact, near-contact and off-contact areas on samples tribostressed in phosphorothionate solution.
4.6 Surface Analysis with X-Ray Photoelectron Spectroscopy

Depth Analysis

In XPS, data are usually collected at a certain emission angle. This provides information about the elements present in the top 5-10 nm of the analysed sample but gives no information about the depth distribution. There are several possibilities to obtain depth-dependent data: angle-resolved XPS [83, 90], sputter depth profiling [83, 147] or comparing signals of an element with different kinetic energies [83]. In this work, all three techniques were applied, while ARXPS was most frequently used.

Comparing the spectra at different emission angles gives a first idea about the depth distribution (e.g. Figure 3.38), while the apparent atomic concentration at different emission angles allows the assignment of elements in different chemical states to different layers and thus to determine the layer-structure of the sample (e.g. Figure 3.39). For layered structures, the thickness of the layers can be determined with the Hill-equation [90]. The drawback of ARXPS is that elastic scattering contributes to signals at high emission angles [83, 147] and that the acquisition takes much time to obtain good signal-to-noise ratios at all emission angles, especially if some elements are present only in traces.

Sputter depth profiling was performed to analyse the depth distribution of an oxidised steel disc (see Figure 7.3). This technique allows thicker samples to be analysed, since in normal XPS only the top 5-10 nm of the sample are probed. The disadvantages of sputter depth profiling are that selective sputtering might change the composition and that the ion-bombardment might affect the chemical state of the elements and increase the roughness of the sample. Often, the exact sputter rate is not known, resulting in an uncertainty of the depth of analysis [83, 147].

On samples tribostressed in ZnDTP solution, both the signals of Zn2p and Zn3s were acquired. The binding energy and thus the kinetic energy of these electrons are very different, 464 eV kinetic energy for Zn2p\textsubscript{3/2} electrons and 1346 eV for Zn3s. This results in very different IMFPs in a pyrophosphate, 1.33 nm for 2p\textsubscript{3/2} and 2.9 nm for 3s electrons. About 65% of the electrons originate from a depth within the surface and $\lambda \cdot \cos(\theta)$ [83], which is 0.9 nm for Zn2p\textsubscript{3/2} and 2.1 nm for Zn3s at an emission angle of 45°. Therefore the 2p\textsubscript{3/2}
Discussion

Figure 4.7: Intensity ratio of the Zn2p3/2 peak to the Zn3s peak corrected for the sensitivity factors.

electrons originate rather from the surface while the 3s electrons come from the bulk as well. Taking the intensity ratio of the Zn2p3/2 to the Zn3s peak, corrected by the sensitivity factor, therefore information about the depth distribution of zinc can be obtained (see Figure 4.7) with this multiline approach. For a homogenous compound, a ratio of 1:1 is expected. Higher ratios are obtained if zinc is present at the very surface of the sample, ratios around 1 if zinc is in the middle or if thick layers are formed. The ratio is below 1 if zinc is covered for example with a thick organic layer. For samples tribostressed with the oscillating-load test, ratios between 1 and 1.3 were obtained, suggesting that thick layers containing zinc were formed. In the non-contact areas thick layers were only present at 150°C while at 30° and 80°C, zinc was on the surface of the sample, that is only thin layers were formed. On the ball, the ratios were lower because thick organic layers were covering the samples.

Modelling

All these findings based on the XPS results utilizing the different sampling depth probes applying the multiline approach or ARXPS suggest that multilayered samples with up to four layers were present. In “classical” XPS, homogenous compounds with sometimes a thin overlayer are investigated [89, 109, 113]. In the past, several groups worked with 3-layer-models to determine the thicknesses and compositions of the layers [54, 117-119, 148]. These models are based on the first-principle model [109, 113] in combination with the Beer-Lambert law for the attenuation of the electrons by overlayers. For all these models there is the assumption that the individual layers are homogenous laterally and in depth and that there is no mixing between the layers.
Based on the same principles and assumptions as mentioned above, a four-layer model was applied in this work in order to determine the thickness and compositions of the oxide, reaction and organic layer on top of the substrate assumed to be constituted of iron. If not enough intensity from the substrate was obtained, a three- or even a two-layer model was applied. Roughness effects are minimal (accuracy ±10%), since spectra acquired with the PHI 5700 and the PHI Quantera were collected at the 'magic' emission angle of 45° [91]. As shown with angle-resolved XPS, the assumptions of homogeneity and no mixing interface are questionable, since longer phosphate chains were found in the outer part of the reaction layer than in the inner part. Nevertheless, applying the multi-layer model is a fast way of data processing taking into account the layered structure, which gives more accurate results than neglecting the layered structure. A comparison of the results obtained with the multi-layer model used in this work with results obtained with the 3-layer model from Rossi et al. [118, 119] applied on the results with the step tests in ZnDTP solution [108] gave similar thicknesses (±0.1 nm) and concentrations (±1%).

**Thin Layers**

In some experiments performed in phosphorothionate solutions, only fractions of a monolayer were obtained. These could not be treated as full layers because this is in disagreement with the assumption of homogenous layers laterally and in depth. Therefore, if the resulting reaction layer thickness was below 3 Ångstroms (dimension of a phosphate group), the elements normally assigned to the reaction layer were included in the organic layer and the system organic layer (containing the reaction layer species) on top of the oxide layer was used for the modelling.

**Composition of the Substrate**

For the sputtercleaned disc (see Appendix) a carbide concentration of 1.8±0.3 wt.% was obtained. This is much higher than the 1 wt.% from the nominal composition. This can be interpreted assuming that not only iron carbide but also interstitial carbon in the martensite contributed to this peak, that selective sputtering took place removing more iron than carbides and that during sputtering a reaction between the carbon of the contamination layer and the iron occurred.
In this chapter the most important conclusions are drawn from this work. This includes the combinatorial testing and the effect of the applied conditions on the performance, thickness and composition of the anti-wear films formed with ZnDTP and different phosphorothionates.
The oscillating-load test allows combinatorial long-term experiments to be performed on a single track under conditions that are close to those in real systems, where long lifetimes with many stress cycles and often varying loads are present. Parameter libraries covering friction and wear coefficients were successfully produced for ZnDTP and phosphorothionate anti-wear additives in dependence on temperature, contact pressure, sliding speed and tribopair. The chemical composition of the surface was investigated with small-area XPS in combination with imaging- and angle-resolved XPS in dependence on the applied temperature and contact pressure both on non-contact area, the wear track of the disc and on the tribostressed region on the ball.

Friction coefficients in the range of 0.14 to 0.25 were found for the steel-steel contacts, slightly higher at low loads and changing in the order ZnDTP < TPPT < base oil at T < 80°C. At 150°C the friction coefficient was highest in the presence of ZnDTP. The wear rate increased proportionally to the applied load. The dimensional wear coefficient was always high, ranging from with 2⋅10⁻⁷ mm³/Nm up to a maximum of 15⋅10⁻⁶ mm³/Nm at low loads in the base oil. In presence of ZnDTP values between 1 and 4⋅10⁻⁶ mm³/Nm were found, indicating severe wear conditions in the boundary-lubrication regime.

Thickness and composition of the tribofilms formed in the wear track changed with test duration, load and temperature. The tribofilms show a layered structure of poly(thio)phosphates with different chain-lengths: at short times (step test) thin films consisting of zinc orthophosphate were formed. These films increased in thickness and transformed to short-chain poly(thio)phosphates at longer test duration (oscillating-load test). Longer chain-length polyphosphates were found in the outer part of the tribofilms. Increasing load (contact pressure) produced more frictional heat resulting in the formation of thicker poly(thio)phosphate films with shorter chain lengths. These films are harder and tougher, resulting in lower friction and dimensional wear coefficients.

**ZnDTP**

Strong temperature dependences of both the oxide and the reaction layer were observed: the oxide layer at low temperatures was found to be an iron oxy-hydroxide. At higher temperature the stoichiometry of the substrate was very close to Fe₃O₄.

The thickness of the reaction layer increased with increasing temperature, reaching values greater than 6 nm. The composition of the non-contact areas changed from adsorbed dialkyldithiophosphate at room temperature through a short-chain zinc phosphate at intermediate temperature to a cross-linked poly-
phosphate at 180°C. Under the tribological stress of the combinatorial step test a thin tribofilm was formed even at room temperature, and consisted of zinc orthophosphate. Increasing temperature led to longer chains. These were shortened in the contact regions due to reaction with the iron ions, which could be incorporated into the tribofilm resulting in a mixture of iron and zinc phosphates. Longer chains were found in the outer part of the reaction layers by means of angle-resolved XPS. Under the tribological stress of the longer lasting combinatorial oscillating-load test, thicker films of short-chain poly(thio)phosphates were formed at all temperatures, with increasing thickness with higher temperature.

A higher contact pressure produced more frictional heat, which causes the formation of thicker tribofilms of poly(thio)phosphates. The higher pressure has a shortening effect on the chain length, resulting in poly(thio)phosphates of 3-5 phosphate units. These films are harder and tougher, resulting in lower friction coefficient and dimensional wear coefficients.

Analysing both the ball and the disc provides a deeper insight into the antiwear mechanism of ZnDTP. The same composition of the tribofilm was found on the ball and on the disc where high contact pressures were applied. This suggests that the same mechanism took place on both the ball and on the disc tribostressed with high contact pressures. While on the disc the pressure dependence was investigated, the reactions behind the tribological contact could be followed on the ball.

**Phosphorothionates**

Strong temperature, contact-pressure and chain-length dependence of the film formation and the resulting film composition was found for the alkylated phosphorothionates. In comparison with ZnDTP, generally thinner films were formed because of a lack of counterions in the system, while in the case of ZnDTP the counterion is already present in the starting molecule.

The activation temperature for thermal decomposition of the TPPTs was at 150°C higher than found for the ZnDTP, therefore the films formed in the non-contact areas were very thin below 125°C and tended to be single molecules adsorbed on the surface rather than continuous overlayers. Only above 150°C were thicker layers formed. These consisted of a mixture of sulphates and polyphosphates.

With higher contact pressures, the local temperature increased and thus thicker reaction layers were formed, which minimized the asperity contacts and thus resulted in lower dimensional wear coefficients at higher pressures. While the tribostress led to thicker tribofilms below 125°C, the thermal films were re-
moved with the tribostress at 150°C and thinner films were formed instead. The composition changed with higher contact pressure: more sulphides and phosphates were present.

Longer alkyl chains bound on the phenyl of the phosphorothionate increase the solubility of the TPPT molecule. Therefore fewer molecules adsorb on the surface, which results in thinner layers formed with longer alkyl chains. In addition, the percentage of sulphur in the reaction layers was higher with longer alkyl chains. The experienced wear was found to vary drastically with the different additives and temperatures. Excellent anti-wear performance with the formation of protective films was observed at lower contact pressures, whereas at 150°C the wear efficiency was similar for the different molecules. In general, the phosphorothionates were not as effective as ZnDTP in forming anti-wear films and protecting the surfaces against wear.

Analysing both the ball and the disc, different mechanisms were found. While on the ball the tribofilm contained, besides the phosphates, mainly sulphides and only traces of sulphates, large amounts of sulphates were present on the disc. This shows that an oxidation of the wear track takes place during the experiment, while this was not possible on the ball, being under permanent tribostress.

The results with the different alkylation of the phosphorothionates show that the performance depends drastically on the applied conditions, and demonstrates the usefulness of the combinatorial testing, which allows different contact pressures to be screened at once and thus to minimize the number of experiments to be performed for additive characterisation.

**Wear Tests**

Using the non-hardened 100Cr6 steel for these experiments resulted in very severe wear denoted by scuffing. Lower friction and dimensional wear coefficients were obtained with lower temperature, higher contact pressure and higher sliding speed. The anti-wear additives ZnDTP and b-TPPT were effective only in the case of the steel-steel tribopair at 150°C, where the thermal energy was high enough to produce protective layers. In the case of the ceramic-steel contact, lower friction and wear resulted compared to the steel-steel contact because under these conditions no microwelding occurred and thus adhesive wear was lowered.
Final Conclusions

XPS analysis in combination with the combinatorial oscillating-load test makes a high-throughput additive characterisation possible.

Based on these libraries the reaction mechanisms could be better understood for both the ZnDTP and the phosphorothionates anti-wear additives under the different conditions. These findings will help to develop more effective ashless anti-wear additives and to optimize the application of the anti-wear additives.
In this chapter, suggestions for improving the setup of combinatorial tests are given, especially regarding the parameter library and the reproducibility of tribological experiments. In the following section, possibilities as to how the surface analysis of tribofilms could be improved, are reported.
Combinatorial Testing

A parameter library covering different contact pressures and temperatures was created in this work for ZnDTP and phosphorothionates with different chain lengths. For future work, the combinatorial oscillating-load test can be applied for testing other anti-wear additives and to determine their mechanisms. It would also be interesting to investigate the films formed by the anti-wear additives in the presence of other additives usually used in lubricant formulation.

The tribometer could be modified installing either a profilometer installed in the tribometer for in situ depth profiling or an optical microscope to follow changes in the tribotrack dimension. Measuring the resistance between the ball and the disc would provide in vivo information about the breakdown of the oxide films and the anti-wear film formation.

Parameter Library

For both the contact pressure and the applied temperature a wide range of conditions was tested, there seems to be no need to expand these ranges. With the wear test it was found that both friction and wear depended on the sliding speed. It would thus be interesting to investigate if this correlates with a change in the chemical composition of the tribofilm.

The time of an experiment increased from 5 minutes/annulus for the combinatorial step tests to 95 minutes for the combinatorial oscillating-load tests. In comparison to technical applications, this is a short time. Therefore the tribofilm formation in dependence on sliding time could be investigated.

The wear experienced with the wear test using non-hardened steel on the disc was so severe that immediate failures would occur in real applications. In order to obtain more significant data therefore only hardened steel discs should be used for both the steel-steel and the ceramic-steel tribopairs.

Reproducibility

As presented in Table 4.2, the contact area of the ball depends on the applied conditions during the running in and the subsequent tribotest. Therefore the running in should be applied according to a standard protocol, e.g. by flattening the ball using sandpaper or by performing the running in under dry conditions at a given temperature. This would allow a better control of the contact area and thus the applied contact pressure.

A parameter, which is often neglected, is the environment in which the experiment takes place. In this work the temperature and relative humidity in the
hood was registered. A more elegant way would be if the environment could actively be controlled, that is the humidity and composition of the air and herewith the oxygen content of the oil could be adjusted or even be varied as an experimental parameter.

**Surface Analysis**

Angle-resolved XP-spectra are proved to be very powerful in providing in-depth information of thin film structure and elemental distribution in a non-destructive way, but they have sometimes a low signal/noise ratio rendering the subsequent data processing challenging. This could be improved increasing the measurement time. In addition, a higher number of collected emission angles could be collected to provide more detailed information of the intensity vs. emission angle and thus facilitating the subsequent modelling of the data for going from the intensity vs. angle plots to concentration vs. depth.

Small-area XPS combined with imaging-XPS allowed lateral changes in the film composition to be ascertained as shown in Figure 3.35. It would be extremely interesting to correlate these local changes with those of the friction and wear coefficients. Furthermore, the application of other surface analytical techniques like Auger electron spectroscopy or time-of-flight secondary ion mass spectrometry (ToF-SIMS) would allow higher spatial resolution and changes at smaller dimensions could, if present, be detected.

In addition, the morphology of tribotacks could be investigated with SEM or AFM, for example to determine the wear mechanisms. SEM in combination with focussed ion beam (FIB) would allow one to analyse the layered structure and could be helpful to confirm the results obtained with angle-resolved XPS.
Chapter 7

Appendix

In this chapter, guidance for calibrating the load cell, the Matlab routines to process tribological data, laser profilometer files and routines to calculate the thickness and composition of the layers using the multilayer model in XPS are given.

In the second part, X-ray photoelectron spectra of reference compounds for peak identification in XPS and the peak-fitting parameters are presented.
7.1 Tribometer

7.1.1 Calibration of the Load Cell

The load cell has to be dismounted from the motor block and laid on its back so that the mounted spring is facing upwards. The load cell is then connected to the measuring unit of the tribometer using an extension cable. The load cell is unbiased (View/Semi-automatic Panel/Data-I and Run/Sensor Unbias) and the screws on the measuring unit (on top of the x-movement, labelled with “Zero Fx” and “Zero Fz”) adjusted until the measured forces Fx and Fz (UMT.exe/View/Automatic Panel) are close to zero. After the sensor has been zeroed (View/Semi-automatic Panel/Data-I and Run/Sensor Bias), the test weight is put onto the spring of the load cell. The measured force Fz is compared with the theoretical force \( F_{th} = g \cdot m_{\text{test weight}} \) and the Fz-proportionality factor (UMT.exe/Options/Data Acquisition/Force: behind “Fz ±”) is adjusted \( \text{factor}_{\text{new}} = \frac{\text{factor}_{\text{old}} \cdot F_{th}}{F_z} \).

The Fx-factor is calibrated with the sensor put on its side and the stylus mounted on the spring. The sensor is zeroed in that position and then the test weight hung on the stylus. The Fx-proportionality factor (behind “Fx ±”) is then adjusted \( \text{factor}_{\text{new}} = \frac{\text{factor}_{\text{old}} \cdot F_{th}}{F_x} \).

7.1.2 Tribological Data Processing

Tribological data are processed with Routine 7.1. It creates a colour plot with the friction coefficient in dependence on the angular position of the disc and the number of turns of the experiment. If the applied load has been constant, the height of the carriage of the tribometer was plotted as a function of the angular position on the left side of the colour plot to check for irregularities in the planarity of the disc. If the load has been oscillating, the applied load is plotted as a function of the angular position in order to visualize the load dependence of the friction coefficient.
Routine 7.1: Matlab routine to create a colour plot of tribological data.

% ----- Choose a tribological file and read in the data -----  
Filename = uigetfile('*.txt', 'Please select the tribo-file'); cd(Filename);
[Fx Fz t z ENC R] = textread(Filename, '%f %f %f %f %f %f');
% ----- Shift-corrections of the load cell -----  
Shift_FxO = input('Shift of Fx at the begin of the experiment [mN]? ');
Shift_FzO = input('Shift of Fz at the begin of the experiment [mN]? ');
Shift_Fx = input('Shift of Fx at the end of the experiment [mN]? ');
Shift_Fz = input('Shift of Fz at the end of the experiment [mN]? ');
Fx=Fx-Shift_FxO; Fz=Fz-Shift_FzO; Shift_Fx=Shift_Fx-Shift_FxO; Shift_Fz=Shift_Fz-Shift_FzO;
% Calculation of the friction coefficient and its position  
ENC=abs(ENC-fix(ENC(1))); Turn=floor(ENC); Position=ENC-Turn;
COF_values(1)=mean(COF); COF_values(2)=std(COF)
% Construction of a matrix with the friction coefficients ----
Boxes=fix(length(find(Turn == 1))/5); Pos_old=0; m=2; Box(1)=COF(1);
for k=length(find(ENC<0))+2:length(ENC)
  Pos=fix(Boxes*Position(k));
  if Pos == Pos_old
    Box(m)=COF(k); m=m+1;
  else
    COF_matrix(Pos_old+1,Turn(k-1)+1)=mean(Box);
    clear Box; Box(1)=COF(k); m=2; Pos_old=Pos;
  end
end
% ----- Create the colour plot -----  
figure2=figure; set_options('Position', [500 350 620 400])
% ----- Create the left part of the plot -----  
figure2_2=subplot(1,2,1);
if std(Fz)<1000
  z=(z-mean(z)).*1000; plot(z,Position,'k.','MarkerSize',1);
else
  Fz=Fz./1000; plot(Fz,Position,'k.','MarkerSize',1);
end
ylabel('angular position');
axis([-15.15 15 0 1]); xlabel('height [um]','Fontsize',18);
end
% ----- Create friction coefficient plot on the right side of the plot -----  
figure2_1=subplot(1,2,2);
matrixplot=surf(COF_matrix);
colormap('hot')
view([0 90])
xlabel('number of turns');
endl
7.2 Laser Profilometry

The settings used for performing laser profilometry measurements are given in Table 7.1. Since the language of the program is German, both the English and the German expressions are given in the table.

Table 7.1: Settings for laser profilometer measurements on the UBM UBC 14.

<table>
<thead>
<tr>
<th>English</th>
<th>German</th>
<th>English</th>
<th>German</th>
</tr>
</thead>
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<tr>
<td>Measurement range</td>
<td>Messbereich</td>
<td>± 50 μm</td>
<td></td>
</tr>
<tr>
<td>Measurement axis X /</td>
<td>Messachse X /</td>
<td></td>
<td></td>
</tr>
<tr>
<td>diagonal axis Y</td>
<td>Querachse Y</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Direction</td>
<td>Richtung</td>
<td>Forward</td>
<td>Vorwärts</td>
</tr>
<tr>
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<td>Startpunkt</td>
<td>Centre(1)</td>
<td>Mitte(1)</td>
</tr>
<tr>
<td>Measure</td>
<td>Messen</td>
<td>Profile; Reflection</td>
<td>Profil; Reflexion</td>
</tr>
<tr>
<td>Option</td>
<td>Option</td>
<td>Acceleration before measuring</td>
<td>Beschleunigung vor Messung</td>
</tr>
<tr>
<td>Speed</td>
<td>Geschwindigkeit</td>
<td>0.36 mm/s</td>
<td></td>
</tr>
<tr>
<td>Measuring frequency</td>
<td>Messfrequenz</td>
<td>43.2 Pt/s</td>
<td></td>
</tr>
<tr>
<td>Continuous measurement</td>
<td>Kontinuierliche</td>
<td></td>
<td></td>
</tr>
<tr>
<td>measurement</td>
<td>Messung</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

7.2.1 Data Processing

Profiles measured with laser profilometry were converted into an ascii file using the macro “asciicon.mac” provided with the UBM software. The resulting file is a matrix that contains the z-values. Using Routine 7.2, the matrix is loaded and a colour plot of the profile is created to give a first impression about the topography of the sample. The radial profiles are determined with Routine 7.3. Assuming a linear background at the wear tracks, the positive and negative integrals of the profiles are determined automatically and afterwards converted into wear and deposition rates. With Routine 7.4, the automatic background of the radial profiles can be checked and changed if necessary. Other routines have been written to measure the average and the root-mean-square roughness of the sample or to determine the centre of the tribostressed sample if it does not correspond with the centre of the measured profile.
Routine 7.2: Matlab routine to create colour plots of the height profile.

% ----- Load the file ----- 
[Filename, Pathname] = uigetfile("*.pr", 'Select the PR-file'); cd (Pathname); 
Profile=dlmread([Filename]); [size_y size_x]=size(Profile); 
% ----- Flatten the profile ----- 
mean_x1=mean(Profile(1:size_y,1)); mean_xx=mean(Profile(1:size_y,size_x)); 
delta_x=mean_xx-mean_x1;delta_x=delta_x/(size_x-1); 
for k=2:size_x 
    Profile(1:size_y,k)=Profile(1:size_y,k)-(k-1)*delta_x-mean_x1; 
end 
mean_y1=mean(Profile(1,1:size_x)); mean_yy=mean(Profile(size_y,1:size_x)); 
delta_y=mean_yy-mean_y1;delta_y=delta_y/(size_y-1); 
for k=2:size_y 
    Profile(k,1:size_x)=Profile(k,1:size_x)-(k-1)*delta_y-mean_y1; 
end 
% ----- Mirror the matrix on the y-axis ----- 
Profile=fliplr(Profile); 
% ----- Create a small matrix for faster plotting ----- 
Comp=5; 
for laufy=1:floor(size_y/Comp) 
    for laufx=1:floor(size_x/Comp) 
        Profile_hilf=Profile(Comp*(laufy-1)+1:laufy*Comp, Comp*(laufx-1)+1:laufx*Comp); 
        Profile_klein(laufy, laufx)=mean(mean(Profile_hilf)); 
    end 
end 
% ----- Create an additional matrix for plotting ----- 
Resolution=120; [size_y_kl size_x_kl]=size(Profile_klein); 
Length=size_x/Resolution; Width=size_y/Resolution; 
[X Y]=meshgrid(linspace(0,Length,size_x_kl),linspace(0,Width,size_y_kl)); 
% ----- Create the colour plot ----- 
image=figure; hold on 
matrixplot=surf(X, Y, Profile_klein); colormap('hot') 
set(matrixplot,'EdgeColor','none') 
axis ([0 Length 0 Width -100 100 -1 1]) 
colorbar 
view ([0 90]) 
% ----- Definition of the theoretical centre of the disc ----- 
Centre_x=size_x/Resolution/2; Centre_y=size_y/Resolution/2;
Routine 7.3: Matlab routine to read out the radial height profiles of the z-value matrix and to determine the wear- and deposition rate automatically.

% ----- Choose inner and outer radius ----- 
inn = input('Inner Radius? '); 
out = input('Outer Radius? '); 
% ----- Set parameters ----- 
clear z_werte position z_wert_rad 
warning off MATLAB:polyfit:RepeatedPointsOrRescale

number_turns=1000; phi_start=-90; phi_end=270;
Radius=r_in:1/Resolution:r_out;
% ---- Set the resolution (delta_phi) and read out the radial profile as a function of the angle----
da|=1
for phi=phi_start:delta_phi:phi_end

clear zwert

phi=(pi/180).*phi;

% ----- Limit the outer radius in case it's larger than the matrix ----- 
[size_y size_x]=size(Profile);
x=round(Centre_x_px+cos(phi).*r_out_px);
if x<1 
    r_out_px=(1-Centre_x_px)/cos(phi);
end
if x>size_x
    r_out_px=(size_x-Centre_x_px)/cos(phi);
end
y=round(Centre_y_px+sin(phi).*r_out_px);
if y<1
    r_out_px=(1-Centre_y_px)/sin(phi);
end
if y>size_y
    r_out_px=(size_y-Centre_y_px)/sin(phi);
end

% ----- Read out the profiles determined by the inner and outer radius and phi ----- 
lauf2=0; z_wert_orig=0;
for R=r_in_px:1:r_out_px
    x=round(Centre_x_px+cos(phi).*R);
    y=round(Centre_y_px+sin(phi).*R);
    lauf2=lauf2+1; z_wert_orig(lauf2)=Profile(y,x);
end

% ----- Flatten with a parabolic fit ----- 
R_position=1:1:length(z_wert_orig);
p = polyfit(R_position, z_wert_orig,2); f = polyval(p, R_position);
z_wert = z_wert_orig - f;
z_werte(lauf,1:length(z_wert))=z_wert; lauf=lauf+1;
end
% ----- Create the mean profile ----- 
z_wert=mean(z_werte);

[m,n]=size(z_werte); [i,j]=find(z_werte == 0);
if length(j)>0
    laufk=1;
    while laufk <= n & length(find(z_werte(1:m,laufk) == 0)) < m-1 
        z_wert(laufk)=z_wert(laufk)*m/(m-length(find(z_werte(1:m,laufk) == 0)));
        laufk=laufk+1;
    end
end

save z_wert_av.txt z_wert -ascii; save Radius.txt Radius -ascii;
% ----- Determine the number of tracks and their position for the automatic integral ----- 
Profileplot=figure; position=Radius(1:length(z_wert)); plot(position, z_wert)
number_tracks=input('Number of tracks? ');
if number_tracks==1
    disp('Choose the track with the mouse')
    [x y]=ginput(1); location=x(1)
end
else
disp('Choose the first and the last track with the mouse')
[x y]=ginput(2); location=x(1):(x(2)-x(1))/(number_tracks-1):x(2)
end
save location.txt location -ascii

% ----- Average spectra of 5 degrees ----- 
for k=1:1:360/5
    clear z_wert_hilf
    z_wert_hilf=z_werte(fix((k-1)*m/(360/5)+1):fix(k*m/(360/5)),1:n);
    z_wert=mean(z_wert_hilf); [mh,nh]=size(z_wert_hilf); [i,j]=find(z_wert==0);
    if length(j)>0
        laufk=j(1);
        while laufk <= nh & length(find(z_wert_hilf(1:mh,laufk)==0)) < mh-1
            z_wert(laufk)=z_wert(laufk)*mh/(mh-length(find(z_wert_hilf(1:mh,laufk)==0)));
            laufk=laufk+1;
        end
    end
end
z_wert_rad(k,1)=(k-1)*5; z_wert_rad(k,2:length(z_wert)+1)=z_wert;

% ----- Determine the wear- and deposition rate automatically ----- 
delta_loc=0.2; Integral_pos=[0 0 0 0 0 0]; Integral_neg=[0 0 0 0 0 0];
for lauf=1:length(location)
    x=[location(lauf)-delta_loc location(lauf)+delta_loc]; n=length(z_wert);
    a=(position(n)-position(1))/(n-1); x_indx=round((x-position(1)+a)/a);
    if x_indx(2)+2<n
        % ----- Determination of a linear background ----- 
        y=[mean(z_wert(x_indx(1)-3:x_indx(1)+3)) mean(z_wert(x_indx(2)-3:x_indx(2)+3))];
        hold on
        Profile_line=plot(x,y); Slope=(y(2)-y(1))/(x(2)-x(1));
        % ----- Sum up the negative and positive values related to the background ----- 
        for k=x_indx(1):1:x_indx(2)
            delta=z_wert(k)-(y(1)+Slope*(position(k)-x(1)));
            if delta>0
                Integral_pos(lauf)=Integral_pos(lauf)+delta;
            else
                Integral_neg(lauf)=Integral_neg(lauf)+delta;
            end
        end
        end
end
% ----- Adjust the area to wear- and deposition rates ----- 
Integral_pos=Integral_pos*(x(2)-x(1))/(x_indx(2)-x_indx(1))/number_turns;
Integral_neg=Integral_neg*(x(2)-x(1))/(x_indx(2)-x_indx(1))/number_turns;
depositrate(k,1)=(k-1)*5; wearrate(k,1)=(k-1)*5;
depositrate(k,2:length(Integral_pos)+1)=Integral_pos;
wearrate(k,2:length(Integral_neg)+1)=-Integral_neg;
end
wearrate(2,13)=0;
save wearrate.txt wearrate -ascii; save depositrate.txt depositrate -ascii;
save z_wert_rad.txt z_wert_rad -ascii;
Routine 7.4: Matlab routine to go through the radial height profiles and to change the background if necessary.

% ----- Choose the range of angles to check -----
Angle_start=input('Starting Angle? '); Angle_end=input('Ending Angle? ');
for Angle=Angle_start:5:Angle_end
    k=Angle/5+1; [m n]=size(z_wert_rad);
    z_wert=z_wert_rad(k,2:n-length(find(z_wert_rad(k,2:n)==0)));
    position=Radius(1:length(z_wert));
    % ----- Plot the radial profile -----
    Profileplot=figure; plot(position, z_wert); axis ([min(position) max(position) -0.5 0.5]);
    Grad=[num2str(Angle) '-' num2str(Angle+5) ' ']; title ([Profile ', Grad,' ','FontSize',18]);
    % ----- Plot the automatic background, or if chosen already by hand, plot that -----
    for track=1 :length(location)
        if wearrate(k,5+4*track)==0
            x=(position(track)-0.2 location(track)+0.2); n=length(z_wert);
            a=(position(n)-position(1))/(n-1); x_indx=round((x-position(1)+a)/a);
            if x_indx(2)+2<n
                % ----- Determination of a linear background -----
                y=[mean(z_wert(x_indx(1)-3:x_indx(1)+3)) mean(z_wert(x_indx(2)-3:x_indx(2)+3))];
                hold on
                Profile_linie=plot (x,y); Slope=(y(2)-y(1))/(x(2)-x(1));
            end
        else
            x(1)=wearrate(k,5+4*track); x(2)=wearrate(k,6+4*track);
            y(1)=wearrate(k,7+4*track); y(2)=wearrate(k,8+4*track); hold on
            Profile_linie=plot (x,y);
        end
    end
    reply=input('Is the fit o.k.? [y/n]','s');
    while reply ~= 'y'
        disp ('Choose the start- and the endpoint of the linear background with the mouse')
        [x y]=ginput(2); hold on
        Profile_linie=plot (x,y); n=length(z_wert);
        a=(position(n)-position(1))/(n-1); x_indx=round((x+r_in+a)/a);
        Slope=(y(2)-y(1))/(x(2)-x(1));
        % ----- Integration of the z-values -----
        Integral_pos=0; Integral_neg=0;
        for k=x_indx(1):1:x_indx(2)
            delta=z_wert(k)-y(1)+Slope*(position(k)-x(1));
            if delta>0
                Integral_pos=Integral_pos+delta;
            else
                Integral_neg=Integral_neg+delta;
            end
        end
        Integral_pos=Integral_pos*(x(2)-x(1))/(x_indx(2)-x_indx(1))/number_turns
        Integral_neg=-Integral_neg*(x(2)-x(1))/(x_indx(2)-x_indx(1))/number_turns
        % ----- Ask for the track, and write rates into the according place -----
        track = input('Which track was it? ');
        if isempty(track)
            disp('not saved')
        else
            wearrate(k,track+1)=Integral_neg; depositrate(k,track+1)=Integral_pos;
            wearrate(k, track*4+5)=x(1);wearrate(k, track*4+6)=x(2);
            wearrate(k, track*4+7)=y(1);wearrate(k, track*4+8)=y(2);
        end
        reply=input('Is the fit now o.k.? [y/n]','s');
    end
end
save wearrate.txt wearrate -ascii; save depositrate.txt depositrate -ascii;
7.3 Multilayer Model for XPS

An example of a Mathematica worksheet to solve the equations described in section 2.4.5 for a sample consisting of four layers is given in Routine 7.5. The text in italics is additional information for the reader to the following part of the worksheet. The idea behind this routine is to copy-paste a list of corrected intensities from an excel sheet between the curly brackets in the first line of the worksheet, then separate the numbers with commas and finally let the program find a numerical solution with the FindRoot command using the Newton's method. The solution is then automatically exported into a tab-separated textfile, which allows a copy-paste of the solution back into an Excel-sheet.

**Routine 7.5**: Example of a Mathematica worksheet to calculate the thicknesses and compositions of the layers in a four-layer model. In this example, the substrate is pure metallic iron, covered with an iron oxide layer. On that a reaction layer (aqueous zinc phosphate was used as model compound) was formed, covered by an organic layer. \(d_o, d_r\) and \(d_c\) are the thicknesses of the oxide, reaction and carbon layer, respectively, and \(w_i\) the weight fraction of the specified element \(i\).

**Intensities** \(l_c\) corrected by the sensitivity factor in the following order: \(\{C(l), C(ll), C(lll), O(ox), O(NBO), O(BO), P, S(sulphide), S(sulphate), Zn3s, Fe(met), Fe(ll), Fe(lll), Fe(OOH), Fe(PO4)\}\); \(l_c =\{12046, 798, 516, 2388, 1778, 239, 231, 202, 76.2, 760, 656, 2028, 470, 1095, 445\}\);

```
FindRoot[{
Metallic iron;
l_c[[11]]/l_c[[1]] == Exp[-d_o/1.184 - d_r/1.449 - d_c/1.822] / (w_C1*(1-Exp[-d_c/2.561])),
Oxide layer;
l_c[[4]]/l_c[[1]] == w_Ox*(1-Exp[-d_o/1.377])*Exp[-d_r/1.690 - d_c/2.136] / (w_C1*(1-Exp[-d_c/2.561])),
l_c[[12]]/l_c[[1]] == w_Fe2*(1-Exp[-d_o/1.181])*Exp[-d_r/1.446 - d_c/1.817] / (w_C1*(1-Exp[-d_c/2.561])),
l_c[[13]]/l_c[[1]] == w_Fe3*(1-Exp[-d_o/1.179])*Exp[-d_r/1.444 - d_c/1.814] / (w_C1*(1-Exp[-d_c/2.561])),
l_c[[14]]/l_c[[1]] == w_FeOOH*(1-Exp[-d_o/1.178])*Exp[-d_r/1.443 - d_c/1.813] / (w_C1*(1-Exp[-d_c/2.561])),
w_Ox + w_Fe2 + w_Fe3 + w_FeOOH == 1,
Reaction layer;
l_c[[5]]/l_c[[1]] == w_NBO*(1-Exp[-d_r/1.686])*Exp[-d_c/2.134] / (w_C1*(1-Exp[-d_c/2.561])),
l_c[[6]]/l_c[[1]] == w_BO*(1-Exp[-d_r/1.686])*Exp[-d_c/2.131] / (w_C1*(1-Exp[-d_c/2.561])),
l_c[[7]]/l_c[[1]] == w_P1*(1-Exp[-d_r/2.209])*Exp[-d_c/2.817] / (w_C1*(1-Exp[-d_c/2.561])),
l_c[[8]]/l_c[[1]] == w_S1*(1-Exp[-d_r/2.172])*Exp[-d_c/2.769] / (w_C1*(1-Exp[-d_c/2.561])),
l_c[[9]]/l_c[[1]] == w_S2*(1-Exp[-d_r/2.164])*Exp[-d_c/2.758] / (w_C1*(1-Exp[-d_c/2.561])),
l_c[[10]]/l_c[[1]] == w_Zn3s*(1-Exp[-d_r/2.200])*Exp[-d_c/2.805] / (w_C1*(1-Exp[-d_c/2.561])),
l_c[[15]]/l_c[[1]] == w_FePO4*(1-Exp[-d_r/1.440])*Exp[-d_c/1.810] / (w_C1*(1-Exp[-d_c/2.561])),
w_NBO + w_BO + w_P1 + w_S1 + w_S2 + w_FePO4 + w_Zn3s == 1,
Organic layer;
l_c[[2]]/l_c[[1]] == w_C2*(1-Exp[-d_c/2.554]) / (w_C1*(1-Exp[-d_c/2.561])),
l_c[[3]]/l_c[[1]] == w_C3*(1-Exp[-d_c/2.554]) / (w_C1*(1-Exp[-d_c/2.561])),
w_C1 + w_C2 + w_C3 == 1,
};
{do, 1}, {dr, 1}, {dc, 1}, {w_Ox, 1/4}, {w_Fe2, 1/4}, {w_Fe3, 1/4}, {w_FeOOH, 1/4}, {w_NBO, 1/7},
{w_BO, 1/7}, {w_P1, 1/7}, {w_S1, 1/7}, {w_S2, 1/7}, {w_FePO4, 1/7}, {w_Zn3s, 1/7}, {w_C1, 1/3}, {w_C2, 1/3}, {w_C3, 1/3}];
```

Save output into a textfile:

```mathematica
a = Out[]; results = {a[[1, 2]], a[[2, 2]], a[[3, 2]], a[[4, 2]], a[[5, 2]], a[[6, 2]], a[[7, 2]], a[[8, 2]], a[[9, 2]], a[[10, 2]], a[[11, 2]], a[[12, 2]], a[[13, 2]], a[[14, 2]], a[[15, 2]], a[[16, 2]], a[[17, 2]]};
Export["results.txt", results, "TSV"]
```
7.4 XPS Reference Spectra

Reference spectra were acquired to extract the peak-fitting parameters to be applied for processing the tribostressed samples and to compare the binding energies and the chemical states of the elements before and after the experiment. This allows changes in the elemental compositions of the additives or of the tribopartners to be tracked.

7.4.1 Sputter-cleaned Disc

Spectra of the disc after sputter-cleaning for 54 seconds are presented in Figure 7.1. The survey spectrum shows numerous peaks of iron: Fe LM\textsubscript{2,3}M\textsubscript{2,3} at 894 eV and Fe L\textsubscript{3}M\textsubscript{4,5}M\textsubscript{4,5} at 784 eV, Fe2s at 843 eV, Fe2p\textsubscript{3/2} at 707 eV, Fe3s at 92 eV and Fe3p at 53 eV. Besides iron, there were traces of chromium (Cr2p\textsubscript{3/2} at 574 eV), oxygen (O1s at 530 eV), carbon (C1s at 283 eV) and argon (Ar2p at 244 eV). The argon peak was due to the argon implantation.

The detailed spectrum of carbon shows two peaks, one at 283.1 eV assigned to carbides [136, 137, 149] and a minor peak at 285.5 eV originating from ali-

![Figure 7.1: XPS survey and detailed spectra of C1s, O1s, Cr2p and Fe2p of a sputter-cleaned disc made of steel 100Cr6. (Data acquired with the PHI Quantera with 100 µm beam size and 26 eV pass energy after 54 seconds Ar-sputtering (4 kV, 3.3 mm\textsuperscript{2}).)
phatic carbon [87, 134] (see Table 7.2). The oxygen signal consisted of two peaks, the oxide peak at 530.0 eV [132, 133] and a peak at 531.5 eV assigned to hydroxides [133].

Both chromium and iron showed two peaks 2p$_{1/2}$ and 2p$_{3/2}$ due to the spin-orbit splitting. The 2p$_{1/2}$ peak is at higher binding energy than 2p$_{3/2}$ and has half of the peak area of the 2p$_{3/2}$ peak. Only the 2p$_{3/2}$ peaks were used for curve synthesis. The chromium 2p$_{3/2}$ consisted of an asymmetric peak at 574.2 eV that was assigned to metallic chromium [87] or chromium carbide [149, 150]. In the iron 2p$_{3/2}$ spectrum, there was an asymmetric peak at 706.7 eV assigned to metallic iron [129, 132].

The peak-fitting parameters are summarized in Table 7.2 for different analysis conditions. The shape of the metallic peak (GL(85)T(0.63)) was used as a reference for the metallic iron present in materials analysed with the PHI Quantera. Changing the beam size from 100 to 20 μm caused a decrease in the

**Table 7.2**: Peak-fitting parameters of a sputter-cleaned 100Cr6 disc acquired with the PHI Quantera. The uncertainty of the positions and fwhm is 0.1 eV and about 5% for the peak areas.

### 100 μm beam size and 26 eV pass energy (after 54 s Ar-sputtering (4 kV, 3.3 mm$^2$)):

<table>
<thead>
<tr>
<th>Name</th>
<th>Position [eV]</th>
<th>FWHM [eV]</th>
<th>Line Shape</th>
<th>Area [Cps·eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$_2$(carbide)</td>
<td>283.1</td>
<td>1.2</td>
<td>GL(30)</td>
<td>243</td>
</tr>
<tr>
<td>Cl$_2$(aliphatic)</td>
<td>285.5</td>
<td>1.2</td>
<td>GL(30)</td>
<td>46</td>
</tr>
<tr>
<td>O$_1$(oxide)</td>
<td>530.0</td>
<td>1.4</td>
<td>GL(20)</td>
<td>344</td>
</tr>
<tr>
<td>O$_1$(hydroxide)</td>
<td>531.5</td>
<td>1.4</td>
<td>GL(20)</td>
<td>426</td>
</tr>
<tr>
<td>Cr$_2$3/2</td>
<td>574.2</td>
<td>1.2</td>
<td>GL(30)T(0.825)</td>
<td>500</td>
</tr>
<tr>
<td>Fe$_2$3/2</td>
<td>706.7</td>
<td>0.9</td>
<td>GL(85)T(0.63)</td>
<td>29682</td>
</tr>
</tbody>
</table>

### 100 μm beam size and 69 eV pass energy (after 4 min Ar-sputtering (1 kV, 3.3 mm$^2$)):

<table>
<thead>
<tr>
<th>Name</th>
<th>Position [eV]</th>
<th>FWHM [eV]</th>
<th>Line Shape</th>
<th>Area [Cps·eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$_2$(carbide)</td>
<td>283.2</td>
<td>1.4</td>
<td>GL(30)</td>
<td>1553</td>
</tr>
<tr>
<td>Cl$_2$(aliphatic)</td>
<td>285.4</td>
<td>1.4</td>
<td>GL(30)</td>
<td>369</td>
</tr>
<tr>
<td>O$_1$(oxide)</td>
<td>530.1</td>
<td>1.6</td>
<td>GL(20)</td>
<td>2728</td>
</tr>
<tr>
<td>O$_1$(hydroxide)</td>
<td>531.6</td>
<td>1.6</td>
<td>GL(20)</td>
<td>2040</td>
</tr>
<tr>
<td>Cr$_2$3/2</td>
<td>574.2</td>
<td>1.2</td>
<td>GL(30)T(0.825)</td>
<td>2256</td>
</tr>
<tr>
<td>Fe$_2$3/2</td>
<td>706.7</td>
<td>0.9</td>
<td>GL(85)T(0.63)</td>
<td>154805</td>
</tr>
</tbody>
</table>

### 20 μm beam size and 69 eV pass energy (after 4 min Ar-sputtering (1 kV, 3.3 mm$^2$)):

<table>
<thead>
<tr>
<th>Name</th>
<th>Position [eV]</th>
<th>FWHM [eV]</th>
<th>Line Shape</th>
<th>Area [Cps·eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$_2$(carbide)</td>
<td>283.4</td>
<td>1.4</td>
<td>GL(30)</td>
<td>400</td>
</tr>
<tr>
<td>Cl$_2$(aliphatic)</td>
<td>285.5</td>
<td>1.4</td>
<td>GL(30)</td>
<td>96</td>
</tr>
<tr>
<td>O$_1$(oxide)</td>
<td>530.0</td>
<td>1.4</td>
<td>GL(20)</td>
<td>721</td>
</tr>
<tr>
<td>O$_1$(hydroxide)</td>
<td>531.5</td>
<td>1.4</td>
<td>GL(20)</td>
<td>360</td>
</tr>
<tr>
<td>Cr$_2$3/2</td>
<td>574.2</td>
<td>1.2</td>
<td>GL(30)T(0.825)</td>
<td>402</td>
</tr>
<tr>
<td>Fe$_2$3/2</td>
<td>706.7</td>
<td>0.9</td>
<td>GL(85)T(0.63)</td>
<td>33498</td>
</tr>
</tbody>
</table>
measured peak areas by a factor 5, but did not affect the shape of the peaks and the fwhm remained unchanged for the intense peaks while for the peaks with a lower S/N ratio as in the case of carbon and chromium a slight increase with the smaller beam size was observed. Changing the pass energy from 69 to 26 eV led to a decrease of the intensities by a factor 3 and the peaks were narrower: the fwhm of the peaks decreased by 0.1-0.2 eV.

**Composition**

There are three possibilities for the binding state of carbon: When the steel is heated to 800-830°C, only few iron carbides and chromium carbides are formed while the major part of carbon is dissolved in the austenitic lattice. During the quenching there is a phase transformation from the austenite to the martensite, whereas there is no time for diffusion and thus the carbon remains at its interstitial positions. From the iron carbide only minor peaks of iron at 707.3 eV [136] or 709 eV [151] are expected, but these are dominated by the metallic iron at 706.7 eV.

The sputter-cleaned steel 100Cr6 contained 1.8±0.3 wt.% carbon and 1.6±0.2 wt.% chromium. These are the mean values over 4 samples. The expected values from the nominal composition are 1 wt.% carbon and 1.5 wt.% chromium. Deviations can be due to selective sputtering where not all elements are sputtered away with the same probability and due to carbon from the contamination layer reacting with metallic iron to form iron carbides.

### 7.4.2 Disc after Polishing

The spectra acquired on a freshly polished disc are shown in Figure 7.2. The survey spectrum shows peaks of oxygen, iron, chromium and carbon only. The carbon peak was more intense compared to the sputter-cleaned disc; especially the aliphatic carbon peak at 285.0 eV was very intense (see Table 7.3). There are high-binding-energy peaks at 286.8 eV due to carbon bound to oxygen [134, 138, 152] and at 288.7 eV because of carboxylic [121, 134] or carbonate groups [129, 135]. The oxygen spectrum shows three peaks at 529.7, 531.3 and 532.5 eV assigned to oxide, hydroxide and adsorbed water [132, 133]. The chromium 2p$_{3/2}$ peak consisted of two peaks assigned to metallic chromium or chromium carbides at 573.9 eV and to oxidized chromium at 576.3 eV [87]. The iron signal consisted, besides the metallic iron peak at 706.4 eV, of the oxides Fe(II) at 709.3 eV [132, 133] (including its satellite at
714.8 eV [132, 133]) and Fe(III) at 710.9 eV [129, 132] and of iron hydroxide at 711.8 eV [4, 128].

**Polished 100Cr6**

**Figure 7.2:** XPS survey and detailed spectra of C1s, O1s, Cr2p and Fe2p of a freshly polished disc made of steel 100Cr6. (Data acquired with the PHI Quantera with 100 µm beam size and 69 eV pass energy.)

**Table 7.3:** Peak-fitting parameters of a freshly polished 100Cr6 disc acquired with the PHI Quantera with 100 µm beam size and 69 eV pass energy. The uncertainty of the positions and fwhm is 0.1 eV and about 5% for the peak areas.

<table>
<thead>
<tr>
<th>Name</th>
<th>Position [eV]</th>
<th>FWHM [eV]</th>
<th>Line Shape</th>
<th>Area [Cps-eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s(carbide)</td>
<td>282.9</td>
<td>1.4</td>
<td>GL(30)</td>
<td>686</td>
</tr>
<tr>
<td>C1s(aliphatic)</td>
<td>285.0</td>
<td>1.4</td>
<td>GL(30)</td>
<td>10380</td>
</tr>
<tr>
<td>C1s(C-O)</td>
<td>286.8</td>
<td>1.4</td>
<td>GL(30)</td>
<td>1206</td>
</tr>
<tr>
<td>C1s(COOX / CO3)</td>
<td>288.7</td>
<td>1.4</td>
<td>GL(30)</td>
<td>997</td>
</tr>
<tr>
<td>O1s(oxide)</td>
<td>529.7</td>
<td>1.3</td>
<td>GL(20)</td>
<td>27689</td>
</tr>
<tr>
<td>O1s(hydroxide)</td>
<td>531.2</td>
<td>1.3</td>
<td>GL(20)</td>
<td>11384</td>
</tr>
<tr>
<td>O1s(H2O)</td>
<td>532.4</td>
<td>1.3</td>
<td>GL(20)</td>
<td>4523</td>
</tr>
<tr>
<td>Cr2p3/2(met)</td>
<td>573.9</td>
<td>1.7</td>
<td>GL(30)T(0.825)</td>
<td>479</td>
</tr>
<tr>
<td>Cr2p3/2(oxide)</td>
<td>576.2</td>
<td>1.7</td>
<td>GL(30)T(1.1)</td>
<td>1164</td>
</tr>
<tr>
<td>Fe2p3/2(met)</td>
<td>706.4</td>
<td>1.1</td>
<td>GL(85)T(0.63)</td>
<td>16136</td>
</tr>
<tr>
<td>Fe2p3/2(II)</td>
<td>709.3</td>
<td>2.8</td>
<td>GL(0)</td>
<td>26179</td>
</tr>
<tr>
<td>Fe2p3/2(III)</td>
<td>711.0</td>
<td>2.7</td>
<td>GL(55)T(1.6)</td>
<td>11769</td>
</tr>
<tr>
<td>Fe2p3/2(OOH)</td>
<td>711.8</td>
<td>3.0</td>
<td>GL(45)</td>
<td>5577</td>
</tr>
<tr>
<td>Fe2p3/2(II)</td>
<td>714.8</td>
<td>2.8</td>
<td>GL(0)</td>
<td>1833</td>
</tr>
</tbody>
</table>
Table 7.4: Peak-fitting parameters of a freshly polished 100Cr6 disc acquired with the PHI Quantera with 20 μm beam size and 69 eV pass energy. The uncertainty of the positions and fwhm is 0.1 eV and about 5% for the peak areas.

<table>
<thead>
<tr>
<th>Name</th>
<th>Position [eV]</th>
<th>FWHM [eV]</th>
<th>Line Shape</th>
<th>Area [Cps-eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s(carbide)</td>
<td>282.9</td>
<td>1.4</td>
<td>GL(30)</td>
<td>820</td>
</tr>
<tr>
<td>C1s(aliphatic)</td>
<td>285.0</td>
<td>1.4</td>
<td>GL(30)</td>
<td>10330</td>
</tr>
<tr>
<td>C1s(C-O)</td>
<td>286.8</td>
<td>1.4</td>
<td>GL(30)</td>
<td>1280</td>
</tr>
<tr>
<td>C1s(COOX / CO₃)</td>
<td>288.7</td>
<td>1.4</td>
<td>GL(30)</td>
<td>980</td>
</tr>
<tr>
<td>O1s(oxide)</td>
<td>529.7</td>
<td>1.3</td>
<td>GL(20)</td>
<td>27352</td>
</tr>
<tr>
<td>O1s(hydroxide)</td>
<td>531.2</td>
<td>1.3</td>
<td>GL(20)</td>
<td>12141</td>
</tr>
<tr>
<td>O1s(H₂O)</td>
<td>532.5</td>
<td>1.3</td>
<td>GL(20)</td>
<td>3969</td>
</tr>
<tr>
<td>Cr2p₃/₂</td>
<td>573.9</td>
<td>2.7</td>
<td>GL(30)T(0.825)</td>
<td>209</td>
</tr>
<tr>
<td>Cr2p₃/₂</td>
<td>575.6</td>
<td>2.7</td>
<td>GL(30)T(1.1)</td>
<td>1446</td>
</tr>
<tr>
<td>Fe2p₃/₂(met)</td>
<td>706.4</td>
<td>1.1</td>
<td>GL(85)T(0.63)</td>
<td>15360</td>
</tr>
<tr>
<td>Fe2p₃/₂(II)</td>
<td>709.3</td>
<td>2.8</td>
<td>GL(0)</td>
<td>23857</td>
</tr>
<tr>
<td>Fe2p₃/₂(III)</td>
<td>710.9</td>
<td>2.7</td>
<td>GL(55)T(1.6)</td>
<td>13474</td>
</tr>
<tr>
<td>Fe2p₃/₂(OOH)</td>
<td>711.8</td>
<td>3.0</td>
<td>GL(45)</td>
<td>4599</td>
</tr>
<tr>
<td>Fe2p₃/₂(II₉₀)</td>
<td>714.8</td>
<td>2.8</td>
<td>GL(0)</td>
<td>1670</td>
</tr>
</tbody>
</table>

Measuring with the different beam sizes of 100 μm and 20 μm but with the same pass energy of 69 eV (see Table 7.3 and Table 7.4) did not significantly change the peak shapes or peak positions (binding energies ±0.1 eV). The fwhm stayed constant with the exception of chromium 2p₃/₂ where the higher noise from using 20 μm instead of 100 μm beam size led to a higher fwhm. Usually, the areas under the peaks were reduced by a factor of 5 when using the smaller beam size.

Depth Distribution

Two different techniques were applied to determine the depth distribution of the elements: The first approach was acquiring the spectra after short times of sputtering in order to remove layer by layer. The disadvantage of sputter profiling is that selective sputtering might change the composition and the bombardment with ions might change the chemical state of the elements. The second approach was angle-resolved XPS where spectra were acquired at different emission angles and therefore with different sampling depth.

The spectra after depth profiling with sputtering are presented in Figure 7.3. The carbon signal before sputtering was very intense and showed four peaks, a small carbide peak at 283.2 eV and more prominent peaks at 285.0, 286.9 and 288.9 eV. Already after six seconds of sputtering, the peaks above 285 eV almost disappeared while the carbide peak became more prominent and was constant with longer sputtering time. This indicates that on top of the sample there was an organic layer and that the carbide was incorporated in the steel.
The oxygen signal consisted of three peaks at 530, 532 and 533 eV. After a short sputter-time, the intensities of the high-binding-energy peaks dropped, while the intensity of the oxide peak at 530 eV first increased and then decreased with increasing sputter time. This suggests that the organic layer on top of the sample contained water and oxygen, which corresponds to the presence of the high-binding-energy peaks in the carbon spectra assigned to carbon bound to oxygen and carboxyl or carbonates groups. Only a small contribution of the 532 eV peak was originating from iron hydroxides.

The chromium signal before sputtering was very noisy and became more prominent after a short time of sputtering. On the surface mainly oxidized chromium was present as indicated by the high-binding-energy peak at 576.5 eV [87]. Going deeper into the material, the fraction of oxidized chromium became weaker while the fraction of metallic chromium and chromium carbide found at 574.2 eV [87] increased.

Before sputtering, the iron signal was very weak and contained mainly contributions of the oxide layer. With increasing sputter time, the total intensity of iron increased and the signal shifted towards lower binding energy. This indicates that the oxide layer was removed and more and more metallic iron was probed. After 24 seconds almost no oxide peaks were detected.

In angle-resolved XPS, spectra were acquired at different emission angles (EA; angle between analyser and surface normal). At smaller EA, the sampling depth is deeper than at higher EA, and therefore the measurements at smaller angles represent more the bulk composition while the measurements at higher EAs are more surface sensitive. Above emission angles of 60°, electrons from Polished 100Cr6: Sputter Depth Profile

![Polished 100Cr6: Sputter Depth Profile](image)

**Figure 7.3:** XPS detailed spectra of C1s, O1s, Cr2p and Fe2p of a freshly polished 100Cr6 disc as received and after 6, 12, 18 and 24 seconds of sputtering (4 kV, 3-3mm²). (Data acquired with the PHI Quantera with 100μm beam size and 26 eV pass energy.)
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Figure 7.4: Apparent atomic concentration vs. emission angle of a freshly polished disc. (Data acquired with the Theta Probe. The measurement was performed with 300 μm beam size and spectra were acquired at 16 emission angles.)

elastic scattering contribute significantly to the signals and become dominant at large angles [90]. Figure 7.4 shows the apparent atomic concentration of a freshly polished disc vs. the EA. The concentration was calculated assuming a homogenous compound of iron oxide within the whole analysed depth. Elements present in the inner part of the investigated volume exhibit a decreasing concentration with increasing EA and elements present in the outer part show higher concentrations at higher EAs.

Both the concentration of metallic iron and carbon assigned to carbides dropped to zero at 77°, which shows that these elements were present at the very bottom of the analysed volume. The oxide concentrations of iron and oxygen exhibited negative slopes but, in contrast to the metallic iron, remained at a relatively high level at high EAs. Therefore the oxide film was placed on top of the metallic iron. The concentrations of carbon except the carbide peak and of oxygen assigned to oxygen bound to carbon and oxygen in water rose with higher EAs. Therefore these elements were attributed to the organic layer on top of the sample.

Thickness and Composition

For the freshly polished sample, the thickness of the oxide layer was 2.3±0.4 nm and the thickness of the organic layer 2.0±0.3 nm. The ratio of oxygen-to-iron in the oxide layer was 2.0±0.2:1. This indicates that the oxide layer
was composed of a mixture of iron oxide and iron hydroxide. The organic layer mainly contained aliphatic carbon with minor contributions of carbon bound to oxygen and adsorbed water.

### 7.4.3 Disc after Polishing and Ageing

The spectra acquired on a polished sample after aging for 24 hours stored in aluminium foil in the hood (RH 23%) were similar to those of the freshly polished sample (see Figure 7.5 and Figure 7.2). The main difference was the increased intensity of the high-binding-energy peak of carbon assigned to carbonates or carboxylic groups, the weaker chromium peak where metallic chromium was almost absent and the peak shape of iron, where the oxide peak changed to higher binding energy. This indicates a transformation of the surface film due to ageing in air.

#### Thickness and Composition

For the aged sample, the thickness of the oxide layer increased slightly from 2.3±0.1 nm to 2.7±0.2 nm while the thickness of the organic layer remained equal to 2.0±0.3 nm. The oxygen-to-iron ratio in the oxide layer was 2.1±0.2:1

**Polished & Aged 100Cr6**

![Figure 7.5: XPS survey and detailed spectra of C1s, O1s, Cr2p and Fe2p of a disc made of 100Cr6 steel. After polishing, the disc was stored, wrapped in aluminium foil, for 24 h prior to the XPS analysis. (Data acquired with the PHI Quantera with 100 μm beam size and 69 eV pass energy.)](image-url)
and Fe(III) to Fe(II) was 3.3±1.2:1. This value is higher than that of 0.9±0.4:1 found in the freshly polished sample. The organic layer contained more carboxylic or carbonate groups, the percentage of the high-binding-energy species increased from 8±5 at.% to 13±3 at.% with the ageing of the sample.

Table 7.5: Peak-fitting parameters of polished and aged 100Cr6 disc acquired with the PHI Quantera with 100 μm beam size and 69 eV pass energy. The uncertainty of the positions and fwhm is 0.1 eV and about 5% for the peak areas.

<table>
<thead>
<tr>
<th>Name</th>
<th>Position [eV]</th>
<th>FWHM [eV]</th>
<th>Line Shape</th>
<th>Area [Cps-eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s(carbide)</td>
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<td>1.5</td>
<td>GL(30)</td>
<td>469</td>
</tr>
<tr>
<td>C1s(aliphatic)</td>
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<td>1.5</td>
<td>GL(30)</td>
<td>7708</td>
</tr>
<tr>
<td>C1s(C-O)</td>
<td>286.8</td>
<td>1.5</td>
<td>GL(30)</td>
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<tr>
<td>C1s(COOX / CO₃)</td>
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<td>1.5</td>
<td>GL(30)</td>
<td>1998</td>
</tr>
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<td>O1s(hydroxide)</td>
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<td>GL(20)</td>
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<td>O1s(H₂O)</td>
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<td>1.3</td>
<td>GL(20)</td>
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</tr>
<tr>
<td>Cr₂p₃/₂(met)</td>
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<td>2.3</td>
<td>GL(30)T(0.825)</td>
<td>181</td>
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<tr>
<td>Cr₂p₃/₂(oxide)</td>
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<td>2.3</td>
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<tr>
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<td>6169</td>
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<tr>
<td>Fe₂p₃/₂(III)</td>
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<td>2.6</td>
<td>GL(55)T(1.6)</td>
<td>32432</td>
</tr>
<tr>
<td>Fe₂p₃/₂(OOH)</td>
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<td>3.0</td>
<td>GL(45)</td>
<td>488</td>
</tr>
<tr>
<td>Fe₂p₃/₂(II₂sat)</td>
<td>715.1</td>
<td>2.4</td>
<td>GL(0)</td>
<td>432</td>
</tr>
</tbody>
</table>

Table 7.6: Peak-fitting parameters of polished and aged 100Cr6 disc acquired with the PHI Quantera with 20 μm beam size and 69 eV pass energy. The uncertainty of the positions and fwhm is 0.1 eV and about 5% for the peak areas.

<table>
<thead>
<tr>
<th>Name</th>
<th>Position [eV]</th>
<th>FWHM [eV]</th>
<th>Line Shape</th>
<th>Area [Cps-eV]</th>
</tr>
</thead>
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<td>GL(30)</td>
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</tr>
<tr>
<td>C1s(aliphatic)</td>
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<td>1.5</td>
<td>GL(30)</td>
<td>1603</td>
</tr>
<tr>
<td>C1s(C-O)</td>
<td>286.8</td>
<td>1.5</td>
<td>GL(30)</td>
<td>243</td>
</tr>
<tr>
<td>C1s(COOX / CO₃)</td>
<td>288.5</td>
<td>1.5</td>
<td>GL(30)</td>
<td>328</td>
</tr>
<tr>
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<td>1.3</td>
<td>GL(20)</td>
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<td>531.4</td>
<td>1.3</td>
<td>GL(20)</td>
<td>2773</td>
</tr>
<tr>
<td>O1s(H₂O)</td>
<td>532.6</td>
<td>1.3</td>
<td>GL(20)</td>
<td>1073</td>
</tr>
<tr>
<td>Cr₂p₃/₂</td>
<td>573.7</td>
<td>2.1</td>
<td>GL(30)T(0.825)</td>
<td>45</td>
</tr>
<tr>
<td>Cr₂p₃/₂</td>
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<td>2.1</td>
<td>GL(30)T(1.1)</td>
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<tr>
<td>Fe₂p₃/₂(met)</td>
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<td>GL(85)T(0.63)</td>
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</tr>
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<td>GL(0)</td>
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<td>Fe₂p₃/₂(III)</td>
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<td>2.8</td>
<td>GL(55)T(1.6)</td>
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<tr>
<td>Fe₂p₃/₂(OOH)</td>
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<td>3.0</td>
<td>GL(45)</td>
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</tr>
<tr>
<td>Fe₂p₃/₂(II₄sat)</td>
<td>715.1</td>
<td>2.5</td>
<td>GL(0)</td>
<td>178</td>
</tr>
</tbody>
</table>
7.4.4 Maghemite

Maghemite ($\gamma$-Fe$_2$O$_3$) is an iron oxide crystal modification with a defect spinel structure, where cation vacancies compensate for the oxidation state +2 [153]. All iron atoms are in the oxidation state +3, and therefore it was chosen as a reference for the peak shape of Fe(III).

Prior to the acquisition of the presented spectra (see Figure 7.6), the sample was sputter-cleaned for 30 seconds with argon ions accelerated with 500 Volts. These mild sputtering conditions were chosen in order not to damage the struc-

![Maghemite Fe$_2$O$_3$](image)

**Figure 7.6:** XPS survey and detailed spectra of C1s, O1s and Fe2p of a maghemite ($\gamma$-Fe$_2$O$_3$). (Data acquired with the PHI Quantera with 100 $\mu$m beam size and 69 eV pass energy after sputter-cleaning for 30 seconds with 500 V, 3.3 mm$^2$.)

<table>
<thead>
<tr>
<th>Name</th>
<th>Position [eV]</th>
<th>FWHM [eV]</th>
<th>Line Shape</th>
<th>Area [Cps·eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s(aliphatic)</td>
<td>285.0</td>
<td>1.5</td>
<td>GL(30)</td>
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<tr>
<td>C1s(C-O)</td>
<td>286.8</td>
<td>1.5</td>
<td>GL(30)</td>
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</tr>
<tr>
<td>C1s(COOX / CO$_3$)</td>
<td>288.5</td>
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<tr>
<td>O1s(oxide)</td>
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</tr>
<tr>
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</tr>
<tr>
<td>O1s(H$_2$O)</td>
<td>532.1</td>
<td>1.2</td>
<td>GL(20)</td>
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</tr>
<tr>
<td>Fe2p$_{3/2}$(III)</td>
<td>710.1</td>
<td>2.9</td>
<td>GL(55)T(1.6)</td>
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<tr>
<td>Fe2p$<em>{3/2}$(III$</em>{sat}$)</td>
<td>718.6</td>
<td>2.9</td>
<td>GL(55)T(1.6)</td>
<td>3240</td>
</tr>
</tbody>
</table>
ture of the crystal. The drawback is that there was still residual carbon, water and hydroxides present on the sample. The spectrum of iron shows the Fe(III) peak at 710.2 eV with its satellite at 718.7 eV. These binding energies are about 1 eV lower than reported by others [129, 132]. With a peak shape of GL(55)T(1.6), the best fit to the experimental data was obtained. This shape was used for further peak fitting. The area of the Fe(III) satellite was 7±1% of the main peak. Usually, this satellite was not within the fitted range but it was added mathematically to the peak area of the Fe(III) peak.

Composition
The ratio of oxygen in the oxide state to iron was found to be 2.2±0.1:1, which was higher than the expected 1.5:1.

7.4.5 Magnetite
Magnetite Fe₃O₄ is an inverse spinel that contains both iron (II) and iron (III) in a ratio of 1:2 [153]. It was chosen as a reference compound to determine the peak shape of the iron (II) since the shape of the iron (III) was known from the maghemite sample.

The survey spectrum presented in Figure 7.7 showed peaks of oxygen, iron

---

**Figure 7.7:** XPS survey and detailed spectra of C1s, O1s and Fe2p of a magnetite (Fe₃O₄). (Data acquired with the PHI Quantera with 100 µm beam size and 69 eV pass energy after sputter-cleaning for 1 minute with 500V3x3.)
Table 7.8: Peak-fitting parameters of magnetite Fe₃O₄ acquired with the PHI Quantera with 100 μm beam size and 69 eV pass energy. The uncertainty of the positions and fwhm is 0.1 eV and about 5% for the peak areas.

<table>
<thead>
<tr>
<th>Name</th>
<th>Position [eV]</th>
<th>FWHM [eV]</th>
<th>Line Shape</th>
<th>Area [Cps·eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s(aliphatic)</td>
<td>285.0</td>
<td>1.6</td>
<td>GL(30)</td>
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</tr>
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<td>C1s(C-O)</td>
<td>286.8</td>
<td>1.6</td>
<td>GL(30)</td>
<td>244</td>
</tr>
<tr>
<td>C1s(COOX / CO₃)</td>
<td>289.0</td>
<td>1.6</td>
<td>GL(30)</td>
<td>268</td>
</tr>
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<td>O1s(oxide)</td>
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<td>1.2</td>
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<td>O1s(hydroxide)</td>
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<td>1.2</td>
<td>GL(50)</td>
<td>7'731</td>
</tr>
<tr>
<td>O1s(H₂O)</td>
<td>532.0</td>
<td>1.2</td>
<td>GL(50)</td>
<td>4'488</td>
</tr>
<tr>
<td>Fe2p₃/₂(II)</td>
<td>709.3</td>
<td>2.8</td>
<td>GL(0)</td>
<td>22'760</td>
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<td>3.1</td>
<td>GL(55)T(1.8)</td>
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and of residual carbon that was not removed after sputtering. The oxygen peak showed a main peak due to the oxide signal and minor peaks of hydroxides and adsorbed water. The iron signal consisted of the iron species Fe(II) and Fe(III), which were fitted by constraining the area of the Fe(II)-peak to be half of the Fe(III)-peak (see areas in Table 7.8.). The best fits were achieved by using a pure Gaussian peak shape for the Fe(II)-peak (and its satellite), the shape of the Fe(III) was taken from the maghemite fit. The area of the Fe(II) satellite was again 7±1% of the main peak, this was used as a constraint for fitting the iron spectra.

Composition
The oxygen-to-iron ratio of the magnetite was found to be 1.8:1, which was lower than found in the maghemite, but still higher than the expected ratio of 1.33:1.

7.4.6 Ball, as Received
Hardened balls from two batches were used in this study: balls of the old batch for the combinatorial step test and balls of the new batch for the combinatorial oscillating-load tests. Balls from both batches were investigated with XPS to check the initial state before starting an experiment.

The survey spectrum of a ball from the new batch (see Figure 7.8) showed peaks of oxygen, iron and carbon. The detailed spectrum of carbon 1s did not exhibit a carbide peak, as was found on the polished disc. The oxygen 1s spectrum contained besides the oxide peak strong peaks due to hydroxides and wa-
Appendix

100Cr6 Ball: As Received

**Survey**

<table>
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<tr>
<th>Intensity [Cps]</th>
<th>Binding Energy [eV]</th>
</tr>
</thead>
<tbody>
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<td></td>
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</tr>
<tr>
<td></td>
<td>1200</td>
</tr>
<tr>
<td></td>
<td>800</td>
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<tr>
<td></td>
<td>400</td>
</tr>
<tr>
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**Carbon 1s**

<table>
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</thead>
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<tr>
<td>284</td>
<td>2000</td>
</tr>
<tr>
<td>286</td>
<td>4000</td>
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</table>

**Oxygen 1s**

<table>
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<tbody>
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<tr>
<td>534</td>
<td>538</td>
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<td>538</td>
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**Chromium 2p**

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</thead>
<tbody>
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<tr>
<td>574</td>
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<tr>
<td>576</td>
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**Iron 2p**

<table>
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</thead>
<tbody>
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<tr>
<td>740</td>
<td>2000</td>
</tr>
</tbody>
</table>

![Figure 7.8: XPS survey and detailed spectra of C1s, O1s, Cr2p and Fe2p of a ball of the new batch made of 100Cr6 steel, as it was received. (Data acquired with the PHI Quantera with 100 μm beam size and 26 eV pass energy.)](image)

No chromium was detected. The iron 2p$_{3/2}$ spectrum showed a small peak of metallic iron and larger peaks of iron (II) and iron (III).

The survey spectrum of the balls of the old batch showed peaks of iron, oxygen and carbon and traces of several contaminants, such as calcium, nitrogen, magnesium and phosphorus. The detailed spectrum of carbon 1s was similar to that presented in Figure 7.8; the oxygen 1s spectrum showed lower intensity of the oxide peak and the iron signal was much weaker and no metallic iron was detected.

**Thickness and Composition**

The thickness of the oxide layer of the balls of the new batch was determined to be 4.3 nm. In the case of the old balls, no metallic iron from the substrate was detected and therefore the thickness of the oxide layer could not be determined. The thickness of the organic layer was 4.1 nm for the new ball and 5.7 nm for the old ball.

The oxygen-to-iron ratio was 2.2:1 for the new ball and 1.5:1 for the old ball. The organic layer contained 16 at.% oxygen bound to carbon and 6% water in the case of the new ball. The old ball contained higher amounts of oxygen and water in addition to the contaminants.
7.4.7 Ball after Sputter-cleaning

The spectra of the sputter-cleaned ball of the new batch are shown in Figure 7.9. Similar spectra were acquired on the old ball, but a doubling of the sputter time was necessary to remove the overlayers.

The survey spectrum shows high intensities of iron and minor peaks of chromium, oxygen, carbon and argon from the sputtering. The carbon peak shows a major peak at 283.0 eV assigned to carbides [136, 137] and a minor peak due to aliphatic carbon. The oxygen spectrum showed the residual oxygen from oxides and hydroxides, likely due to oxides and hydroxides that were not sputtered away. The chromium 2p signal shows a main peak at 574.1±0.1 eV due to metallic chromium [87] or chromium carbide [149, 150] and a minor peak at 576.8±0.2 eV due to oxidized chromium [87]. The iron spectrum has a very intense peak due to metallic iron at 706.6 eV (fwhm 0.8 eV) [129, 132] and less intense oxide peaks at higher binding energies.

Composition

1.5 wt.% chromium was found in the balls of both batches. This is exactly the expected value from the nominal composition. The carbon content in the new ball was 1.9 wt.% and in the old ball 1.2 wt.%, which was for both higher than

Sputter-cleaned 100Cr6 Ball

![XPS spectra](image)

*Figure 7.9: XPS survey and detailed spectra of C1s, O1s, Cr2p and Fe2p of a sputter-cleaned ball of the new batch made of steel 100Cr6. (Data acquired with the PHI Quantera with 100 μm beam size and 26 eV pass energy after 1 min Ar-sputtering (3 kV, 3·3mm²).)*
the expected 1 wt.%. The carbon is mainly bound to chromium resulting in chromium carbides, but the presence of iron carbides cannot be excluded (see sputter-cleaned disc).

7.4.8 Phosphorothionate b-TPPT

The pure b-TPPT was investigated with XPS in order to detect changes in the binding energies of phosphorus, sulphur and oxygen when the tribofilm is formed. A drop of b-TPPT was deposited on a piece of freshly cleaved mica mounted on a sample holder that was cooled with liquid nitrogen. The drop froze solid immediately and after pumping down the introduction chamber of the spectrometer, the sample holder was introduced into the ultra-high vacuum. The experiments were performed at liquid nitrogen temperature.

The survey spectrum (see Figure 7.10) exhibited the sulphur, phosphorus (2p and 2s orbitals of both), carbon 1s and oxygen (1s and KLL) peaks. The detailed spectra of phosphorus 2p and sulphur 2p exhibited two peaks (2p_{3/2} and 2p_{1/2}) due to the spin-orbit splitting. The peak-fitting parameters are listed in Table 7.9. There were four peaks detected in the carbon signal originating from the phenyl groups at 284.7 eV, from aliphatic carbon at 285.0 eV, from carbon atoms bound to oxygen at 286.5 eV and from the \( \pi \rightarrow \pi^* \) shake up at 291.7 eV [134]. The main peak of oxygen was found at 533.4 eV and was assigned to

Frozen Irgalube®232

![Survey](image)

![Phosphorus 2p](image)

![Carbon 1s](image)

![Oxygen 1s](image)

Figure 7.10: Survey and detailed spectra of frozen b-TPPT on mica. (Data acquired with the PHI 5700.)
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oxygen linking the phenyl groups to the phosphate group (see chemical formula in chapter 2.2.3). There was a small peak at 531.7 eV likely caused by the X-ray degradation of the molecule when the phenyl-group was separated from the phosphate group.

**Composition**

The calculated composition (see Table 7.9) was close to the expected composition from the chemical formula. Slightly higher concentrations of phosphorus and sulphur were found while the carbon concentration was slightly lower.

**Table 7.9:** Fitting parameters and concentrations of the peaks found in frozen b-TPPT. The uncertainty of the positions and fwhm is 0.1 eV, 5% for the peak areas and 10% for the concentrations. (Data acquired with the PHI 5700.)

<table>
<thead>
<tr>
<th></th>
<th>P2p3/2</th>
<th>S2p3/2</th>
<th>Carbon C1s</th>
<th>O1s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>phenyl</td>
<td>aliphatic</td>
<td>C-O</td>
<td>shake up</td>
</tr>
<tr>
<td></td>
<td>fwhm [eV]</td>
<td>1.6</td>
<td>1.5</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>peak area [Cps-eV]</td>
<td>190</td>
<td>241</td>
<td>2318</td>
</tr>
<tr>
<td></td>
<td>calculated at.%</td>
<td>4</td>
<td>4</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>expected at.%</td>
<td>3</td>
<td>3</td>
<td>52</td>
</tr>
</tbody>
</table>
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Curriculum Vitae

Name                  Roman Christian Heuberger
Date of Birth         4th November, 1976
Citizenship           Kirchberg (SG), Switzerland
Marital status        single

Education

2003-2007              Doctoral student at the ETH Zurich, Switzerland, Laboratory for Surface Science and Technology, Department of Materials
1998-2003              Studies in Material Science at the ETH Zurich, Switzerland. Graduation with the degree Dipl. Werkstoff-Ing. ETH.
                       Diploma thesis performed at BiointerfaceGroup, Laboratory of Surface Science, Zurich and Max-Planck Institute for Colloids and Interfaces, Potsdam/Golm (Germany): Biofunctional polyelectrolyte multilayers and microcapsules: Control of non-specific and bio-specific protein adsorption.
1984-1991              Primary school in Mettmenhasli, Switzerland.

Employment

2003-2007              Scientific assistant at the ETH Zurich, Laboratory for Surface Science and Technology, Department of Materials
2002                   Industrial placement at Serto AG, Aadorf, Switzerland: Tests of fittings and preliminary studies for material choice.
2001                   Industrial placement at Nortel Networks, Zurich, Switzerland: selective etching of gallium-arsenide wafers to visualize lattice errors.
1999                   Basic industrial placement at Wärtsilä NSD, Winterthur, Switzerland.
1998-2002              Part-time accounting clerk as investigator in payment transactions, Credit Suisse, Zurich, Switzerland.
Publications


Presentations


R. Heuberger, A. Rossi and N. D. Spencer (poster): “Comparison of the Tribochemistry of Metal-containing and Metal-free lubricant Additives”, France, Lyon, April 9-14, 2006, Frontiers of Boundary Lubricating Films
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